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In The Name of God


یازدهمین
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ایران
11th Annual Electrochemistry
Seminar of Iran

Proceeding of

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11th Electrochemistry Seminar of Iran

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Seminar Chairman: Prof. Hossein Gharibi

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Welcome to the 11th Annual Electrochemistry Seminar of Iran

Dear attendants

On behalf of organizing committee of the 11th Annual Electrochemistry Seminar of Iran, I'm delighted to welcome you all to Tarbiat Modares University.

Over decades, Iranian researchers have concerned the electrochemical phenomena from both theoretical and applied standpoints mainly the electrochemical aspects of biological, energy storage systems, and corrosion processes. Characterization and analytical considerations have been the most important concerns of researches in this field.

We are pleased to host researchers of electrochemistry field held at Tarbiat Modares University, Tehran, Iran. It's noteworthy that the seminar includes 6 major fields including *Nano electrochemistry, Computational electrochemistry, Electrochemical synthesis, Bio electrochemistry, Corrosion, Energy generation and storage.*

We whole heartedly hope that your participation in the 11th Annual Electrochemistry Seminar of Iran in Tehran will be fruitful.

Cordially
Hossein Gharibi

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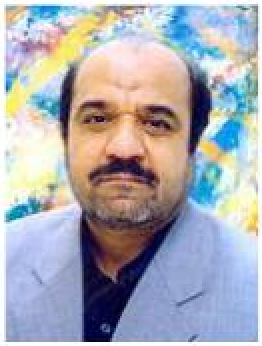

Professor Majid Jafarian

“Review on Recent Trends on electrochemistry of lead, aluminum and nikel”

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Biography
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Review on Recent Trends on electrochemistry of lead, aluminum and nikel

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In this review we present some of our investigation in electrochemistry of Pb Al and Ni. We have already presented details of the studies in a number of published papers [1-3]. Lead chal. pbS, pbSe and pbTe and their alloys have importance technological application. This respect semiconducting properties of PbS was studied. The voltammetric of PbS film in SO4Na2 solution shows that oxidative dissolution of PbS film accrues at about 0.21 V vs Ag/AgCl and total film detachment from the surface occurred with increasing potential .The flat band potential and carrier concentration determined to be -0.32V and 1.6*10 23 m-3 respectively .The film was P type semiconductor [1]. The electrocrystallization of metal on foreign substrate has attracted a great deal of interest in modern electrochemistry due to its technological advantage. Electrochemical deposition of aluminum and lead from basic molten AlCl3 – NaCl-KCl mixture on an aluminum electrode at 180 c was studied by cyclic voltammetry .the deposition of aluminum was found to be diffusion control .The diffusion calculated for Pb+2 ions in basic melt by voltammetry was obtained . The deposition process of lead on al substrate was controlled by 3d diffusion control, nucleation and growth [2]. Intensive research have been directed towards the development of electro-catalysis aiming at lowering the normaly large overpotential encountered in the electrooxidation of materials and in particular the fuel cells in the merging fuel cell systems. We studied electrocatalytic oxidation of methane at nickel hydroxide modified nickel electrode in alkaline solution. Our results demonstrate the preparation of modified nickel electrodes through the electrochemical formatin ofNiOOhsurface film .The possible usefulness of the modified electroes in the mediated electro oxidation of methane in alkaline solution .The mechanism of methane oxidation is reported in terms of formation of intermediates [3].

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Key Speaker

Dr Pablo Fanjul Bolado

“*Electerochemical transducers based on Graphene Materials”*

Biograghy

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CV: 18 scientific papers, 5 patents and more than 50 communications in conferences

During recent years, he has dealt with the development of electrochemical sensors based on screen printed electrodes and joining electrochemical detection systems to immuno and DNA assays.

In 2006 started as entrepeneur transfering some technology developed in the University to the market by founding the spin off DropSens Company, a well stablished technology based firm located in Asturias, Spain.

Since 2006, Pablo is R&D Director of the company dealing with international, national, and regional research projects in collaboration with other institutions (Universities and Companies).

His last research interest is focused in the development of miniaturised analytical instrumentation (potentiostats/galvanostats, spectrometers, flow injection analysis systems, and electrochemical detectors for HPLC).

ELECTROCHEMICAL TRANSDUCERS BASED ON GRAPHENE MATERIALS

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The use of sensors in the field of clinical analysis has encouraged the development of new technologies and more suitable methodologies. One of the most promising techniques is based on the use of screen printed electrochemical sensors (electrochemical transducers) which incorpore graphene-based materials as sensing element. Screen-printing technology allows mass production of low cost thick film electrodes with good electrochemical properties.

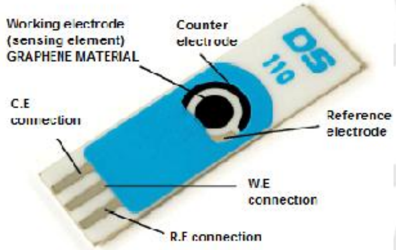

Figure 1: Screen printed electrode

The graphene materials using as sensing element have been obtained from graphene oxides prepared from coke and reduced, in the working electrode, via electrochemical process. The coke, which has not been subjected to graphitization treatment, is prepared using pitches of anthracene oil as raw material[1]. The use of these raw materials derives in high purity, free from impurities graphenes. Besides, allows the modification of the crystalline structure of the materials obtained. The control of the crystalline structures, together with the reduction process selected, results in sensing elements with different electrochemical behaviours. This work is supported by Spanish agency IDEPA and European Regional Development Fund programs, aimed at the implementation of I+D+i tractor projects in the Principality of Asturias.

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11th Annual Electrochemistry Seminar of Iran

Corrosion

A review of corrosion resistance of metals coated with graphene

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Introduction

Corrosion is a serious global problem. Chemical reaction occurs when metal surface comes in contact with oxygen in air, resulting metals being oxidized and corroded [1, 2]. Various methods have been employed by the industries to protect metal from corroding, such as coating with other metal(s), chemical modification, anodizing, using an oxide layer and organic layer/polymer coating [2].

Recently, graphene, which was successfully grown on large-area metals substrates by different methods was tested as a barrier and shown to protect metals surfaces from oxidation [1-5] because of its impermeability [6]. The purpose of this study is a review of low cost method for protection of metal surface from oxidation with graphene.

Methods

Some authors conducted studies on the oxidation resistance of graphene and graphene base composite materials [7- 10] coated Cu [1, 2], Ni [5], Cu/Ni alloys, Fe [2], Pt [9], Ti [10], Co [9], Mg [3] and stainless steel [8]. However, all the above mentioned graphene coatings were deposited via chemical vapor deposition (CVD) which involve tedious and high vacuum system. Electrophoretic deposition (EPD) is a simple electrochemical method used to deposit thin layer of coating onto any conducting substrate [1].

Results and discussion

Graphene, which was successfully grown on large-area metal substrates by a CVD method was tested as a barrier and shown to protect Cu and Cu/Ni alloy surfaces from oxidation. Fe can also be used for CVD graphene growth. However, uniform graphene layers have not been achieved on Fe substrates. Reduced graphene oxide (rG-O), when deposited as a thin film, is an alternative candidate for protecting Fe and Cu surfaces because large thin films can be readily formed by a solution process [2- 5].

Results showed the possibility of CVD graphene as a layer of corrosion barrier. It was confirmed that chemical vapor deposition (CVD) graphene layer works as a barrier for Cu and Cu/Ni alloy against air oxidation and chemical oxidation in the solution of 30% hydrogen peroxide [1, 8]. Fig. 1 shows the polarization curve for the bare copper and Cu+G samples that GO solution used as the electrolyte in the electrophoretic deposition (EPD) process.

The polarization curve enables the corrosion potential and the current densities, i_{CORR} to be determined and compared between the graphene coated and uncoated copper sample. The corrosion potential, E_{CORR} is a measurement of sample resistance towards corrosion. From the polarization curve, it can be seen that there is a shift in the E_{CORR} towards the positive direction for the Cu+G sample. It proves the graphene coating acts as a corrosion resistance barrier [1].

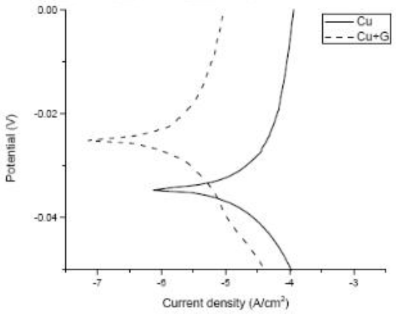

Fig.1. Polarization curves of bare copper and Cu+G [1].

Conclusion

In summary, this review shown that graphene can work effectively as a corrosion inhibiting coating on metal surfaces against O_2 exposure at partial pressures. It is believed that agraphene material which is coated on the metal surface would be an effective strategy for improving the anticorrosion performance of various engineering materials. This proposed method of corrosion passivation is quite versatile and is applicable to arbitrary metallic surfaces that are either smooth or rough [3].

Keywords*: Graphene, Corrosion, CVD, EPD, Oxidation*

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Corrosion performance of epoxy containing Na-MMT/$CoFe_2O_4$ nanopowder on 3105 aluminium and the study of molecular dynamics simulation

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Abstract

Organic coatings are used to protect metals from corrosion mainly by two mechanisms: a passive barrier mechanism to protect against exposure to aggressive substances (oxygen, water, salts etc.) or an active protection mechanism by the release of anticorrosive pigments (inhibitors) [1,2]. Na-montmorillonite is one of the most affordable materials that have shown promising results in polymers. In recent years, epoxy/clay nanocomposites have been noticed in coating, aerospace, defense and automobile industries due to their excellent properties, such as high-dimensional stability, reduced permeability and enhanced mechanical properties [3, 4].

Epoxy nanocomposites matrix, with 1wt% Na-montmorillonite (Na-MMT)/$CoFe_2O_4$ nanopowder, have been employed as coatings for an AA3105 aluminum specimen. Epoxy-based nanocomposite coating was applied for the first time to the synthesis of a series of Na- MMT/$CoFe_2O_4$ nanopowder (below 1wt% nano clay) in a wide range of compositions (from 1 to 5wt% nano clay). $CoFe_2O_4$ nanocrystals were synthesized by a wet chemical coprecipitation approach. The Na-montmorillonite Na-MMT/$CoFe_2O_4$ nanopowders were prepared by doping method. Composition and structure of nanopowders and nanoparticles were investigated by Fourier transform infrared spectroscopy and X-ray diffraction (XRD) technique and field emission scanning electron microscopy (FE-SEM). The effects of Na-MMT/$CoFe_2O_4$ nanopowders in the anticorrosion properties of epoxy-coated AA3105 aluminum were studied by means of electrochemical impedance spectroscopy, potentiodynamic polarization. In this work, molecular dynamics (MD) in the materials studio modeling environment was used to analyze the interface structures, and the interaction energy of the bisphenol-A (DGEBA) molecule anchored on the silicate layer of Na-MMT [5]. As the result, the epoxy nanocomposite with 80wt% Na-MMT and 20wt% $CoFe_2O_4$ showed better protection and prolonged lifetime than the other nanocomposites.

Keywords: *Organic Coating, AA 3105 Aluminium, EIS, Polarization, X-Ray Diffraction, Molecular Dynamics Simulation*

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Thermodynamics and Electrochemical Studies of Corrosion at Stainless Steel 316 by Aurin tricarboxylic acid ammonium salt in hydrochloric acid

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Abstract

The influence of the concentration of Aurin tricarboxylic acid ammonium salt the corrosion of 316 stainless steel (SS) in chloride acid 1M solutions was studied. The potentiodynamics polarization and scanning electron microscopy (SEM) have been used. The inhibition efficiency increased with an increase in the concentration of Aurin tricarboxylic acid ammonium salt.The adsorption of Aurin tricarboxylic acid ammonium salt onto the SS surface occure according to the Langmuir isotherm. The corrosion kinetic parameters of 316 stainless steel and thermodynamic adsorption parameters for Aurin tricarboxylic acid ammonium salt were determined and discussed.

Keywords: *stainless steel 316; Aurin tricarboxylic acid ammonium salt; Potentiodynamics polarization; Corrosion inhibition; Kinetic parameters*

Introduction, Experimental, Results and Discussion aouther

The Schiff base is an organic compound formed by the condensation of an amine and a carbonyl group having general formula of R_1 –CH = N– R_2 where R_1 and R_2 are aryl, alkyl, cycloalkyl or heterocyclic groups. The primary advantages of many Schiff base compounds are that they can be conveniently and easily synthesized from relatively cheap materials and those they are eco-friendly or exhibit low toxicity. These compounds in general are adsorbed on the metal surface blocking the active corrosion sites. Inhibition efficiency of an inhibitor depends on the number of adsorption active centers in the molecule and their charge densities, the molecule size, and the mode of adsorption on the metal surface.

The electrolytes were prepared using analytical grade HCl reagents (Merck). The testing material was stainless steel type 316. The 1-H-benzoteriazol was dissolved at concentrations in the range of 100 - 500 ppm in chloride solutions.

The polarization measurements were performed using an AutoLab PGSTAT 30 potentiostat.

The surface morphology of the specimens after immersion in 1M HCl solution in the absence and presence of Aurin tricarboxylic acid ammonium salt were tested on a Seron Technology-AIS2300C scanning electron microscope (SEM).

Activation parameters, Thermodynamic activation parameters have an important role in understanding the inhibitive mechanism of organic inhibitors. Activation parameters such as: the activation of energies (Ea), the enthalpy of activation (ΔHa), and the entropy of activation (ΔSa) were calculated from an Arrhenius-type plot:

$$j_C \quad = A\,e \quad \left(\frac{-E_a}{R}\right) \quad \text{A} \quad \text{t} \qquad - \text{s} \quad : \quad j_C \quad = \left(\frac{R}{Nh}\right)e \quad \left(\frac{\Delta S_a}{R}\right)e \quad \left(\frac{-\Delta H_a}{R}\right)$$

Adsorption of Aurin tricarboxylic acid ammonium salt from hydrochloric acid solutions onto the SS surface at the studied temperatures obeys a Langmuir adsorption isotherm which is representedby: $\frac{C_{i\ h}}{\theta} = \frac{1}{K_a} + C_{i\ h}$

From the intercepts of the straight lines on the Aurin tricarboxylic acid ammonium salt axis one can calculated, K_{ads} values that relate the standard free energy of adsorption by:

$$\Delta G_a^0 \quad = -R \quad \ln(55.5 \times K_a \quad)$$

Thermodynamically (ΔG^0_{ads}) is related to the standard enthalpy (ΔH^0_{ads}) and entropy (ΔS^0_{ads}) ofthe adsorption process according equation: $\Delta G_a^0 \quad = \Delta H_a^0 \quad - T\Delta S_a^0$

The standard enthalpy of adsorption can be calculated according to the Van’t Hoff equation:

$$l\!\!\;n\, K_a \quad = \frac{-\Delta H_a^0}{R}$$

Conclusion

The corrosion of 316 SS in a 1 M HCl solution is significantly reduced by addition of Aurin tricarboxylic acid ammonium salt. The Aurin tricarboxylic acid ammonium salt behaves as mixed type corrosion inhibitor. Langmuir adsorption isotherm exhibited the best fit to the experimental data. SEM micrographs showed that the Aurin tricarboxylic acid ammonium salt molecules form a protective film onto the SS surface.

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Evaluation of the properties of nanoclay/ $ZnFe_2O_4$ as epoxy coating of 3105 aluminium

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Abstract

The interest in magnetic nanoparticles and nanocomposites has greatly increased in recent years because of their broad applications in several technological fields and their relevance from the point of fundamental physics [1–3]. Nanoclay is one of the most affordable materials that have shown promising results in polymers. In recent years, epoxy/ clay nanocomposites have been noticed in coating due to their excellent properties, such as high-dimensional stability, reduced permeability and enhanced mechanical properties [4].

The present findings support the significance of epoxy nanocomposites in the protection of aluminum and its alloys by nanoclay/ $ZnFe_2O_4$ nanopowder. In this work, Crystalline $ZnFe_2O_4$ nanoparticles were prepared via sol-gel method. Furthermore, nanoclay/ ZnFe2O4 nanopowder were successfully synthesized by doping method. Then, epoxy-based nanocomposite coatings were applied to the synthesis of a series of nanoclay/ $ZnFe_2O_4$ nanopowder (Below 1%wt nano clay) in a wide range of compositions. Therefore, the epoxy nanocomposite coatings with various contents of nanoclay/ $ZnFe_2O_4$ nanoparticles were coated on the surface of an AA3105 aluminum specimen. X-ray diffraction (XRD) technique and ultraviolet–visible spectroscopy and Fourier transform infrared spectroscopy were used to investigate the structural properties of the samples. The morphology and composition of the films were probed by FE-SEM, EDS. The effects of addition of nanopowder on the corrosion resistance of the coating were studied by an electrochemical technique (potentiodynamic polarization and electrochemical impedance spectroscopy (EIS)). Impedance and Potentiodynamic polarization testing results, evidenced the improvement of the corrosion protection properties of the coatings in the presence of the formulations with superior anticorrosion of EF90.

***Keywords**: Magnetic Nanoparticles, Epoxy Nanocomposites, X-Ray Diffraction, EIS, Polarization*

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Corrosion behavior of nanocomposite PEO coatings on titanium fabricated in electrolyte containing penicillin

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Abstract

Nanocomposite coating was applied on commercial pure titanium (CP-Ti) using plasma electrolytic oxidation (PEO) process in phosphate electrolyte containing penicillin and alumina nanopowder. Effect of penicillin concentration on morphology and corrosion behavior of coating was investigated. The results revealed that the use of penicillin as an electrolyte additive increases the thickness of the PEO coating and reduces the passive current density.

Keywords: *Titanium, Corrosion, Plasma Electrolytic Oxidation, Nanocomposite, Penicillin*

Introduction

The use of titanium and its alloys are increasing due to excellent properties such as high strength to weight ratio, high melting point and biocompatibility [1]. PEO as a relatively new surface modification process can improve biocompatibility and corrosion resistance of titanium [2]. The aim of this study is to investigate the effect of penicillin G benzathine corrosion inhibitors as an electrolyte additive on morphology and corrosion resistance of PEO nanocomposite coating on CP-Ti. The effect of penicillin in the sodium phosphate based electrolyte containing alumina nanoparticle (as non-toxic additive) were evaluated.

Methods

PEO coating have been deposited on CP-Ti at constant current density in an aqueous suspension of alumina nanoparticle. Penicillin was used as an additive in electrolyte. α-Al2O3 nanopowders was investigated by transmission electron microscopy (Figure 1). The average particle size of the alumina is 22nm. In order to evaluate the effect of famotidine additive, concentrations of 1.5gr/L and 4.5 gr/L were used. Morphology of cross section of oxide coating was investigated by field emission scanning electron microscope. Corrosion resistance of coatings was evaluated after immersion in Ringer's solution. Cyclic polarization test with the scan rate of 1mV/sec was performed by using Potentiostat/Galvanostat.

Results and Discussion

SEM images of cross-section of the coatings in different electrolytes (Figure 2) reveal that by increasing the concentration of penicillin in the absence of nanopowders, coating thickness increased more than twice and reach to 10.1 µm. In the case of coatings containing nanopowder, by increasing the penicillin concentration, the coating thickness is halved and reach to 1.2 µm. Potentiodynamic cyclic polarization curves of coated samples in different electrolytes (Figure 3) show that all samples have a polarization curve with negative hysteresis which this behavior is features of most titanium alloys in this solution. The results show the presence of penicillin can partly reduce the corrosion current density, which can be due to increasing in coating thickness. According to the results, increasing the concentration of penicillin in the absence of nanoparticles reduces the passive current density and its presence leads to an increase in the passive current density. This is maybe due to thicker coating for samples with less concentration of penicillin [3].

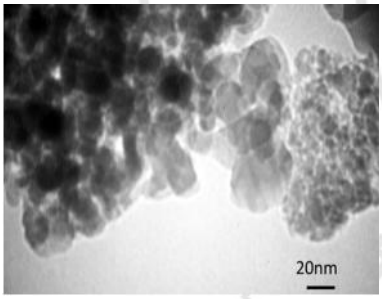

Fig. 1. TEM image of alumina nanopowder.

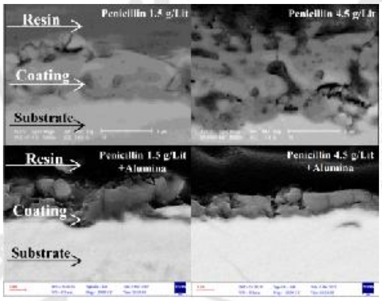

Fig. 2. FESEM images from cross-section of coated samples.

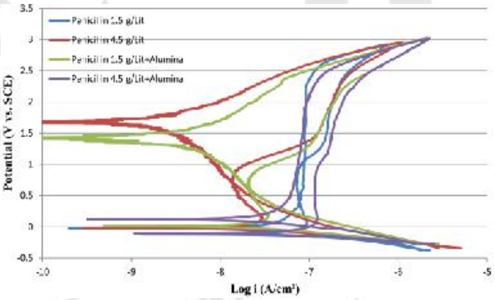

Fig. 3. Cyclic polarization curves for coated samples.

Conclusions

The use of penicillin as an electrolyte additive increases the thickness of the PEO coating. The presence of alumina nanoparticles with penicillin leads to a reduction in the thickness of the coating. The presence of penicillin can partly reduce the corrosion current density, which can be due to increasing in coating thickness. Increasing the concentration of penicillin in the absence of nanoparticles reduces the passive current density and its presence leads to an increase in the corrosion current density.

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Synthesis and characterization of soluble polyanline for Corrosion Protection of Carbon steel

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Abstract

Polyaniline (PANI) is a unique member of conducting polymers family due to its excellent mechanical and chemical properties [1]. These unique properties made PANI a suitable candidate for different technological applications such as corrosion protection of metals [2].Despite its good characteristics PANI has the drawback of poor processability and solubility in commonly used organic solvents. This limits the application of PANI to its full potential [3]. In this work an easily soluble PANI was formed via emulsion synthesis method. In this method different amounts of Dodecylbenzenesulfonic acid (DBSA) was used as emulsifying agent. In this procedure optimized concentrations of aniline (0.5 M) and DBSA (0.1 M) were dissolved in 50 ml of chloroform and vigorously stirred. 30 minute later 50 ml solution containing phosphoric acid (1 M) and ammonium persulfate (0.6 M) was slowly added to previous solution. Stirring was continued for 1 hour in room temperature. After that a green PANI containing DBSA was formed in the solution. The solvents were evaporated in an oven over night and obtained PANI-DBSA powder was thoroughly washed with deionized water. This green powder was first characterized using Energy-dispersive X-ray spectroscopy (edx) and X-ray diffraction spectroscopy (XRD) and then used to formulate an anti corrosion coating based on epoxy resin matrix and xylene as a solvent for epoxy resin. Different carbon steel samples were prepared using this formulation included bare carbon steel electrodes, electrodes with epoxy coating and electrodes with different percent of PANI-DBSA in resin matrix. Corrosion protection performance of samples was investigated in a three electrode cell containing Ag/AgCl and platinum disk as reference and counter electrode respectively in NaCl 3.5% as electrolyte solution. These test proved that PANI-DBSA has high potential in corrosion protection of carbon steel. As it can be seen in Fig.1 Tafel polarization showed a 0.2 V potential change toward more noble potentials in case of 0.1 gr of PANI-DBSA mixed with 3.6 gr of resin. Electrochemical impedance spectroscopy was also used

to evaluate coatings performance. The results showed a relatively smooth surface with very high resistance is formed on carbon steel electrodes. In conclusion we prepared and examined a processable PANI derivate with good corrosion protection performance.

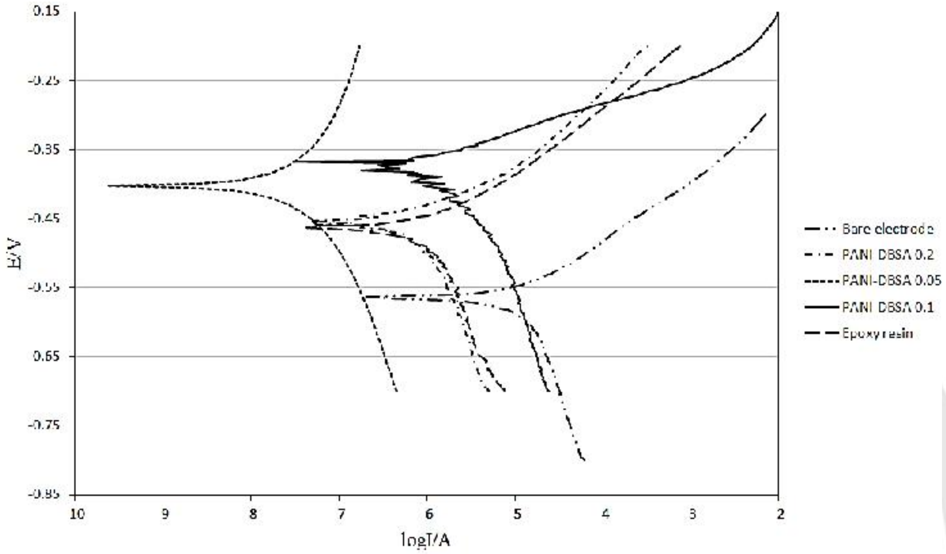

Fig.1: Tafel polarization plots of different carbon steel samples in NaCl 3.5% solution.

Key words: *Emulsion synthesis PANI-DBSA, Epoxy resin, Corrosion protection, Carbon steel,.*

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Electrochemical study of a novel schiff bases as a corrosion inhibitor for galvanized steel in 1M hydrochloric acid

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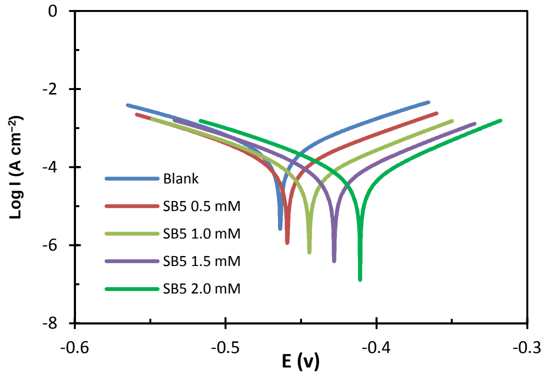
Abstract

The use of inhibitors is the most important method for protecting metals from corrosion. Some Schiff base compounds have been reported as effective corrosion inhibitors for mild steel and other metals [1]. The efficient adsorption is the result of either the π-electron of the aromatic system and multiple bonds, or the presence of electronegative atoms (O or N) in the inhibitors molecular structure [2]. Availability of π electron would facilitate electron interact with d-orbital of iron [3, 4].In this work, the corrosion inhibition effect of new synthesized Schiff bases were investigated using potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and gravimetric methods.The results show that the inhibition by the Schiff baseswere attributable to the adsorption of the Schiff base moleculeson galvanized steel electrode.

Keywords: Corrosion inhibitor, Schiff base, electrochemical impedance spectroscopy (EIS), Polarization.



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EIS study of nanoAlumina-polyester nanocomposite coatings and the effect of curing type on the corrosion properties

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Abstract

In this study, polyester coating and polyester-10%wt Al_2O_3 nanocomposite coating were applied on carbon steel substrate by electrostatic device and were cured in two different regime: microwave and oven. Morphology of nanoparticles was investigated by TEM and morphology of Coatings was evaluated by SEM. the effect of curing type and adding Alumina nanoparticles on corrosion properties was studied by EIS. Results indicate a significant increase in corrosion protection performance of nanocomposite coatings than pure polyester coatings and better corrosion resistance for nanocomposite coatings cured in microwave.

Keywords: *Nanocomposite, EIS, NanoAlumina, Electrostatic.*

Introduction

In this paper, polyester coating as the matrix was combined with 10wt% of Al_2O_3 nanoparticle and polyester-based nanocomposite was formed. The objective of this research is to improve the corrosion resistance properties and increase the service life and study the effect of adding Alomina nanoparticles to coating.

Experimental

SEM[1] image of polyester powder (10-70 µm, iranian Company) and TEM[2] image of Al_2O_3 nanoparticles (15-30 nm, commercial type) is shown in Fig. 1. Production of nanocomposite powder coating was performed in 2 steps: dispersing nanoAlomina and polyester in distilled water by ultrasonic homogenizer, drying the created solution and finally ball milling. Electrostatic device was used to apply powder coating on steel panels. Coatings were cured by microwave (referred as PM for pure polyester and PAM-10 for nanocomposite coating) and oven (denoted by PC for pure polyester and PAC-10 for nanocomposite coating) for the appropriate time. The thickness of all coatings is almost 65±10 µm. Corrosion protection

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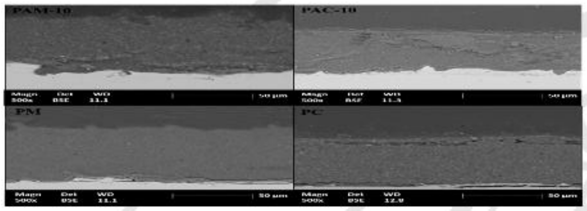
[1] Scanning electron microscope
[2] Transmission electron microscope

properties was investigated by EIS[3] test that was performed by EG&G Potentiostat-Galvanostat equipped with Frequency Response Analyser. All tests have been carried out in open circuit potential.

Results and Discussion

Fig.2 shows SEM micrograph of cross section related to polyester and nanocomposite coatings. SEM images of the cross section of nanocomposite coatings containing 10%wt nanoAlumina represents a homogeneous structure, no cracks, good adhesion to the substrate and almost compact for PAM-10 and PAC-10.



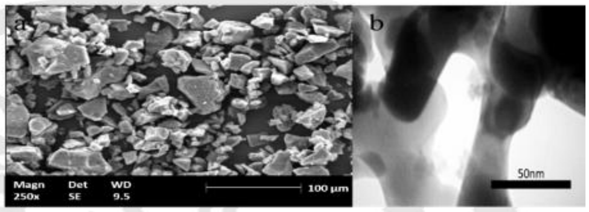


Fig 1. (a) SEM image of pure polyester powder, (b) TEM image of nano Alumina **Fig. 2. SEM images from cross-section of coated samples.**

Nyquist diagrams of coated steel samples after one hour immersion in 3.5% NaCl solution is presented in Fig. 3. Due to features of the coated metal, an equivalent electrical circuit with 2 time constant was used to analyze EIS data. Impedance parameters calculated is shown in Table 1. Corrosion resistance of the coating can be explained inversely with the rate of corrosion [3]. As is clear from Table 1 and Fig. 3, corrosion resistance of PAM-10 and PAC-10 nanocomposite coatings is markedly higher than PM and PC coatings. It can be argued that the presence of nanoparticles in the coating has a positive effect on both coating resistance and coating capacitance due to the delays in the penetration of water, oxygen and ion components through the coating contains nanoparticles. Also corrosion properties of nanocomposite coatings cured in microwave is better than samples cured in oven. A comparison of the results for nanocomposite sample determined that condition of curing in microwave was better than curing in oven, and high curing percent and more crosslinking were achieved for samples cured in the microwave

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[3] Electrochemical impedance spectroscopy

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Fig 3. Fitted Nyquist impedance spectra of coated

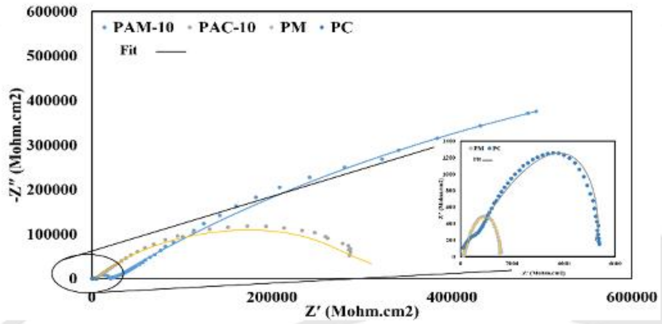

Table 1. Impedance parameters obtained by fitting of Nyquist diagrams.

Samples	C_{coat} (F/cm^2)	R_{coat} (Ωcm^2)	C_{EDL} (F/cm^2)	R_{corr} (Ωcm^2)
PAC-10	1.5*10^{-9}	25632	1.46*10^{-6}	1.7*10^{6}
PAM-10	1.13*10^{-9}	160230	1.3*10^{-6}	442040
PC	1.8*10^{-7}	5204	4.1*10^{-6}	26630
PM	3.6*10^{-7}	98	1.7*10^{-4}	2927

Conclusion

The absence of pores and flaw in nanocomposite coatings, as well as creating a barrier against corrosive electrolytes penetration leads that corrosion resistance properties of nanocomposite coating will be higher than the pure coatings. In general it can be concluded that the presence of nanoparticles will be effective greatly to increase the corrosion protection properties of polyester coating.

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Investigation of corrosion protection properties of SiAlON-epoxy nanocomposite coatings

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Abstract

In this study, the effect of adding 10wt% and 20wt% SiAlON nanoparticles in epoxy powder to improve anticorrosive properties of the nanocomposite powder coatings was investigated. Morphology of SiAlON nanoparticles and coatings were evaluated by TEM and SEM respectively. Results of Tafel and immersion test indicate that SiAlON nanoparticles have important role in improving the protective properties. Also Penetration of the electrolyte through the coatings is decreased significantly in coating with 10wt% SiAlON.

Keywords: *Nanocomposite, Tafel, Immersion test, SiAlON nanoparticles, Electrostatic.*

Introduction

In this paper, the effect of SiAlON nanoparticles to corrosion properties of epoxy powder was investigated. The main purpose of adding SiAlON nanoparticles to the epoxy powder is evaluation of possible increasing in corrosion protection of coatings. By performing Tafel and immersion tests on the coated samples, observed that by adding SiAlON nanoparticles, resistance to corrosion will improve greatly.

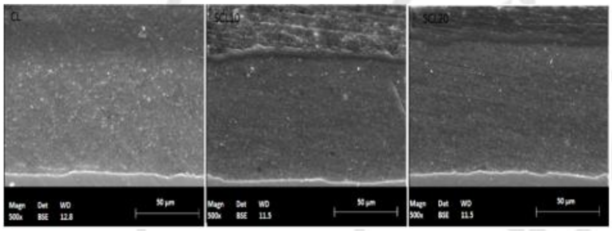
Experimental

Scanning electron microscope (SEM) micrograph of pure epoxy powder (10-70µm, Iranian Company) as well as transmission electron microscopic (TEM) image of SiAlON nanoparticles (15-30nm, commercial type) are shown in Fig. 1. Production of nanocomposite powder coating was performed in 2 steps: mixing epoxy powder with 10 & 20wt% SiAlON nanoparticles in turbo mixer and then ball milling. To apply powder coating on steel panels, electrostatic device was used. Coatings were cured by oven that denoted by CL for pure epoxy and SCL10 and

SCL20 for nanocomposite coating respectively. The thickness of all coatings is almost 70±15 µm. Corrosion resistance was studied by Tafel and immersion tests. Tafel test was performed in the potential range of -250mV to + 250mV versus open circuit potential (OCP) by EG&G Potentiostat-Galvanostat device with using three-electrode systems that immersed in 3.5% NaCl solution.

Results and Discussion

Fig.2 shows SEM micrograph of cross section of epoxy coating and nanocomposite coatings on the metal substrate. As shown, nanocomposite coatings (SCL10 & SCL20 samples) represent a homogeneous structure, no cracks, good adhesion to the substrate and almost compact in comparison with CL sample.



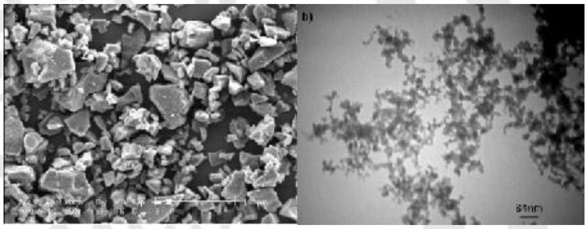


Fig 1. (a) SEM micrograph of pure epoxy powder, (b) TEM image of SiAlON nanoparticle. Fig. 2. SEM micrograph of cross-section of coated samples.

As shown in Fig. 3, OCP values of the coating contains nanoparticles over the time is more positive than pure epoxy coatings. Immersion test results show that with the passage of time, penetration of corrosive solvent in the nanocomposite coatings is less than pure coating[1]. As shown in Fig. 4, corrosion current density of nanocomposite coatings is lower than pure epoxy coatings and they will have higher polarization resistance, so exhibits better corrosion resistance. Therefore, nanoparticles improves the corrosion behavior by filling surface defects such as cavities, holes and cracks, and acts as a barrier against penetration of corrosive ions[2]. As is clear from the Tafel diagrams, SCL10 sample, provided excellent corrosion protection performance than pure epoxy coating. The reason for higher corrosion resistance of coating contains nanoparticles can be found in delay created for penetration of water, oxygen and ionic components through coating[3]. Lower corrosion resistance of SCL20 than SCL10 sample could be due to agglomeration of nanoparticles in epoxy matrix and thus reduce the barrier effectiveness of them.

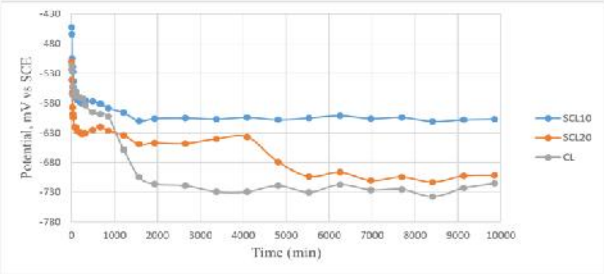


Fig 3. OCP changes compared to the immersion time for different samples.

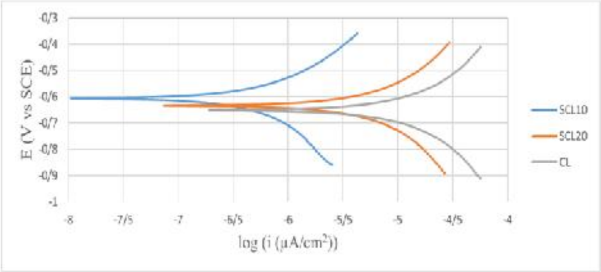


Fig 4. Polarization curves for coated samples

Conclusion

Incorporation of SiAlON nanoparticles in epoxy matrix leads that nanocomposite coating are denser, more uniform and with less pores in comparison of pure epoxy coating. Corrosion resistance properties of nanocomposite coatings will be higher than the pure coatings because of barrier properties against corrosive electrolytes penetration and lower pores and flaw in these coatings.

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Electropolymerized coatings of polyaniline-CNT on stainless steel 310 and their corrosion protection performance in chloride environment

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Abstract

Stainless steel 310 (SS 310) is widely used in many fields due to its good corrosion resistance as well as its mechanical properties. The resistance to corrosion in aqueous media is attributed to the presence of a thin protective chromium-enriched oxide film. Several strategies have been used to generate more protective interfaces on stainless steels, including the use of conducting polymers [1, 2]. In this work, homogeneous, uniform and adherent polyaniline-carbon nanotube (PANI-CNT) nanocomposite coatings were electrosynthesized on SS 310 by using the current density fixed in the under galvanostatic conditions method. The synthesized coatings were characterized by Fourier transform infrared spectroscopy (FT-IR), SEM and UV-Vis spectroscopy. Optical absorption spectroscopy shows the synthesis polymers of the emeraldine state that is suitable for a corrosion purposes. The corrosion performances of coatings were investigated in 5000 ppm NaCl solution used by the potentiodynamic polarization technique and electrochemical impedance spectroscopy (EIS).

The current corrosion decreases significantly from 140.39 μA cm^{-2} for blank electrode SS 310 to 0.27 μAcm^{-2} for PANI-CNT nanocomposite coatings, under optimal conditions. Also, the potential corrosion increases from -386.42 mV versus Ag/AgCl for blank electrode SS 310 to -40.19 mV versus Ag/AgCl for PANI-CNT nanocomposite coated stainless steel electrodes under optimal conditions. The results of this study clearly ascertain that the PANI-CNT has outstanding potential to protect the SS 310 against corrosion in a chloride environment.

Keywords: *Nanocomposite, Electrochemical synthesis, Corrosion, Stainless steel 310*

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Effect of ultrafine-grained structure on the electrochemical behavior of 1050 aluminum alloy

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Abstract

In this study, the effect of ultrafine-grained (UFG) structure on the passivation behavior of 1050 aluminum alloy in a borate buffer solution (pH=5.5) has been investigated. UFG sample was fabricated by accumulative roll bonding (ARB) technique as a severe plastic deformation process for the industrial production of UFG and nano structure sheets with excellent mechanical properties. X-ray diffraction pattern (XRD) and Atomic force microscopy (AFM) were used for determination of microstructure and grain size refining after 7 cycles of ARB process. Passivation behaviors of annealed sample compared to 3 and 7 cycles number of ARBed samples by using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) after 2 h immersion in test solution. The potentiodynamic polarization plots revealed that the higher number of cycles for samples processed with the ARB method rather than annealed sample yield to lower corrosion and passive current densities and more noble corrosion potential values. Moreover, electrochemical impedance spectroscopy (EIS) measurements showed that increasing the number of ARB cycles offer better conditions for forming the passive film. Compared to annealed sample, it was found that passivation behavior of the ARBed samples improved and their grain size decreased.

Keywords**:** *Al alloy, UFG, ARB, Passive film.*

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Simultaneous Removal of Heavy Metals from water: Effect of pH and Removal Time

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Abstract

Recently many scientists are focused on removal of pollutants from wastewater. Toxic Heavy metals have harmful and hazardous effects on human health and ecology. Up to now several methods such as chemical precipitation, ion-exchange, membrane filtration, adsorption, electrochemical treatment have been used to remove toxic heavy metal ions from wastewaters and minimize their health risks. Although all of these techniques can be employed for wastewater treatment, they also have some inherent advantages and limitations [1-3]. Antimony is one of the toxic metals and has much concern in terms of toxicological and environmental. Antimony has been extensively used in power transmission equipment, alloys, batteries, cable sheathing, and bearing metal. Among the most important uses of antimony in nonmetal products are ceramic enamels, paints, textiles, rubber compounds, glass and pottery abrasives phosphorus, and certain types of matches. Antimony and its compounds were listed as priority pollutants by the united states environ- mental protection agency and the european union due to its toxicity and implication in cancer development [4-6]. Antimony exists in environment as a result of natural processes and human activities [7-10]. The toxicological effects of antimony depend on its chemical form and oxidation state. In the environmental samples, antimony exists mainly in the pentavalent and trivalent oxidation states. The Sb(III) compounds have ten times higher acute toxicity than the Sb(V) species [4-6]. Lead is another toxic heavy metal and its toxicity is well established. All over the world guidelines set the maximum acceptable concentration of lead in drinking water at very low levels [11]. In this study, the simultaneous removal of both antimony and lead from water has been studied by iron sacrificial plates. The effect of removal time and pH of the water sample on removal of heavy metal ions has been

investigated. Scanning electron microscope images of the precipitate obtained after water treatment show the formation of small nanoparticles with this method. Inductively coupled plasma–mass spectrometry results showed that the concentration of antimony and lead in water depends on both time and pH of the water. Based on these results we found that the pH of water and the removal time play important role on removal efficiency. We suggest this easy, inexpensive, high efficiency, and promising method for removal of heavy metals from water.

Keywords: *Antimony, Lead, Water treatment, Nanoparticles.*

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The influence of high nitrogen austenitic surface layer formation on the corrosion resistance of Fe-23Cr-2.4Mo ferritic stainless steel

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Abstract

In the work the corrosion resistance of ferritic- austenitic dual layer steel composed of ferritic core and nickel-free high nitrogen austenitic stainless steel (HNASS) sell, in 0.5M H_2SO_4solution was investigated and was compared with the initial ferritic and conventional 316L austenitic steels. Austenitic high nitrogen layer was produced by high temperature gas nitriding if initial ferritic steel at 1200°C for 2 hour. Corrosion resistance was investigated by recording open circuit potential, potentiodynamic polarization curves and electrochemical impedance spectra. Results showed that HNASS steel has a high general corrosion resistance compared with the intial ferritic and conventional 316L Austenitice stainless steels which was related to the formation of the thicker protective passive film on the HNASS steel.

Keywords: *ferritic- austenitic dual layer steel, nickel-free high nitrogen austenitic stainless steel, open circuit potential, potentiodynamic polarization, electrochemical impedance spectra, general corrosion resistance*

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Hydride cracking of zirconium alloys

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Abstract

Hydride cracking in Zirconium alloys is one of the major causes of failure and considering the importance of this type failure we have reviewed the situation that makes Zirconium alloys vulnerable to cracking. The results show that most of atomic hydrogen is produced in normal corrosion process albeit; absorption depends on various factors. The recent investigations revealed that, radial hydrides are more disastrous compared to circumferential hydrides.

***Keywords**: corrosion, Hydride, cracking, zirconium*

Introduction

Although Zirconium has a very low solubility, once the solubility limit is surpassed, hydrogen precipitates as a zirconium hydride phase[1]. As a result, the following effects have been reported to occur in the cladding: hydrogen embrittlement, delayed hydride cracking (DHC), and acceleration of corrosion and of irradiation growth[2]. The ductility reduction due to hydrogen embrittlement is dependent on the volume fraction of hydride present, the orientation of the hydride precipitates in the cladding, and their degree of agglomeration[3].

Discussion

Absorption of hydrogen is a major contributor to degradation of zirconium alloys during service. This degradation is primarily attributed to the formation of zirconium hydrides thus enhancing the susceptibility to cracking. Recent studies have also shown that the addition of hydrogen can increase the creep rates in Zr–2.5Nb and possibly irradiation growth[4]. The hydrogen can be provided from a variety of sources. The oxide itself generally presents an effective barrier to the absorption of hydrogen such that the structure of the oxide and the electron transport mechanism can be linked to hydrogen uptake. There is some evidence that the nickel content in Zircaloy-2 increases the absorption of hydrogen, either by supporting direct dissociation of water or by mitigating recombination of hydrogen and oxygen. This was one reason why the nickel was removed in the formulation of Zircaloy-4. Specifically, the electron current increasing applied load. The hydrides, if formed, can be circumferential or radial. The embrittlement is influenced by the orientation of hydrides relative to the stress. Hydrides that are oriented normal to the tensile load enhance embrittlement provide an easy path for the growth of cracks through the hydrides[5]. Radial hydrides are of greater concern, as they are oriented perpendicular to the hoop stress that arises during operation. The classic theory of DHC comes from the work of Dutton and Puls. The basis of the theory is that the crack tip hydride grows as hydrogen migrates from hydrides in the bulk of the material to the crack tip[6].

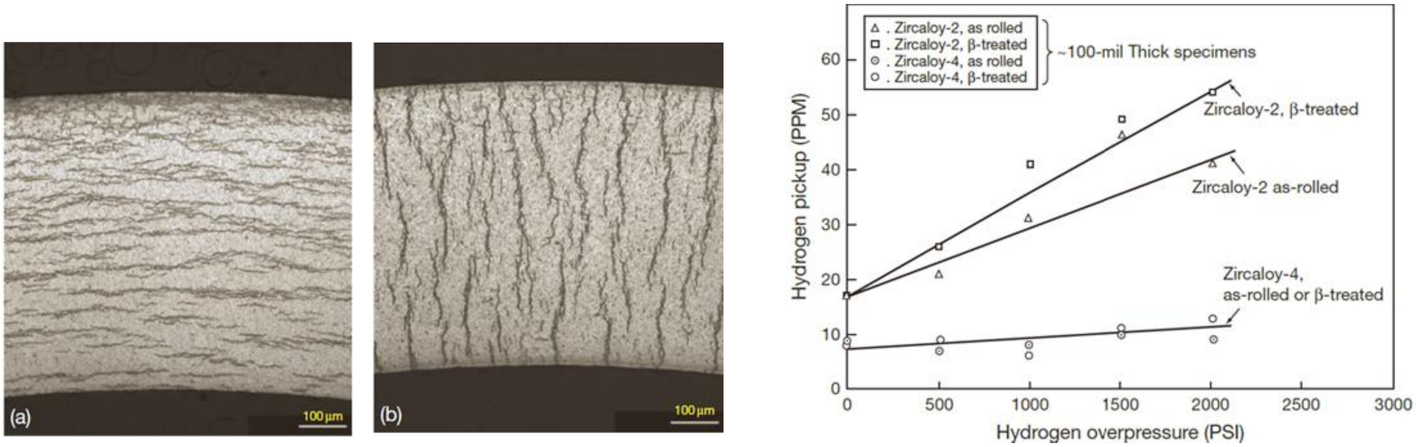

Figure1:(a) Circumferential and (b) radial hydrides (c) Hydrogen pickup in Zircaloy-2 and Zircaloy-4[2].

Conclusion

Zirconium alloy undergoes corrosion when subjected to the environment. The corrosion is related to the oxidation and is associated with hydrogen uptake into the cladding. The hydrogen pickup fraction can vary from alloy to alloy and for different environments and corrosion times. The hydrogen pickup mechanisms and the influence of the alloy on the process are still under study.

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Influence of Multi- walled Carbon Nanotube Addition on the Zinc-Rich Paint Coating Corrosion in NaCl solution

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Abstract

Zinc-rich paints (ZRPs) are one of the most effective coatings used to protect steel from corrosion [1]. They are used in many aggressive medium: sea water, marine and industrial environments. For solvent-based zinc-rich paints, it seems to be established that, at least at the beginning of immersion, zinc particles provide a cathodic protection of the steel substrate [1,2]. Then, a long term protection develops due to the formation of zinc corrosion products, reinforcing the barrier affect of the paint [1, 3].

The effect of addition of conductive pigments like multi-walled carbon nanotubes on the corrosion behavior of zinc-rich paints (ZRP) coated steel in 3.5% NaCl solution was investigated. Open circuit potential measurements were used to characterize the cathodic protection ability and duration. Electrochemical Impedance spectroscopy and Tafel analysis was performed in order to identify the corrosion rate and to follow the corrosion mechanism. Also, the Scanning Electron Microscope (SEM) analysis was used for study the morphology changes in the coating due to corrosion. Two different effects were pointed out: increase of the porosity induced by multi-walled carbon nanotubes addition and a galvanic action between zinc and multi-walled carbon nanotubes.

Keywords: *zinc-rich paint; Corrosion; Electrochemical Impedance spectroscopy; Multi-walled carbon nanotubes; Tafel.*

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Influence of composition and process conditions on corrosion of Pb-Sn-Ca Alloys in Lead- Acid battery positive grid

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Abstract

In the recent years, Pb-Sn-Ca as dominant alloy uses for production of lead-acid battery positive grid. Regards on corrosion phenomenon as one of the most critical battery aging ingredient, the effects of alloying elements and process conditions on corrosion properties of positive grid have been studied.

This study has been done on the Pb-Sn-Ca alloy which produced by different percentage of tin and calcium, also different rolling temperatures and cooling rates. For quantitative analysis, microstructure characterizing and tafel polarization test, quantometer, optical microscope and IVIUMSTAT device have been used respectively. The results have been shown that reduction in calcium and increasing in tin, led to the corrosion properties improvement. Similarly enhancement of cooling rates and decreasing in rolling temperatures had significant effects on corrosion resistance increment.

Keywords: *Corrosion, Lead-Acid battery, Pb-Sn-Ca alloy, Rolled grids*

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Study of effect of super hydrophobicity on corrosion resistance

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Abstract

Corrosion is the decaying or destruction of a material due to chemical reactions with its surroundings. In other words, corrosion is the wearing away of metals due to a chemical reaction. Super hydrophobic coatings on metallic substrates have shown, during the past two decades, remarkable corrosion resistance in highly aggressive media.

Keywords*: *Corrosion, super hydrophobic, contact angle

1- Introduction

In 1997 two German botanist, Neinhuis and Barthlott, using SEM discovered the two scaled structure of the lotus leaf and investigated its chemical composition. That study was a revolution revealed two important guidelines for researchers who study on super hydrophobic surfaces. First one is the roughening of the surface of materials with low surface energy and the second one is modification and creation of the rough surfaces using low surface energy materials. So the unusual surface wettability in the nature can be created by controlling the microstructure of the geometry of the surface and low surface energy. After that discovery (by German scientists) a lot of research and review articles related to the super hydrophobic surfaces were published, which they explained the applications of the super hydrophobic surface in the day life. In many reviews and research articles the “Lotus Effect” was investigated and the Micro/Nano scaled structure was suggested to create and develop super hydrophobic surfaces[1].

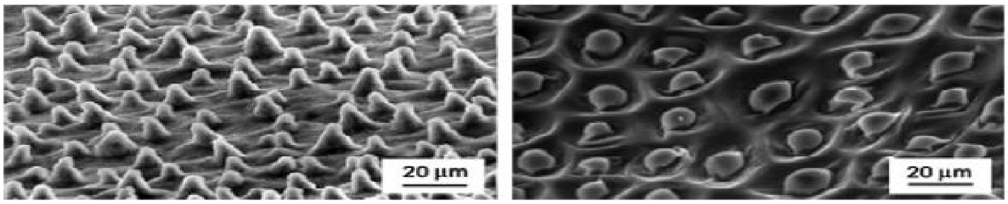

Fig1- Micrographs of two hydrophobic leaves, lotus (left) and Colocasia esculenta (right)[2].

2- Theory

2-1- wettability on rough surface

The effect of surface roughness on wettability was discussed by Wenzel in 1936 and later by Cassie and Baxter in 1944. Wenzel suggested that when a surface becomes rough, the area of the effective surface increases which results in the more tendency of water to be more widespread on the hydrophilic surface and increased the contact of liquid and the surface; While spreading on the rough hydrophobic surface decreases in order to decrease the contact angle[3].

2-2- Contact angle Hysteresis

Another parameter in addition to the contact angle, which is measured in the static state, is needed to specify the wettability.The hysteresis of the contact angle is the difference between the advancing contact angle (θ_a) and receding contact angle (θ_r), which appears due to the roughness and the heterogeneity of the solid surface[4].

2-3- Contact angle and corrosion resistance

Corrosion of metals in the electrolyte is dependent on the surface reactions and any agent which repels the corrosion agents or reduces the reaction rate can increase the corrosion resistance; for example, inhibitors that reduce the contact surface or the coatings which reduce the contact surface and increase the resistance as well. One of these agents is the contact angle of the water on the surface. A lot of studies investigated the effect of super hydrophobic contact angle on the corrosion rate[5]

2-4- State-of-the-art studies on corrosion resistant coatings using super hydrophobic coatings

Some authors summarized that the current state-of-the-art studies on anti-corrosion using super hydrophobic coatings. Although the idea of using the air retained on the super hydrophobic surface as a passivation layer is promising as a new efficient anti-corrosion scheme, potentially superior to the other conventional methods, it should be noted that all the super hydrophobic surfaces tested thus far were based on irregular Coatings resulting in a random surface roughness in micron Scale[6, 7].

Conclusion

Many techniques of preparing such surfaces, as well as various methods of characterization and analysis were applied, but the conclusion was the same and it states that super hydrophobic coatings prevent metallic substrates from corrosion. The air retained on such super hydrophobic surface can prevent corrosive processes

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A Study upon the Corrosion Behavior of MoC-Co-Nb Alloys in the Bromide Media

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Abstract

It's known that hard metals are sintered composites of metal-ceramic powders. In this case, the mixtures of one or more finely divided hard carbides particles, such as tungsten, molybdenum, titanium, tantalum, and vanadium, embedded in a matrix of soft and ductile binding materials such as cobalt, iron, or nickel. These metals are hard and have very good wear resistance, and this make them suitable alloys in several industrial applications, such as cutting tools or seal rings, linings, valves, jet nozzles, saw blades, fluid mixers, and conveyor belt scrapers. A series of MoC-Co-Nb alloys was evaluated in different bromide containing media to investigate their corrosion resistance. Standard electrochemical corrosion tests, chronoamperometric measurements, and surface analyses with Raman spectroscopy were conducted. An increasing amount of Nb improves the corrosion resistance of all the alloys. The effect is not as dramatic as that observed with stainless steels containing Nb in corrosive media. In both corrosive media Nb decreased the cathodic Tafel constant and has a retarding influence on the cathodic part of the corrosion reaction. Raman analyses indicated the presence of molybdenum oxide, hydrated molybdenum oxide compounds, and CoO and Co_3O_4 formed on the alloy surfaces during the corrosion process.

Keywords: *corrosion, electrochemical, alloy, SEM*

1. Introduction

Although, this fact is very well known that corrosion resistance is not a prime requirement of hard metals. This property is very important in its industrial uses. Since the cobalt binder phase is the most susceptible to corrosion in acidic and neutral media, it follows that improvement of the corrosion resistance of the binder will have a major influence on the overall corrosion resistance. In principle, Co-based cemented carbide does not passivate. Aggressive media preferentially attack the binder while the molybdenum carbide itself remains immune [1]. Corrosion attack proceeds predominantly at different locations [1,2].

2. Experimental Methods

2.1. Scanning Electron Microscopy (SEM). Morphological and qualitative analyses of the samples were performed using scanning electron microscopy (SEM) equipped with energy dispersive spectroscopy (EDX). The SEM provided information on the physical properties and morphology of the materials, while EDX provided information on their chemistry.

2.2. Raman Spectroscopy. In order to identify the thin surface films (corrosion products) at high resolution, Raman spectroscopy was used. A laser source of Ar^+ was used to capture the scan patterns at room temperature, whereas the image on the surface of the alloy was captured, with a light microscope. The samples were scanned from 105 to 2545 cm^{-1} wavenumbers, with a resolution of 4.12 cm^{-1} .

3. Results and Discussion

3.1. Sodium Bromide (1 M NaCl) Electrolyte

3.1.1. Open Circuit Potential (OCP). The variations in the open circuit potential values of the samples measured for two hours in 1 M sodium bromide are confirmed . It was observed that the open circuit potential values of the samples were unstable and showed random fluctuations in their curves. The alloy containing 3.0 wt% Nb content had the highest (more noble) starting potential when compared to the other alloys containing lower ruthenium contents. However, as the time progressed, the potential dropped and this alloy stabilized at a slightly lower potential compared to the alloys containing 1.5 wt% Nb and 2.0 wt% Nb. It is not clear why the alloy with 3.1% Nb has a slightly lower final potential than the one with 1.54% and 2.1%, but the variation is small and within the experimental variation often observed.

3.2. Synthetic Mine Water

3.2.1. Open Circuit Potential (OCP). The variation of the open circuit corrosion potentials (OCPs) of the MoC-Co-Nb/VC alloys for the period of two hours after exposure to synthetic mine water is obtained. The reference alloy containing 0 wt% Nb revealed the lowest OCP values when compared to the other alloys. It was observed that as the amount of ruthenium increased, the potential values slightly increased. However, there was a drastic increase in potential values of the alloy containing 3.1 wt% Nb stabilizing at the positive potential of 0.03 V. The potential values at 7200 s illustrate that the alloys with increasing amounts of the niobium are nobler than the one without niobium and the one containing VC. Selected micrographs of some of the microstructures, along with the chemical composition of the various elements observed on the surfaces of the alloys after exposure to synthetic mine water, are given in Figure 1.

4. Conclusions

All the alloys evaluated experienced more corrosion in the sodium bromide alone than to the synthetic mine water solution, which consists of a mixture of bromide and sulphate salts, albeit at lower amounts. An increasing amount of Nb improves the corrosion resistance of all the alloys, although the effect is not as dramatic as that observed with stainless steels containing Nb that were placed in corrosive media. Nevertheless, the decrease in corrosion rate in sodium bromide and synthetic mine water is spectacular for the two alloys containing the highest amounts of Nb (2.1 and 3.1 wt%, respectively.) when compared to the other alloys and especially the base one without any Nb. The alloy containing VC has a lower corrosion resistance in synthetic mine water than the one with a similar amount of Nb. SEM micrographs indicated that crystalline corrosion products formed on all the alloys exposed in the two bromide media. In the case of the sodium bromide solution, these were sodium bromide crystals, while the salt-like crystals detected on the various alloy surfaces exposed in synthetic mine water were rich in sulphur, oxygen, and chlorine, thus implying the crystallization of bromide and sulphate type salts on the alloy surfaces.

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Figure 1: SEM micrograph of the 0.4 wt% VC containing alloy after exposure to synthetic mine water solution

Study of cathodic disbondment mechanism from the electrochemistry point of view

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Abstract

The cathodic disbondment (CD) of organic coatings is a continual problem in applications of cathodically protected steel in civil infrastructure and petrochemical production and transportation. Multiple researchers have proposed that the degree of disbondment is a function of factors such as service temperature, coating thickness and applied cathodic potential. While the mechanism by which disbondment occurs has received a fair amount of attention the objective of this paper is to Study of cathodic disbondment mechanism from the point view of Electrochemistry.

Keywords: *Cathodic disbondment, Electrochemical, Organic coating.*

1-Introduction

The cathodic disbondment process is a complex and multi-stage phenomena. Several explanations have been reported in the literature with regard to the time necessary to initiate, propagate and grow cathodic delamination. Watts and Castle suggested a two-stage theory of disbondment. The first stage is dissolution of the metal oxide following a logarithmic rate. The second stage is due to the failure at the metal oxide/polymer interface at a linear rate [1]. A third stage reported by Higgins that suggests a change in the failure kinetics from metal oxide/polymer degradation, although the reasoning is still a bit unclear [2]. Since, in general one of the most important cause of corrosion is electrochemical process, so here we want to study the effect of electrochemical process on the cathodic disbondment.

2- Electrochemical study

The major driving force for cathodic delamination is electrochemical processes in the presence of air (Oxygen reduction): $H_2O + \frac{1}{2}O_2 + 2e^- = 2OH^-$ (1)

When a stronger potential is applied, another the important reaction may be initiated (Hydrogen evolution): $2H^+ + 2e^- = H_2$ (2)

At a potential of -0.8V the dominant reaction is oxygen reduction and at potentials more negative than -1V (vs. SCE) the dominant reaction is hydrogen evolution [3]. Polarization at -0.8V (vs. SCE) of polymer-coated steel containing a defect in the absence of oxygen leads to no significant delamination from the defect, whereas in the presence of air there is significant delamination [3, 4].

2-1- Cathodic potential

The application of more negative cathodic potentials yields a more severely alkaline environment leading to higher disbondment areas of organic coatings. Steinsmo and Skar showed that decreasing the cathodic potential from -1.0V (vs. SCE) to -1.4 V (vs. SCE) increased the disbonding rate 1.6 times [5]. A similar experiment by Jin et. al. reported an increased disbonding rate of nearly 2 times [6]. Generally, the minimum potential required for immunity of the steel substrate should be applied for cathodic protection.

2-2- Electrolyte and pH

Cathodic disbondment does not occur in the absence of oxygen or when the applied potential is maintained in the range where the oxygen reduction reaction is the predominant cathodic reaction [7]. Disbondment of organic coatings of cathodically protected steel is typically the result of high pH at the coating/metal interface generated from oxygen reduction reactions. While this is a widely excepted cause of CD, the direct mechanism by which high pH destroys the integrity of the coating is a bit more uncertain [7].

2-3- Anion and Cation migration

Anion diffusion plays a limited role in the CD process because the metal surface already has contact with negative OH^- ions due to the cathodic electrochemical reaction [8]. Negatively charged hydroxyl ions are the product of the oxygen reduction reaction occurring on cathodically protected steel surfaces. These anions (hydroxyls and peroxides) seek to be balanced by cations which may dissociate from the soil environment or immersion electrolyte [9].

3-Conclusions

The nature of the environment surrounding a buried pipeline has an important effect on the rate of cathodic disbondment. Covering the metal surface with a non-conductive layer, such as a phosphate, reduces the availability of electrons for the cathodic reaction and can minimize the disbondment of organic coatings.

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Physioelectrochemical Study on the Inhibition of Copper Corrosion in Acidic Solution by Newly Synthesized Organic Compound

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Abstract

Copper has wide applications in industry owing to its high electrical and thermal conductivities, mechanical workability, and its relatively noble properties. It is employed extensively for condensers, evaporators, and fractionating columns in the chemical industry [1]. A variety of environmental factors can easily cause corrosion of copper. Scale and corrosion products have a negative effect on heat transfer, and they cause a decrease in heating efficiency of the equipment. That is why periodic cleaning in hydrochloric acid and nitric acid pickling solutions are necessary. In order to reduce the corrosion of metals, several techniques have been applied. The use of chemical inhibitors is one of the most practical methods for the protection against corrosion in acidic media. Most of the excellent acid inhibitors are organic compounds containing nitrogen, oxygen, phosphorus and sulphur. Studies of the relation between adsorption and corrosion inhibition are of considerable importance. Copper dissolution involves at first, single electron transfer process leading to oxidation thereby forming Cu(I) complex .The action of inhibitors is electrochemical in nature and involves the discharge of positively charged particles at the cathodic area that form an adsorbed layer. The adsorption of inhibitors takes place by virtue of their physical and chemical properties and also depends on the nature of metal and the type of the electrolyte solution used [2]. Herein, we investigated inhibitive effect of organic compound (Fig. 1) on the corrosion of copper in sulfuric acid by means of potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). The results of investigation show that this compound is a good inhibitor against the corrosion of copper in acidic solution and its inhibition efficiency increase by increasing the inhibitor concentration. The adsorption of organic compound onto the copper surface followed the Langmuir adsorption model with the negative free energy of adsorption. Quantum chemical calculations were employed to give further insight into the mechanism of inhibition action of inhibitor.

Figure 1. Optimized molecular structure of the organic inhibitor

Keywords**:** *Copper, Inhibitor, Potentiodynamic polarization, electrochemical impedance spectroscopy*

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Electrochemical Study on the Inhibition of Aluminum Corrosion in Acidic Medium by Newly Synthesized Adsorbable Organic Compound

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Abstract

Aluminum and its alloys are widely used in many industries such as reaction vessels, pipes, machinery, and chemical batteries due to their excellent combination of properties, e.g. good corrosion resistance, excellent thermal conductivity, high strength to weight ratio, easy to deform, and high ductility [1]. The most important feature of aluminum is its corrosion resistance due to the presence of a thin, adherent, and protective surface oxide film. However, when exposed to aggressive environments, such as the use of acid solutions for pickling, chemical and electrochemical etching of aluminum, industrial acid cleaning, cleaning of oil refinery equipment, oil well acidizing and acid descaling, these processes usually lead to substantial loss of the metal due to corrosion. The failure of aluminum equipment due to acid corrosion in industries is widely reported, and the use of chemical inhibitors is the most practical and cost effective by means of controlling corrosion of metals in acid solutions. There is always a need for developing new organic corrosion inhibitors result from a number of inhibitors of acid corrosion of aluminum is toxic, non-biodegradable and expensive. In the present work, new organic compound (Fig. 1) was synthesized and its inhibiting action on the corrosion of Al in sulfuric acid was investigated by means of potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). Electrochemical measurements were carried out by Zahner Ennium and a conventional three-electrode system was used throughout this work. Saturated Ag/AgCl electrode, a Pt wire and an Al disk electrode were employed as the reference, counter and working electrodes, respectively. The experimental results indicate that the newly synthesized compound shows excellent inhibition efficiencies against the corrosion of Al in acidic solution. The adsorption of organic compound onto the Al surface followed the Langmuir adsorption model with the negative free energy of adsorption. Quantum chemical calculations were employed to give further insight into the mechanism of inhibition action of organic compound.

Figure 2. Optimized molecular structure of organic inhibitor

Keywords**:** *Aluminum, Corrosion, Potentiodynamic polarization, Electrochemical impedance spectroscopy*

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Discoloration of C.I. Reactive Yellow 145 solution using TiO_2 nanoparticles coupled with Sonoelectrochemistry process

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Introduction

Various processes have been utilized for decolorization of textile industries wastewater including physical, chemical, and biological methods. One of the most advanced oxidation processes is sonoelectrochemical technology used to decompose and treat dye [1]. In this process, hydroxyl radical is released as a result of cavitation phenomenon caused by ultrasonic vibrations inside the liquid in a high temperature and pressure, decomposing the compounds. This attractive combinatory technology has received a great deal of attention thanks to having the following advantages: adaptability to the environment, usage of clean energy, recovery of heavy metals, treatment of wastes with a high toxicity, no generation of secondary pollution in the environment, and being more economical [2-4]. The aim of this study is to determine the efficiency of the sonoelectrochemical process in the decomposition of C.I. Reactive Yellow 145 from aqueous media.

Methods

A CCD was used for determining the optimum conditions for discoloration of RY145. The experimental results were analyzed using Design-Expert Version8.0.5, and the regression model was proposed. The initial pH (2.0-11.0), nano-TiO_2 (0.1-1.0 $g.L^{-1}$), time (300-7200 s) and applied voltage (0.5 – 1.5 V) were selected as four independent variables in the degradation process of RY145.

Result and discussion

In figure 1, the response surface and 3D plots were shown as a function of pH (from 4.25 to 8.75) and applied potential (at range 0.825 – 1.475 V) at constant condition of 4800 s and 0.0272 g nanoTiO_2. The decolorization percentage increased with increased potential at both acidic and basic conditions. However, higher rate was again obtained at acidic medium (i.e. pH = 4.25). The

$OH^{\bullet}$ production rate was increased with increasing potential, and thus, more $OH^{\bullet}$ can diffuse from the surface of the electrode into the solution.

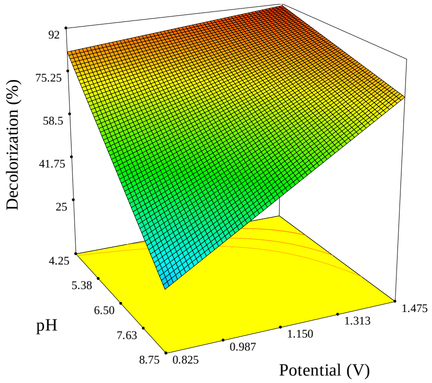

Fig.1.3 Response surface graph for the discoloration of RY145 by sonoelectrochemical treatment.

Conclusion

The degradation of the RY145 was optimized with sonoelectrochemistry system using RSM. The effects of four important operational parameters including pH of solution, Amount of TiO_2, time, and potential were evaluated by the response surface and counter plots. Analysis of variance (ANOVA) showed the relative significance of process parameters in decolorization process. This result indicated that pH was the main factor, and the interactions of other parameters were discussed in detail. Optimization results showed that the optimal conditions for significant experimental factors were pH= 4.25, applied potential= 1.4 V, TiO_2 amount=0.0235 g and contact time= 5700 s. At this conditions, predicted maximum of decolorization efficiency was over 91%. The present results showed that sonoelectrochemistry assisted by CCD have a good potential for dye removal from aqueous solution in the industrial application.

Keywords: *Sono- Electrochemical, Reactive Dye, Discoloration, RSM.*

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Study of Electrolytes effect on corrosion of oxide layer created on magnesium alloys by PEO

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Abstract

In this study, we review the studies conducted in the field of plasma electrolytic oxidation (PEO) on magnesium based to type of electrolytes and additives. The most studies are focused on phosphate and silicate based electrolytes with varying amount of hydroxide species. The study showed that increase of KOH content, decreases sparking voltage and increases corrosion resistance also it was revealed that sulphate species create stable passive film and increase corrosion resistance. Corrosion and wear resistance of coating conducted by PEO was higher than parent material.

Keywords: *corrosion, PEO, magnesium, electrolyte.*

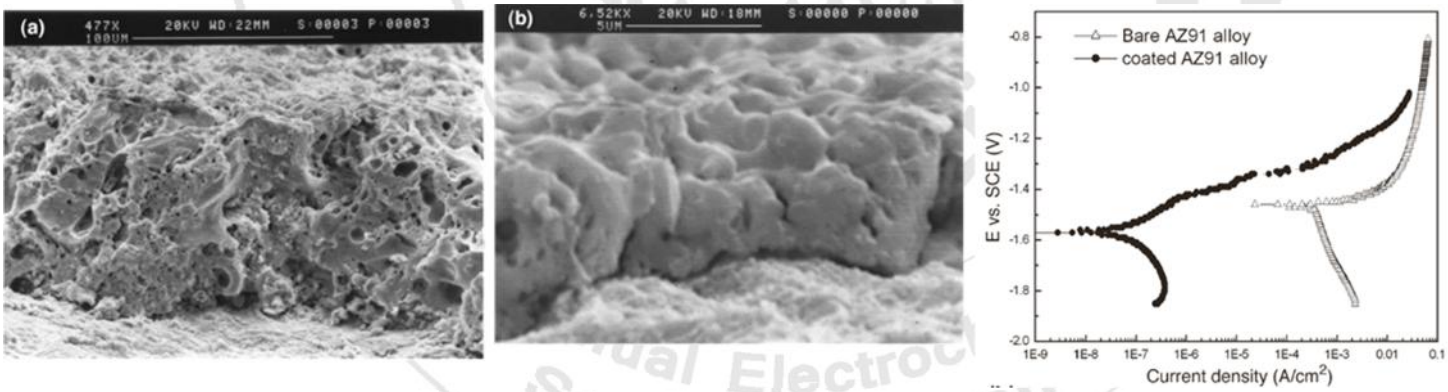
Introduction

The method of plasma electrolyte oxidation is based on anodic polarization of material in the aqueous electrolyte in terms of discharge plasma on the surface of anode [1] . One of the main reasons for use of this coating on the surface of Aluminum, Magnesium and their alloys is the high corrosion resistance of this coating [2].

Results and Discussion

Among the electrolytes used in the PEO, some of them have weak passivation properties while others can passive the surface strongly. For instance Phosphate and Silicate have good sparking properties and they are suitable for PEO coating of magnesium. In terms of contribution of electrolytes into the oxide coating, electrolytes that have anionic and cationic compounds, provide the best performance because in addition to the oxidation of substrate the deposition of other elements in the electrolyte to the oxide layer is allowed. It is possible to create a wide range of coatings with different properties and composition. Therefore, use of these two groups of electrolytes is more considered. In addition to electrolyte type, KOH, NaOH, NaF additives are used to increase the electrical conductivity of the solution and adjust the alkaline pH. Thus, there are wide ranges of electrolyte composition that can be selected to provide the desired properties of coating [3, 4]. In case of electrolyte type, effect on oxide properties of magnesium alloy AZ31B a study was done by Yerokhin[5]. the effects of phosphate and silicate electrolytes was studied that concluded that silicate electrolytes can cause severe sparking on the surface and phosphate electrolyte created film with a smooth surface and almost no defects[5]. Additives may be added to improve the wear and corrosion resistant of coating. For instance, Ko et al. observed that increase of KOH content, decrease sparking voltage and increase corrosion resistance. It is for this reason that, the increase of KOH content , increase MgO in the surface [6].

Figure: Cross-section fracture micrographs of PEO films produced in the following electrolytes, a. silicate,b. phosphate, c.polarization curve of AZ31B without coating and PEO [6].



Conclusion

As was seen in the case of parameter changes in electrolytes have an important impact in the final properties of the coating. The electrolyte have different factors that are important such as the composition, temperature, pH, etc. that increase of KOH content, decrease sparking voltage and increase corrosion resistance also the study clear that sulphate species create stable passive film and increase corrosion resistance.

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Effect of Nano-Grained Structure on the Electrochemical Behavior of Pure Copper in an alkaline solution

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Abstract

Effect of nano-grained structure on the electrochemical behavior of pure copper has been studied in this work. For this purpose, nano-grained structure was produced by accumulative roll bonding (ARB) process. To evaluate the microstructure and grain size refining after 8 cycles of ARB process, atomic force microscopy (AFM) was used. AFM image showed that nano-grained structure with average size of below 100 nm appeared after 8 cycles of ARB. Electrochemical behavior of annealed and 8 cycles number of ARB process has been studied by potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and Mott-Schottky analysis in an alkaline solution. All electrochemical tests revealed that as a result of grain refinement, the electrochemical behavior of the nano-grained structure significantly improves compared to the annealed pure copper.

Keywords: *Pure copper; AFM; Polarization; EIS; Passive film.*

Electrochemical Study of Anti-Corrosion Property of Fe_3O_4/Polyaniline Nanocomposite

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Abstract

Herein, a nanocomposite of polyaniline and Fe_3O_4 nanoparticles (Fe_3O_4/PANI) were prepared through a two-step oxidative polymerization in mass ratio of 1:1, 1:2 and 2:1. Prepared Fe_3O_4/PANI nanocomposites were characterized by FT-IR, XRD, TEM, SEM and EDXA. A thin layer of the Fe_3O_4/PANI nanocomposites were used to coating a carbon steel as corrosion inhibitor in NaCl 3.5%. Anti-corrosion performance of the Fe_3O_4/PANI nanocomposites was investigated through electrochemical techniques such as open circuit potential (OCP), potentiodynamic polarization and electrochemical impedance (EIS). Observed results showed a dramatic shift in corrosion potential and a decrease in cathodic and anodic reactions rate in Tafel plots. Also, EIS data showed charge transfer resistance was increase after coating the carbon steel with Fe_3O_4/PANI nanocomposite. Affecting parameters like mass ratio, amount of nanocomposite and incubation time, were optimized. Our electrochemical results showed that 100 mg/l of Fe_3O_4/PANI (1:1) nanocomposite in 60 mine can achieved to inhibition efficiency of 96% in 3.5% NaCl. Finally ability of proposed coting as an anticorrosive layer was further proofed by using surface methods i.e. SEM and EDXA. Observed results will be presented and discussed.

Keywords**:** *Corrosion, Polyaniline, Fe_3O_4 nanoparticles, Nanocomposite, 3.5% NaCl, EIS.*

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Electrochemical study of corrosion behavior of Zr-1%Nb in LiOH and KOH solutions

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Abstract

Zirconium alloys are widely used for fuel cladding and in pressure tubes in most water-cooled reactors, because of its low neutron absorption cross section and high corrosion resistance. The primary coolant in pressurized water reactors (PWR) contains lithium hydroxide (LiOH), which is used for pH control since it has been recognized that a more constant pH is desirable to reduce radiation field and fuel depositions. But it has been known that LiOH accelerate corrosion of nuclear fuel cladding [1-4]. Therefore, in this work the potential of KOH instead of LiOH for PWR application was investigated.

Corrosion properties of the Zr-1%Nb alloys were assessed by Autolab potentiostat/galvanostat (model 302N, Netherlands), in naturally-aerated 1 M LiOH and 1 M KOH solutions at room temperature. A conventional three-electrode cell was employed for the measurements, with an Ag/AgCl electrode and a platinum counter electrode. Zirconium plates with ~1 cm^2 area that used as working electrodes were immerged 90 minutes prior to the tests in the solution to allow the stabilization of open-circuit potential. The electrochemical impedance spectroscopy (EIS) tests were carried out at a frequency range of 10 mHz to 100 kHz at the open circuit potential and the perturbation amplitude was 10 mV. The scan rate and perturbation for potentiodynamic polarization (PDP) were 1 mV/s and ±10 mV, respectively.

The polarization curves of the zirconium electrode in the 1.0 M LiOH and KOH solutions were shown in figure 1-a, and the electrochemical parameters that are obtained from the polarization curves are summarized in table 1. The experimental impedance plots altogether with simulated spectra by equivalent circuit were shown in figure 1-b. The electrochemical parameters of the equivalent circuit elements are listed in table 2.

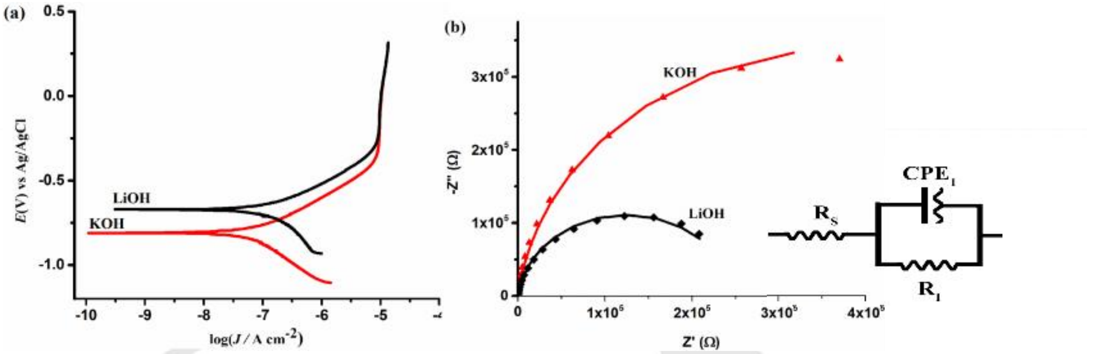

Fig.1. a) Polarization curves and b) Impedance plots in 1 M LiOH and KOH solutions together with the proposed equivalent circuit. Dotted lines represent measured spectra and solid lines represent simulated spectra, fitted by the equivalent circuit.

Table 1. Electrochemical parameters obtained from polarization curves

Media	*Ecorr (V vs Ag/AgCl)*	*Jcorr (μA/cm²)*	*Rp(kΩ)*	*β_a(V/dec)*	*β_c (V/dec)*	*Corrosion Rate (μm/y)*
KOH	-816	69	556	159	202	0.8
LiOH	-673	187	254	207	357	2.1

Table 2. Parameters of the equivalent circuit elements obtained by fitting of experimental impedance data with equivalent circuit shown in -b

Media	***R_S(Ω)***	***R_1(kΩ)***	***Y_0(CPE_1) (μ $\Omega^{-1}s^{-n}$)***	***n_1***
KOH	25.6±0.2	755±25	20.7±0.1	0.931±0.001
LiOH	3.99±0.07	248±7	20.7±0.3	0.928±0.002

As can be seen in Fig. 1-b, the radius of Nyquist plot in LiOH media is less than that in KOH media, which is indicate that the corrosion resistance of the alloy in LiOH media are less than that in KOH media. Similar results can be obtained from table 1 and table 2. In other words, the results show that KOH was not affect significantly to the corrosion of the alloy. Therefore, it has a potential for PWR application only from the point of view of Zr-1%Nb corrosion.

Keywords: *Zirconium, corrosion behavior, LiOH, KOH, potentiodynamic polarization, EIS.*

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Sonoelectrochemical Oxidation for Decolorization of Basic Blue 41 based on Central Composite Design

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Introduction

As an auxiliary to electrochemical processing, ultrasonic cavitation at/near a solid surface has potential advantages: (i) ultrasonic degassing at an electrode surface prevents gas bubble accumulation, which interferes with the passage of current; (ii) agitation via cavitation at the electrode surface assists in ion transport through the diffusion layer; and (iii) cavitation at the electrode surface results in continuous cleaning and activation of the electrode [1, 2]. Power ultrasound can be applied as a hydrodynamic tool to increase the signal-to-background ratio for diffusion controlled redox systems and to remove the effects of electrode surface fouling. A combination of sonication and electrochemical oxidation is a hybrid technology developed for the treatment of organic pollutant [3, 4]. In this study, a four-factor five-level Central Composite Design (CCD) was applied to develop mathematical model and optimize process parameters for Basic Blue 41 dye (BB41) decolorization from aqueous solutions using sonoelectrochemical process.

Methods

Generally, at optimum condition, 5.0 mL of BB41 (1.0 g L^{-1}), 5.0 mL buffer solution with pH =6.0 were added to 50 mL volumetric flask and diluted to the volume with double-distilled water. The solution was moved to the electro analyzer cell, which placed in ultrasound bath and potential of 0.65 V was applied the working electrode for 118 min. The initial and final adsorption of the dye solution were determined at the maximum wave length λ_{max}= 617 nm using a UV-VIS spectrophotometer. The percentage removal of dye was calculated as follows:

$$\%\text{ dye removal} = 1 - A/A_0 \times 100$$

Where A_0 and A is the initial and final absorbance of solution, respectively and the removal was taken as a response (Y) of the experimental design.

Results and Discussion

The discoloration rate constantly increases with the increase in the time. By increasing of time, the free radicals such as $^{\bullet}OH$ and $HOO^{\bullet}$ would be increased, which promotes the discoloration rate. More dye molecules was also moved to electrode and was oxidized on electrode. Moreover, the dye removal percentage increased with increased the applied potential. The $OH^{\bullet}$ production rate was increased with increasing potential, and thus, more $OH^{\bullet}$ can diffuse from the surface of the electrode into the solution.

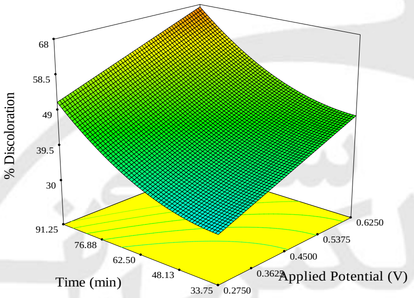

Fig 1. Three-dimensional response surface graph for the decolorization of Basic Blue 41 by sonoelectrochemical treatment.

Conclusion

Based on ANOVA results, the order of factors from high to low contribution on decolorization efficiency was found as initial dye concentration, time, pH and applied potential with respect to sum of squares. Optimization results showed that the optimal settings for significant experimental factors were initial dye concentration= 108 mg L^{-1}, pH= 6.0, applied potential= 0.67 V and contact time= 118 min. At this condition, predicted maximum removal efficiency was over 99%.

Keywords: *Sonochemistry, Electrochemical, Basic Dye, decolorization*.

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Electrochemical Study of Corrosion Inhibition Properties of Polyvinyl Alcohol/Graphene Nanocomposites on Carbon Steel

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Abstract

In this work, anti-corrosion behavior of synthesized water soluble poly vinyl alcohol/graphene (PVA/G) nanocomposite was investigated. Firstly, prepared PVA/G was characterized by FTIR, SEM-EDX, and XRD techniques. Then, electrochemical techniques such as open circuit potential (OCP), potentiodynamic polarization and electrochemical impedance (EIS) were employed to study the corrosion protection performance of PVA/G on carbon steel in NaCl 3.5% environment. The role of concentration of PVA/G, incubation time of film formation on the carbon steel corrosion has been investigated. Observed results showed the PVA/G acts as mixed-type inhibitor and could serve as an effective corrosion inhibitor for carbon steel in NaCl 3.5% environment. Surface morphology of the protected carbon steel specimen with PVA/G was investigated by SEM and EDXA that confirms the protection of mild steel surface by strong adsorption of nanocomposite. Observed results will be presented and discussed.

Keywords: *Corrosion, Polyvinyl alcohol, Graphene, EIS, Tafel.*

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Study of Inhibitory Effect of Walnut Leaf Extract on Corrosion of Carbon Steel in NaCl 3.5%

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Abstract

Assessment of corrosion inhibitors for metals in aggressive media is important for some industrial facilities. While choosing an inhibitor, several factors such as its cost, toxicity, availability and environment friendliness need to be taken into account. In spite of the high efficiency of many commonly used synthetic compounds, they are often toxic, carcinogenic or even allergenic, green inhibitors are used as corrosion inhibitors. In the present work, attention has been focused on the corrosion inhibiting properties of walnut leaf extract carbon steel in NaCl 3.5% environment. Walnut leaf extract contain phenolic substances that can naturally prevent the corrosion of ferrous metals. The performance of the inhibitor in different concentrations of 5%, 10%, 15%, 20%, 25% and 30% of walnut leaf extract in NaCl 3.5% was studied electrochemicaly by using open circuit potential (OCP), potentiodynamic polarization and electrochemical impedance (EIS) techniques. Observed results showed addition of walnut leaf extract to NaCl 3.5% environment, led to a shift in corrosion potential and a decrease in the corrosion rate. Observed results will be presented and discussed.

***Keywords**: Inhibitor, Walnut leaf extract, Carbon steel, Nacl 3.5%*

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Polyvinylpyrrolidone/Fe_3O_4 (PVP/Fe_3O_4) as a Coating on Carbon Steel for Increasing Its Corrosion Resistance in NaCl 3.5%

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Abstract

Polymers can be used as corrosion inhibitors due to their functional groups, which form complexes with metal ions on the metal surfaces. These complexes occupy a large surface area, thereby blanketing the surface and protecting the metals from corrosive agents that presence in the solution. The corrosion inhibition by various cationic polymers such as polyethyleneimine derivative, polyacrylamide derivative, polydicyanodiamide derivative, and anionic polymers such as polymaleic acid derivative, polyacrylic acid derivative, and Polyvinylpyrrolidone (PVP), have been investigated previously. In the present work, known property of PVP combined with excellent property of nanoscale magnetite (Fe_3O_4), to produce an anti-corrosion film on carbon steel. Therefore, firstly a PVP/Fe_3O_4 nanocomposite was prepared and characterized by FT-IR, XRD, SEM and EDXA. Then, electrochemical techniques such as open circuit potential (OCP), potentiodynamic polarization and electrochemical impedance (EIS) were employed to study the corrosion protection performance of PVP/Fe_3O_4 on carbon steel in NaCl 3.5% environment. The role of concentration of PVA/G, incubation time of film formation on the carbon steel corrosion has been investigated. Observed results showed the PVP/Fe_3O_4 acts as mixed-type inhibitor affecting the iron dissolution and the cathodic reaction as well. Surface morphology of the protected carbon steel specimen with PVP/Fe_3O_4 was investigated by SEM and EDXA that confirms the protection of mild steel surface by strong adsorption of nanocomposite. Observed results will be presented and discussed.

***Keywords**: Corrosion, Polyvinylpyrrolidone, Magnetite (Fe_3O_4), NaCl 3.5%, Carbon steel.*

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Evaluation of corrosion inhibition role of conventional surfactants for zinc in alkaline battery solution

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Abstract

One of the most important changes in the characteristics of the MnO2-Zn dry cell as known before the 1960s occurred when caustic electrolytes were introduced to the technology of this system on a large scale. The current-carrying capability, capacity, and shelf life increased considerably, and today this type of galvanic cell has a wide range of application. Despite the mentioned advantages, these type of batteries suffer from a serious drawback of corrosion in alkaline medium which often results in a leakage. To overcome this problem, the employment of environmentally friendly surfactants, as corrosion inhibitors is gaining large preference and interest due to its safe effect, practical use and low cost. Most of the surfactants used as corrosion inhibitors are organic molecules having a notable inhibition efficiency in their CMC values.

The corrosion inhibition mechanism of surfactants at the metal surface includes the adsorption of these species on the metal surface. Electrochemical characterization of the studied system was done in an three electrode array including Ag/AgCl (satd), Zink specimen, and Pt as reference, working, and counter electrodes, respectively, in The aggressive solution 7.0 M KOH prepared using 99% KOH. Corrosion inhibition efficiency of Dotab surfactant on zinc in 7.0 M KOH solution was evaluated by polarization as EIS techniques. Results evidenced that Dotab surfactant can improve the corrosion inhibition of zinc and enhance the capacity of battery. The inhibition efficiency enhances with increasing the surfactant concentration. The maximum inhibition efficiency is above 90% at CMC (0.4 mM). Polarization curves proved that Dotab surfactant is an efficient corrosion inhibitor.

***Keywords**: Alkaline batteries, Corrosion inhibition, Discharge capacity, Polarization, Surfactant*

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Hot Corrosion and oxidation Investigation of the sermaLoy j coating on the Rene 41 Nickel based superalloy

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Abstract

Slurry coating has spawned a considerably interest in gas turbine coating industry regarding their low cost and straightforward process. Among conventional standard methods, SermaLoy J slurry is widely used in gas turbine engine to protect Vanes and blades from hot corrosion and oxidation[1, 2]. In this work, SermaLoy J was deposited on the Rene 41 Nickel based superalloy with different thickness and process. Also, heat treatment operation was done to diffuse Al, Si, and Cr in lattice. Then, Microstructure and chemical composition of the coated specimens were analyzed using Scanning Electron Microscopy (SEM), Energy Dispersive X-ray spectroscopy (EDX), Metallography, and Quantometery. Physical characterization done by SEM and EDX showed a homogeneous coating including Si, Al, and Cr elements. Finally, the hot oxidation and corrosion resistance of them is analyzed on the 1100 °C. As shown on the result, Coating in which has 40-50 micro meter coating has best quality to hot corrosion and oxidation.

Keywords*: *SermaLoy J, Coating, Hot corrosion, and Oxidation

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Simulation of CO_2 Corrosion for Copper Pipes in Different PH and Temperatures

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Abstract

A flow mixture of carbon dioxide and water that passing through a copper pipe can cause significant copper corrosion. Rate of the corrosion depends to Properties such as pH and temperature. In this paper, the effect of changing the temperature and pH to corrosion rate is investigated [1,2]. To this aim we selected 1-12 as pH and 20-100°C as different temperatures. Simulation of models helps us to understand complex dynamic processes. The corrosion process was simulated in Comsol Multiphysics software.

Keywords: *Carbon Dioxide, Corrosion, Copper Pipes, PH, Temperature*.

Introduction

Copper plays an indispensable role in our life. Despite superior thermal and electrical conductivity of copper, this metal shows good resistance to corrosion in many industrial and urban industrial atmospheres environmental applications. Copper pipes play an important role in the household drinking water distribution systems [3, 4, 5, 6]. We know that in a small number of cases that the high quality water in Melbourne is affected by copper corrosion - a condition that mainly occurs within a customer's own plumbing. Copper corrosion leads to release copper into drinking water. Temperature and PH are two main factors of corrosion in copper pipes. In this work, depending of carbon dioxide corrosion of copper pipes to pH and temperature have been studied.

There are some equilibrium reactions that present in water:

$$H_2O(l) \Leftrightarrow H^+(aq) + OH^-(aq)$$
$$CO_2(aq) + H_2O(aq) \Leftrightarrow H_2CO_3(aq)$$
$$H_2CO_3(aq) \Leftrightarrow H^+(aq) + HCO_3^-(aq)$$

$$HCO_3^-(aq) \Leftrightarrow H^+(aq) + CO_3^{2-}(aq)$$

At the pipe surface this electrochemical reactions are present:

$$Fe(s) \rightarrow Fe^{2+} + 2e^-$$

$$H^+ + e^- \rightarrow H$$

$$H_2O + e^- \rightarrow H + OH^-$$

$$H_2CO_3 + e^- \rightarrow H + HCO_3^-$$

Above reactions can lead to corrosion on the surface of copper pipes.

Result

Figure 1 shows concentration of some elements versus distance from copper surface at pH=7 (water pH) and different temperatures (thickness of pipe assumed 1mm):

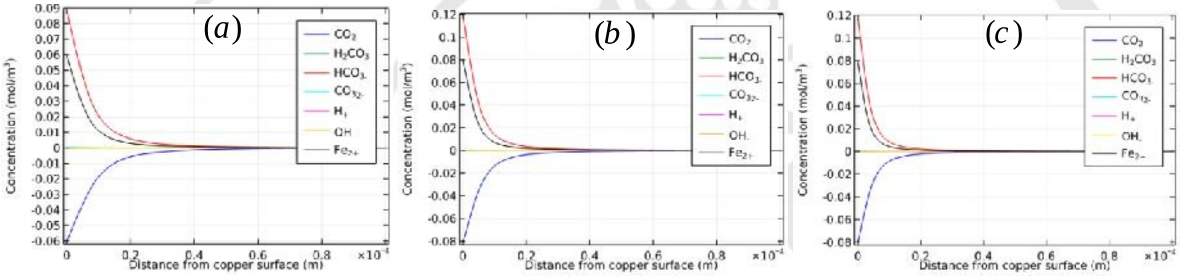

Figure 1: Concentration versus distance from copper surface at: (a) 20°C, (b) 60°C and (c) 100°C.

We can see that in near distances to the copper pipe surface, the concentration of elements is more than far distances.

In figure 2 we can see Corrosion rate versus temperatures for various pHs:

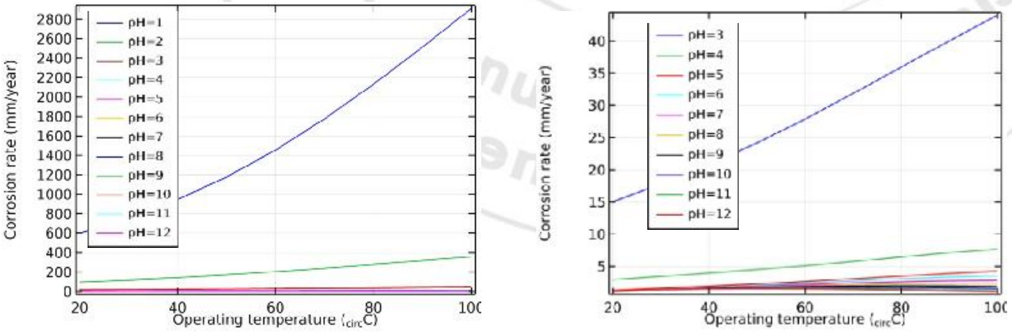

Figure 2: Corrosion rate versus temperatures for various pHs

It’s found that Corrosion rate for acidic pHs if higher than Alkalin pHs.

Conclusion

In summary, it’s found that for copper pipes, high temperatures and low pHs lead to an increase in the corrosion rate. For water at low temperatures (20-40°C) we can use copper pipes but in high temperatures it isn’t a good choice. So we can use plastic and galvanized pipes at high temperatures (80-100°C).

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Generation and storage of energy

Analyzing the battery chargers and analyzers with aviation application

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Abstract

Nowadays batteries and electrochemical capacitors after oil and its derivatives are going to be the primary energy resources for us. Despite the fact that oil productions are going to be finished in some decades and regarding the prices of preparing them for practical use, batteries and electrochemical capacitors will take their place. As a consequence, one of the most important factors which should be considered in these kinds of energy resources is their maintenance. Analyzing the electrochemical capacitors can be done by numbers of method. In this study tests like cyclic voltammetry, cyclic charge/discharge and electrochemical impedance spectroscopy are going to be analyzed.

Keywords: *Battery analyzers, cyclic Voltammetry, cyclic charge/discharge, impedance spectroscopy.*

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Electrochemical Study of a Novel High Performance Supercapacitor Based on MnO_2/Nitrogen-Doped Graphene Nanocomposite

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Abstract

Supercapacitors as energy storage devices have advantages in comparison to the batteries such as higher power densities, fast charging/discharging rates, and excellent cycling stabilities. Supercapacitors are used particularly for the applications involving in high power electronics, electrical utilities, transportation, medical electronics and military defense systems [1]. MnO_2 as a supercapacitor electrode has attracted many attentions due to its relatively low cost, and being environmental friendly as neutral aqueous electrolytes [2]. However, the low electrical conductivity (10^{-5}-10^{-6} S cm^{-1}) and low electrochemical kinetic of MnO_2 limit its charge storage and thus its commercial usage. The electrical conductivity of MnO_2 could be improved by incorporating various types of carbonaceous compounds such as graphite, graphene oxide, graphene, carbon nanotube, mesoporous carbon, and carbon black by various methods [1-3].

Nitrogen doped reduced graphene oxide (NRGO) can increase the conductivity of metal oxide-based supercapacitors. In the present study, a simple method for preparation of MnO_2/NRGO as the supercapacitor electrodes is introduced using ultrasonic vibration. Applying ultrasonic waves is a simple method for the synthesis of nanostructures [23]. The process, known as cavitation, is based on incorporating bubbles in the liquid, where they grow up and finally collapse. The bursting of bubbles results in very high local temperature and pressure leading to reactions in the solution [4]. The structure and morphology of MnO_2/NRGO nanocomposites are characterized by X-ray diffraction, X-ray photoemission spectroscopy (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Raman spectroscopy. The electrochemical supercapacitive performance of the nanocomposite was investigated by cyclic voltammetry (CV), FFT Continuous cyclic voltammetry (CCV), galvanostatic charge/discharge, and electrochemical impedance spectroscopy (EIS) methods.

The supercapacitive performance of the RGO, NRGO, pure MnO_2, MnO_2/RGO and MnO_2/NRGO electrodes were studied by CV method, using a three-electrode system using Ag/AgCl as the reference and platinum foil as the counter-electrode. Fig. 1a illustrations the typical CV curves of the MnO_2, RGO/MnO_2 and NRGO/MnO_2 electrodes were measured at 50 mV s^{-1} in 0.5 M Na_2SO_4. The results show that the CV curves of the RGO/MnO_2 and NRGO/MnO_2 electrodes are symmetrical respect to the zero-current line and a rapid current change around the potential reversal at the end each scan. In fact, existing a quasi-rectangular shapes and symmetric I–V responses indicates the ideal pseudocapacitive behavior of the materials. The measured currents of the MnO_2 and MnO_2/RGO electrodes, under the same conditions, were smaller than the measured current for the MnO_2/NRGO electrode. However, for the case MnO_2/NRGO electrode, the current enhancement could be the results of synergistic effect for the combination MnO_2 and NRGO, which cause an improvement of the electronic conductivity of the nanocomposite. These results also, shows the calculated SC values for the MnO_2, MnO_2/RGO, and MnO_2/NRGO samples are equal 298, 437 and 522 F g^{-1} at scan rate 2 mV s^{-1}, respectively. Fig. 1b shows the CV curves of the MnO_2/NRGO electrode at scan rates of 5, 10, 20, 30, 40 and 50 mV s^{-1}. As shown on the figure, there is not a notable change in the rectangular shape with scan rate, which is an indication of a fast and reversible process at the electrode surface.

The CCV technique could be considered the best tools for examination of the monitoring in the CVs and charge storage of a capacitor during that time [2, 4]. In this method, under a long-term potential cycling, the stability of the electrodes are evaluated. The calculated SC as a function of time are presented in Fig. 1c. As shown in Fig. 1c, after applying 4000 CVs, the value of SC decrease 17.9%, 7.0% and 3.7%for the MnO_2, MnO_2/RGO and MnO_2/NRGO electrodes, respectively. The above results prove that the MnO_2/NRGO electrode are highly stable during potential cycling test compared to MnO_2 and MnO_2/RGO electrodes. Fig. 1d shows three-dimensional (3D) CCVs, which was performed at a scan rate of 200 mV s^{-1}. In these two 3D-plots, the changes in the CVs over time are more noticeable.

***Keywords**: Supercapacitor, Nanocomposite, N-doped Graphene, MnO_2 nanoparticles, Sonochemistry.*

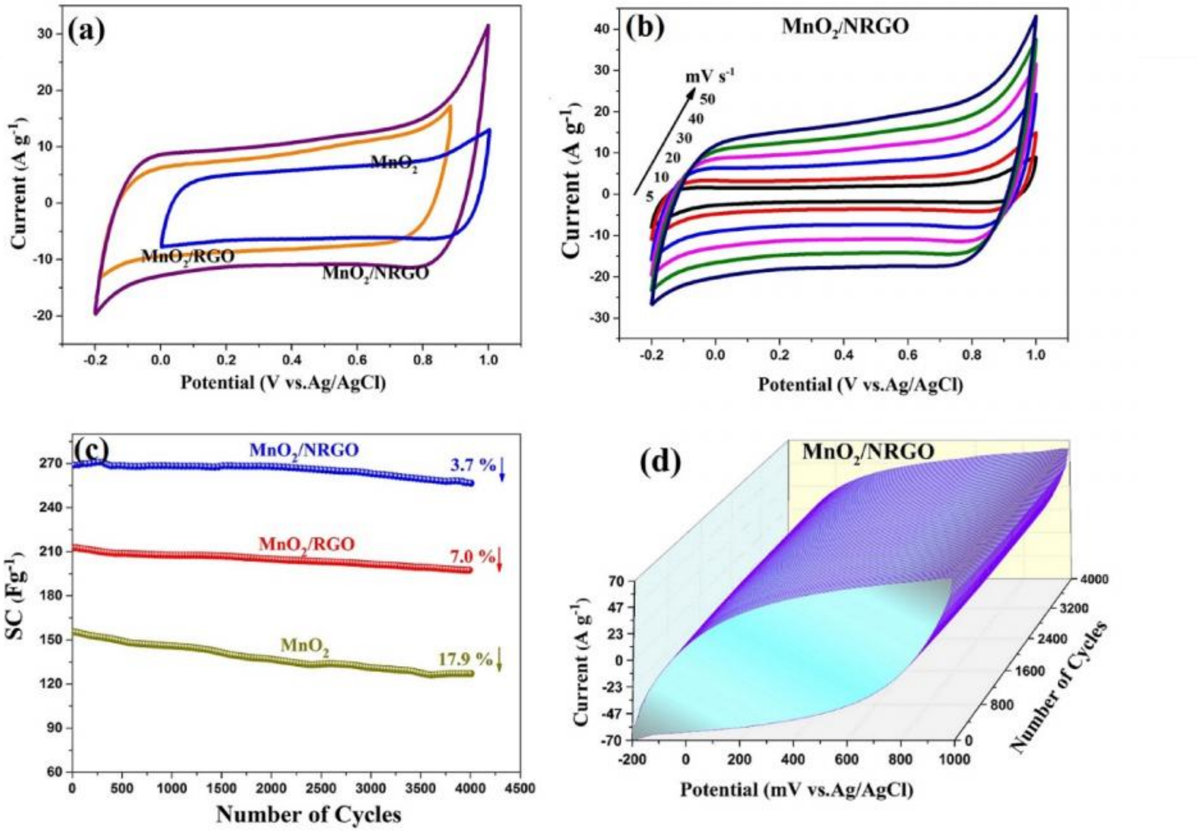

Fig. 1. (a) CVs of the pure MnO_2, MnO_2/RGO and MnO_2/NRGO electrodes, at a scan rate of 50 mV s^{-1} in 0.5 M Na_2SO_4 aqueous electrolyte, (b) CVs of the MnO_2/NRGO electrode, different scan rates of 5, 10, 20, 30, 40 and 50 mV s^{-1} in a potential range of -0.2 to 1.0 V, (c) Variation of the specific capacitance of the MnO_2/NRGO electrode as a function of time measured at 200 mV s^{-1} and (d) 3D-CCV curves of the MnO_2/NRGO electrode measured at scan 200 mV s^{-1}.

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Synthesis of a novel Magnetite/Nitrogen-doped Reduced Graphene Oxide nanocomposite as High Performance Supercapacitor

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Abstract

In today's world, electrochemical supercapacitors (ESs) could be considered as one of the most important energy storage devices for a larger number of power portable electronics and electrical vehicles. They can be classified into two major groups based on the charge-storage mechanisms in them, electrical double-layer capacitors (EDLCs) and pseudocapacitors [1-2].The pseudocapacitors, could have an individual capacitance due to their electrochemically active materials through rapid and faradic redox reaction. Numerous materials are used in construction of them, such as transition metal oxides, and conductive polymers. Indeed, these materials have shown a higher capacity than those carbon-based materials. A number of metal oxides such RuO_2, NiO, MnO_2, Co_3O_4, and Fe_3O_4 have found to be very suitable for making pseudocapacitors [3].

But the high internal resistance and lower the cyclic stability of metal oxides could be the main reason for the limitation in their use in commercial ESs. There are many attempt to solve this problem, such as application of the Metal oxides with carbon-based materials as nanocomposite, for examples; exfoliated graphite, mesoporous carbon, carbon black, carbon nanotubes, and graphene oxide [4].

In the present study, a simple method for preparation of nanostructured Fe_3O_4/NRGO as the ES electrodes is introduced using ultrasonic vibration. Applying ultrasonic waves is a simple method for the synthesis of nanostructures. The pseudocapacitive behaviors of the Fe_3O_4 and Fe_3O_4/NRGO composite electrodes were examined by cyclic voltammetry (CV), Continuous cyclic voltammetry (CCV), galvanostatic charge/discharge, and electrochemical impedance spectroscopy (EIS) in a 0.5 M Na_2SO_4 electrolyte.

The supercapacitive performance of the NRGO, Fe_3O_4, Fe_3O_4/RGO and Fe_3O_4/NRGO electrodes were studied by CV method, using a three-electrode system using Ag/AgCl as the reference and

platinum foil as the counter-electrode. Fig. 1a illustrations the typical CV curves of the NRGO, Fe_3O_4, Fe_3O_4/RGO and Fe_3O_4/NRGO electrodes were measured at 50 mV s^{-1} in 0.5 M Na_2SO_4. The results show that the CV curves of the Fe_3O_4/RGO and Fe_3O_4/NRGO electrodes are symmetrical respect to the zero-current line and a rapid current change around the potential reversal at the end each scan. In fact, existing a quasi-rectangular shapes and symmetric I–V responses indicates the ideal pseudocapacitive behavior of the materials. The measured currents of the Fe_3O_4 and Fe_3O_4/RGO electrodes, under the same conditions, were smaller than the measured current for the Fe_3O_4/NRGO electrode. However, for the case Fe_3O_4/NRGO electrode, the current enhancement could be the results of synergistic effect for the combination $Fe_3O_4$and NRGO, which cause an improvement of the electronic conductivity of the nanocomposite. These results also, shows the calculated specific capacitance values for the Fe_3O_4, Fe_3O_4/RGO, and Fe_3O_4/NRGO electrodes are equal 143, 271 and 355 F g^{-1} at scan rate 2 mV s^{-1}, respectively. Fig. 1b shows the CV curves of the Fe_3O_4/NRGO electrode at different scan rates. As shown on the figure, there is not a notable change in the rectangular shape with scan rate, which is an indication of a fast and reversible process at the electrode surface.

In order to gain further understanding about the supercapacitive performance, the galvanostatic charge/discharge of the Fe_3O_4, Fe_3O_4/RGO, and Fe_3O_4/NRGO electrodes are measured at the potential range of –0.8–0.2 V at charge/discharge current density of 2.0 A g^{-1} (Fig. 1c). The electrodes have stable electrochemical properties in the 0.5 M Na_2SO_4 electrolyte where the capacitor voltage is varied linearly with the time during both charging and discharging. Almost no voltage drop was observed during the discharge process, giving high values of charge/discharge efficiency. Fig. 1d shows the charge/discharge of the Fe_3O_4/NRGO electrode at different current densities. A good linear variation of potential versus time was observed for all the curves, which is another typical characteristic of an ideal capacitor. The small iR drop indicates a conductive characteristic of a composite material. This is related to the formation of a highly conductive network by adding NRGO, which facilitates the interface contact between the electrolyte and the Fe_3O_4 of the composite electrode. Therefore, the internal resistance within the composite electrode itself is reduced and good electronically conducting pathways are provided for protonic and electronic transportation during the rapid charge/discharge process. The shape of the charge/discharge curves shows agreement with the result of the CV curves.

Keywords: *Supercapacitor, Nanocomposite, N-doped Graphene, Fe_3O_4 nanoparticles.*

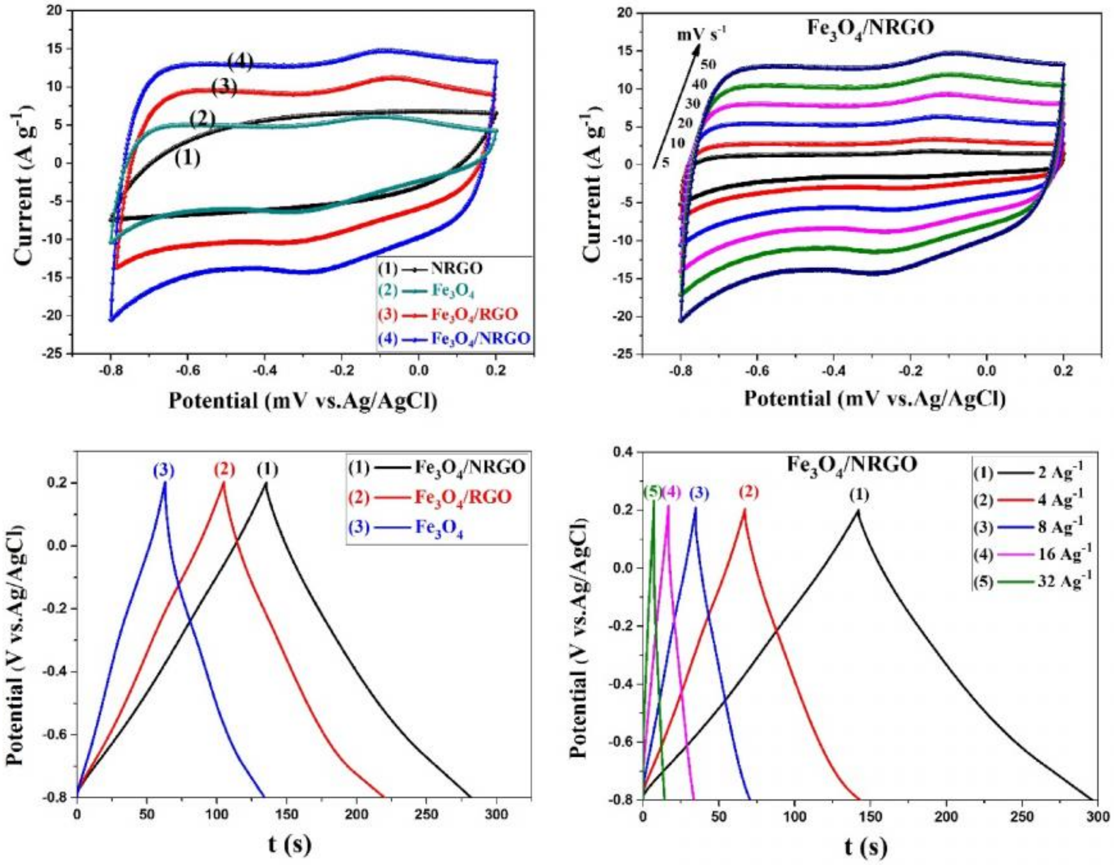

Fig. 1. (a) CVs of the NRGO, Fe_3O_4, Fe_3O_4/RGO and Fe_3O_4/NRGO electrodes, at a scan rate of 50 mV s^{-1} in 0.5 M Na_2SO_4 aqueous electrolyte, (b) CVs of the Fe_3O_4/NRGO electrode, different scan rates of 5, 10, 20, 30, 40 and 50 mV s^{-1} in a potential range of -0.2 to 1.0 V, (c) Chronopotentiograms of Fe_3O_4, Fe_3O_4/RGO and Fe_3O_4/NRGO electrodes between potential range of –0.8–0.2 V at charge/discharge current density of 2.0 A g^{-1}, and (d) Chronopotentiograms of Fe_3O_4/NRGO electrode at different discharge current densities (2, 4, 8, 16 and 32 A g^{-1}).

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One-step Electrochemical Preparation of Fe_3O_4 Particles/PVA Composite as High Performance Electrode Materials for Supercapacitors

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Abstract

Supercapacitors or ultracapacitors, have recently attracted considerable attention owing to their high energy density, high charge/discharge rates, and long cycle life performance [1]. Based on the types of energy storage, supercapacitors are also classified into electric double layer capacitors (EDLCs) and pseudocapacitors [2]. In particular, pseudocapacitors, typically including transition metal oxides (MnO_2, RuO_2, NiO, Co_3O_4, Fe_3O_4, etc) or hydroxides ($Ni(OH)_2$, $Co(OH)_2$, etc), as well as electrically conductive polymers (polyaniline, polypyrroles, and polythiophenes), use a reversible faradaic redox reaction at the electrode surface [3]. They generally show higher specific capacitance than EDLCs, made of carbonaceous materials for double-layer charge storage [4]. Among various metal oxides, Fe_3O_4 has attracted great attention due to its low cost and environmentally benign nature [5]. Fe_3O_4 has been reported to exhibit a high theoretical Li storage capacity, suggesting that it can offer potentially high pseudocapacitance through redox reaction. However, when directly used as a supercapacitor electrode, Fe_3O_4 alone exhibits a low rate capability owing to its inadequate conductivity, which limits the fast electron transport required by high rate applications [5]. To circumvent this hindrance, an effective method is to fabricate hybrid electrodes by integrating Fe_3O_4 with a carbon host, such as graphene (CNTs) [3], carbon nanofibers (CNFs) [4] or carbon nanoparticles (CNPs) [5], which can work as conductive channel for ion diffusion.

In this work, PVA-coated Fe_3O_4 and pure Fe_3O_4 nanoparticles were synthesized *via* electrochemical deposition method. The as-prepared products characterized by XRD and SEM indicate that PVA coating does not affect the structure and morphology of Fe_3O_4. The electrochemical properties measured by cyclic voltammetry, galvanostatic charge–discharge

cycling and electrochemical impedance spectroscopy tests showed that PVA coated Fe_3O_4 nanoparticles present improved electrochemical performance (as seen in Fig. 1).

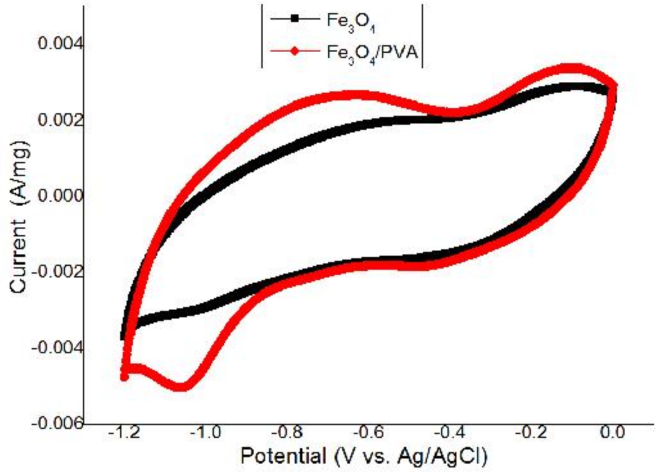

Fig. 1. CVs of PVA-coated Fe_3O_4 and pure Fe_3O_4 nanoparticles at the scan rate of 5 mV/s.

A specific capacitance of 115.9 F g^{-1} is achieved at a scan rate of 5 mV s^{-1} in 1 M Na_2SO_3 aqueous solution for the Fe_3O_4/PVA composite in comparison to that of 88.6 F g^{-1} for pure Fe_3O_4. As a result, the composite exhibit enhanced capacitances in comparison with pure iron oxides.

Keywords: *Magnetite, PVA, Nanoparticles, Supercapacitors*

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Method of Recovering Metals from Lithium Batteries

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Abstract

Lithium ion batteries are the most common rechargeable batteries in consumer electronics [1]. There is an inconsistent policy about the fate of discarded lithium ion batteries in e-waste that is distributed internationally. Lithium batteries contain potentially toxic materials including metals, such as copper, nickel and lead, and organic chemicals, such as toxic and flammable electrolytes. Defunct Li-ion batteries are classified as hazardous due to their lead (Pb) (6.29 mg/kg), cobalt (163,544 mg/kg), copper (98,694 mg/kg) and nickel (9525 mg/kg) contents with exceeded limits of chromium, lead, arsenic and thallium [2].

Also the resources of some metals such as Lithium and Cobalt are limited in worldwide [3]. These reasons encourage us to recover and recycle the components of spent batteries, especially laptop batteries. In present project we tried to recycle and recover the components of Cylindrical Lithium ion secondary battery with functional pin by different physical and chemical processes.

Keywords**:** *Lithium, Cobalt, Leaching, Thermal treatment, Separation*

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Supercapacitive Behavior of Co_3O_4 Nanoplates Prepared via Pulse Electrosynthesis Followed by Heat-treatment

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Abstract

Cobalt oxide (Co_3O_4) with a spinel structure has received considerable attention because of its diverse applications in many fields such as catalysis [1], sensor [2], batteries [3] and supercapacitors [4-6]. An emerging application of Co_3O_4 as an electrode material in electrochemical supercapacitors can prove itself as a promising alternate to expensive RuO_2, which has been used extensively as electrode material. In the supercapacitive application, the sheet or plate-like structures are beneficial to improvement the electrochemical performance of Co_3O_4 [5]. These structures can provide large inter-sheet spacing for transferring the ions rapidly and increasing the electroactive material–electrolyte interface area i.e. electrolyte penetration which results high utilization of the electrode materials. In addition to the inter-sheet spacing, the microstructure or morphology of sheets i.e. their thickness and porous nature has an important role in electrochemical performance of these structures. It is obvious that the thin and porous sheets can result a high surface area which produces large reaction sites and shortened ion diffusion paths, and a lot of pores cause better electrolyte penetration, respectively.

In this work, we applied pulse current in the deposition of hydroxide precursor, and then heat-treatment at 400 ^{o}C for 3 h. The results showed that the high surface and thin nanoplates are easily achievable. The supercapacitive performance of the prepared nanoplates was evaluated by cyclic voltammetry (CV) and charge-discharge techniques. Fig. 1a shows XRD pattern of the oxide product. The observed peaks in this pattern are fully matched with the corresponding crystalline cubic Co_3O_4 phase (JCPDS no. 42-1467). No other phase peaks were observed, demonstrating that the deposited hydroxide was completely transformed into Co_3O_4 after heat-treatment at 400 ^{o}C for 3h. SEM observation showed a plate-like structure with regular uniformity (Fig. 1b).

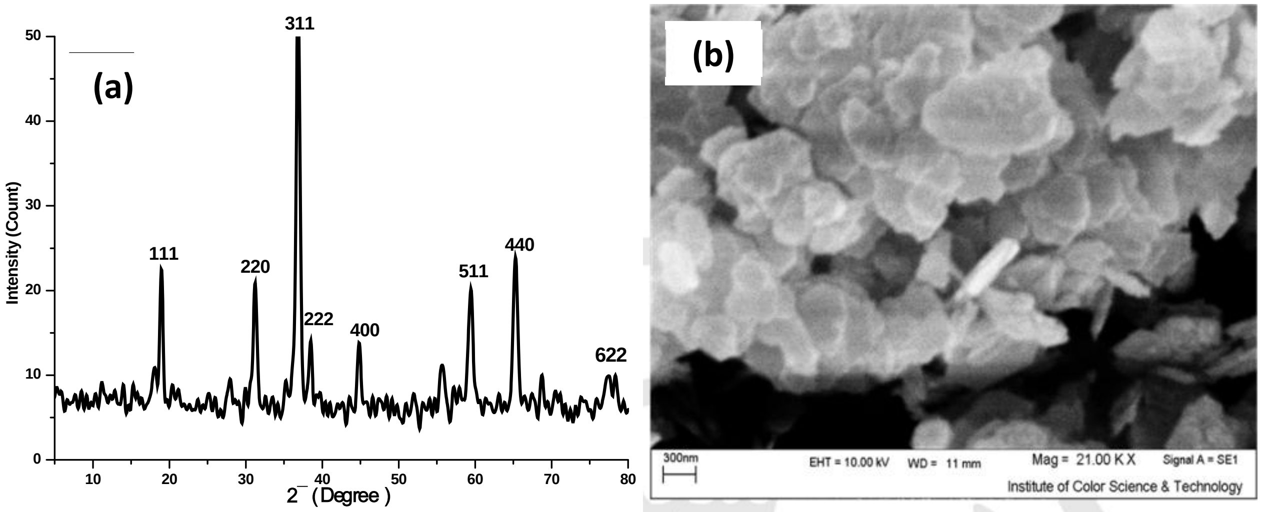

Fig. 1. (a) XRD pattern and (b) SEM image of nanoplates.

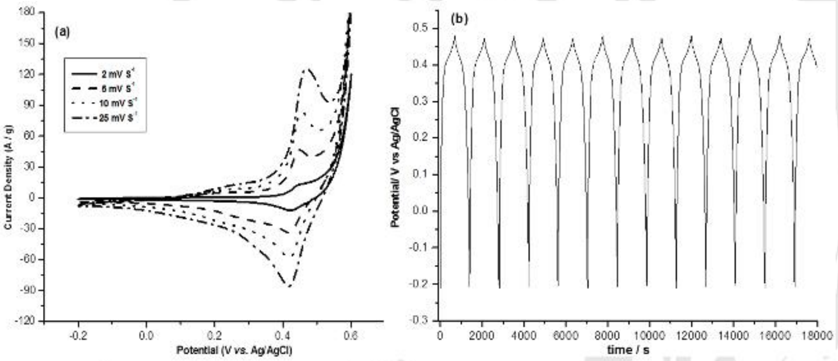

Fig. 2. (a) CVs and (b) CPs of Co_3O_4 nanoplates**.**

Fig. 2 shows the supercapacitive behavior of the prepared nanoplates. The specific capacitances of Co_3O_4 nanoplates was calculated to be 563.1, 505.8, 437.5 and 388.5 F g^{-1} at the scan rates of 2, 5, 10 and 25 mV s^{-1}, respectively. These values showed excellent supercapacitive performance of the nanoplates, which resulted from their plate and thin texture, and high surface area.

Keywords: *Co_3O_4, Pulse electrosynthesis, Nanoplates, Supercapacitors*

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Electrochemical Performance for Methanol Oxidation of Pt/Carbon Quantum Dot Nanocomposites in Acid Media

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Abstract

The composites of carbon quantum dots decorated by Pt nanoparticles have been prepared via reduction of carbon quantum dots and H_2PtCl_6 by sodium borohydride in one pot and the electrochemical activity for methanol oxidation was investigated. Experimental results demonstrate that, in comparison to the widely-used Pt-C catalyst, carbon quantum dot-supported Pt nanoparticles demonstrate enhanced efficiency for methanol electro-oxidation. For instance, by comparison the cyclic voltammofram of Pt-CQD catalyst in acid media and presence methanol observed that active surface area enhanced by increasing methanol, while Pt-C catalyst performance is not like that [1, 2]. Second experiment was investigation effect of the number cycles on ratio of forward peak current density to the backward peak current density of methanol oxidation. Results show that, this ratio increases by increasing the number of cycles. The other work was investigation of effect of increasing of scan rate on oxidation of methanol. Results show that, increases of scan rate can help to improving performance of electocatalyst toward methanol oxidation

Finally, the effect of methanol concentration on Pt-CQD catalyst performance checked out and observed that this catalyst did not show any signs of poisoning. This findings favor the use of carbon quantum dots as catalyst supports for direct methanol fuel cell [3-5].

Keywords: *Carbon Quantum Dot, Methanol Electro-oxidation, Current density, backward peak.*

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Electrochemical Evaluation of Liquid Electrolyte for Dye-Sensitized Solar Cells (DSSCs) by Cyclic Voltammetry

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Introduction

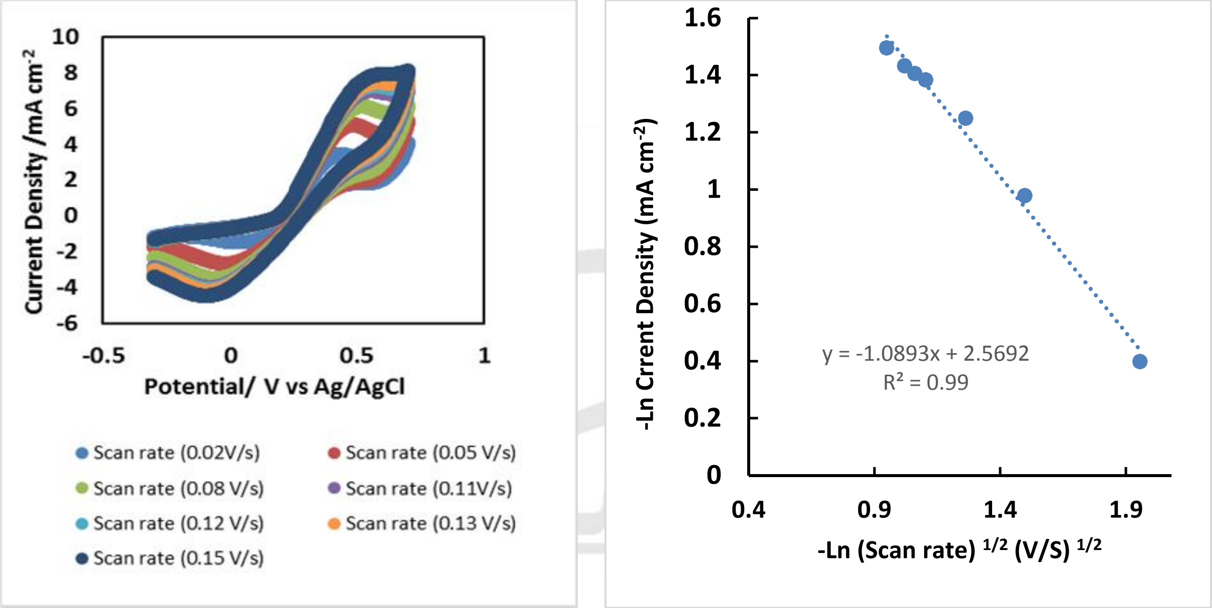
While Prof Grätzel invented dye-sensitized solar cells (DSSCs) in 1991, the research on different parts of this photovoltaic device for increasing efficiency has attracted great attention [1]. Electrolyte is one of key component for DSSCs and its properties have much effect on the conversion efficiency and stability of the solar cells [2]. Several studies have used cyclic voltammetry technique in order to explain the effect of electrochemical properties of electrolyte on the performance of DSSCs [3-5]. So the aim of this work is studying reduction mechanism of I_3^- at Pt electrode by cyclic voltammetry.

Method

Cyclic voltammograms for the electrolyte were recorded in three-electrode electrochemical cell containing a Pt-electrode as the working electrode, Pt- wire as counter and an Ag/AgCl as a reference electrode dipped in acetonitrile solution containing 1 mM I_2, 10 mM KI and 0.1 M $NaNO_3$ at different scan rates, using an electrochemical workstation (PGSTAT. 302N, Autolab, Eco-Chemie, The Netherlands).

Result and Discussion

Fig.1. (a) shows the cyclic voltammograms of electrolytes in different scan rates and Fig. (b) Shows the relationship between redox peak and scan rate. Linear relationship between peak currents and square roots of scan rates indicates the redox reaction of I^-/I_3^- on the surface of Pt electrode is a diffusion-limited reaction, which may be related to the transport of iodine species from Pt surface to electrolyte solution. These results suggest that there is no specific interaction between I^-/I_3^-- redox couple and Pt counter electrode.



(a) (b)

Fig 1: (a) Cyclic voltammograms of acetonitrile solution containing 1 mM I_2, 10 mM KI and 0.1 M $NaNO_3$ at different scan rates. (b) Relationship between redox peak and scan rate.

Conclusion

The electrochemical evaluation of DSSCs liquid electrolyte showed the reduction of I_3^- on the Pt electrode was limited by diffusion of I_3^- species from electrode to electrolyte solution. Therefore, additions of chemical compounds which accelerate the diffusion of I_3^- can enhance the performance of DSSCs.

Keywords: Dye Sensitized Solar Cells, Cyclic Voltammetry, Electrolyte, Diffusion

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Pt.Ni nanoparticles supported on Graphene as an effective catalyst for oxygen reduction

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Abstract

The oxygen reduction reaction (ORR) is one of the key processes of energy systems. The ORR is catalyzed by Pt. The ORR sluggish kinetics requires a substantial amount of Pt, which has limited the scaling-up of technologies. Alloying Pt with 3d transition metals such as Ni has been reported as a successful approach for reducing the cost of catalysts [1]. Another approach is Pt-loaded onto graphene (G). Graphene have a large specific surface area and good conductivity. In this study, we report the synthesis of Pt.Ni alloy nanoparticles supported on graphene by *in-situ* reduction of metal on graphene oxide (GO) that provides enhanced activity toward the ORR. GO was prepared using Hummers method reported previously [2]. 50 mg of GO was ultrasonically dispersed in de-ionized water. $H_2PtCl_6.xH_2O$ and $NiCl_2$ (1:1) and the total metal content was 20 wt%. Then 10 mL of $NaBH_4$ solution in excess was added. The solid particles were separated by filtration, washed and dried. The catalyst inks were prepared by mixing 30 mg of catalysts with 2-propanole, de-ionized water and 5wt% nafion solution. After the painting of catalyst inks on the carbon paper, the final electrodes were dried at 120 ^oC for 1 h. The electrochemical measurements were carried out using three-electrode compartment. An Ag/AgCl electrode was used as the reference electrode and platinum as the counter electrode. Cyclic voltammetry (CV) was applying a scan rate of 50 mV s^{-1} between -0.1 and +1.2 V vs. RHE in the O_2 saturated NaOH solution. EIS measurements were performed over a frequency range of 100 KHz to 0.01 Hz. The CV results of Pt.Ni/G revealed the onset ORR peak of 0.7 V/RHE and ORR peak of 0.46 V/RHE, which is in good agreement with other studies [3]. Polarization curves were produced at a scan rate of 1 mV s^{-1} and the kinetic parameters were extracted by the Tafel equation. The Tafel slope and current density of electrode were 62 mV/decade and 5.7×10^{-3} mA cm^{-2}. A Tafel slope of 60 mV per decade is observed because the electrode surfaces are a mixture of M and MO and on the M/MO surface, the rate determining step is a pseudo 2-electron procedure. The EIS study

was carried out at different dc potentials. The Nyquist plots are shown in Fig. 1. The Nyquist plots of E≥0.6 V show two loops, while the OCP indicate one loop in the high frequency region and semi-infinite diffusive manner in the low frequency region. According to the Tafel results, the two electron transfer mechanism is suggested to be accrued at E≥0.6 V:

$$[O_2 \cdot (H_2O)_n]_{aq} + 2e^- \rightarrow (HO_2^-)_{ads} + OH^- + (H_2O)_{n-1} \quad (1)$$

$$(HO_2^-)_{ads} + H_2O + 2e^- \rightarrow 3OH^- \quad (2)$$

Two electric circuits were employed to obtain quantitative information (inside Fig. 1) . The electric circuits of (a) and (b) were used to simulate the impedance response of OCP and applied dc potentials, respectively. In the model (a), R_1 and R_2 indicate the double layer charge-discharge and the adsorption of reactants or intermediates resistance, respectively. In model (b), the R_1 and R_2 are the charge transfer reaction according to Eq. (1) and Eq. (2). By increasing the positive potential, the R_1 and R_2 values decrease (Fig. 2). It is due to O_2 molecule adsorption by the oxygen atom orientation and the charge transfer happens more easily and the resistance values decrease. The R_2 of Pt.Ni supported on Vulcan carbon was measured 26 Ω cm^{-2} at 0.9 V in our previous work, which was 3 times greater than Pt.Ni supported on Graphene resistance.

Keywords: *Platinum, Nickel, Graphene, Electrocatalysts, Oxygen reduction*

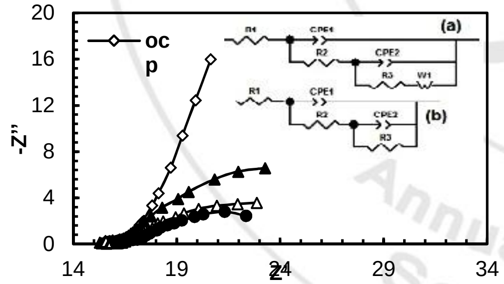

Fig. 1. Nyquist plot of Pt.Ni/G, recorded in 0.1 M O_2 saturated NaOH media. The electrical equivalent circuits of open circuit potential (a) and applied dc potentials (b)

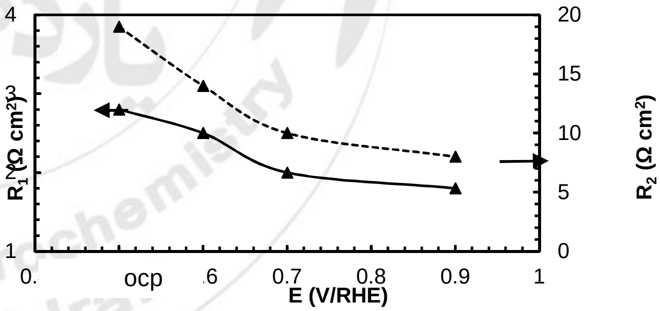

Fig. 2. Dependence of the R_1 and R_2 values of the electrode as a function of different applied potentials; recorded in 0.1 M O_2 saturated NaOH media.

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Changing Electro-deposition Parameters to Enhance Co Nanoflakes as Electro-catalyst

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Abstract

In this paper, the effect of electro-deposition, time and current density, on cobalt nanoflakes as electro-catalyst for water oxidation reaction have been studied. We have selected steel-mesh, 5, 10, 20 $\frac{m}{c\quad 2}$ as the flexible substrate and different current densities, respectively. Deposition time have been also changed between 500-2000s. LSV and SEM results revealed that the minimum overpotential was attributed to Co nanoflakes obtained from 5 $\frac{m}{c\quad 2}\ ı\imath\ 2000s$.

Keywords: *Cobalt nanoflake, Electrocatalyst, Current density, Electrodeposition time, Overpotential*.

Introduction

Considering limit of fossil resources and negative their effect on environment using the renewable energies such as solar cells and producing hydrogen by water splitting is unavoidable. One criterion to improve the performance of a H2 production system based on solar energy is to decrease required input electrical power.

Since reduction of electro-catalyst overpotential is very important for increasing the efficiency of water splitting, selecting the best electro-catalyst for artificial photosynthesis is one of the big challenges. Electro-catalyst must be have low overpotential, high mechanical resistance, low cost and furthermore it must be earth abundant. While Ru and Ir shows best efficiency in artificial photosynthesis, this materials aren’t earth abundant and, hence, it is necessary to utilize low cost and potentially suitable materials like Ni, Co, Cu, Fe and Zn and try to optimize their performance [1,2,3,4,5].

In this work, we studied effect of current density and time of electrodeposition on morphology of cobalt nanoflakes as well as their electro-catalytic performance.

Result

In figure 1 we can see that electrodepositing sample with 5 $\frac{m}{c\quad 2}$ current density for 2000s shows suitable morphology with higher flakes surface density and aspect ratio than others. Both high current densities and low times show unsuitable morphologies. In high current densities cobalt particles can't grows regularly on steel-mesh substrate and lead to some areas without any flakes and in low times the density of cobalt nanoflakes is lower than other samples.

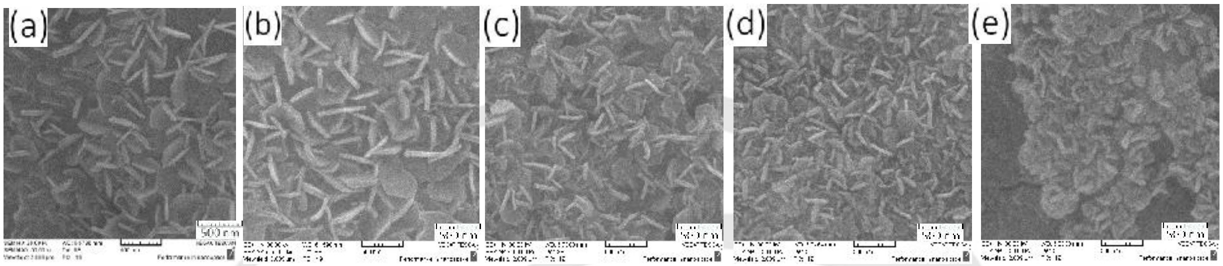

Figure 1: SEM images of electrodeposited samples with different current density/time: (a) 5 $\frac{m}{c\quad 2}$ / 500s, (b) 5 $\frac{m}{c\quad 2}$ / 1000s, (c) 5 $\frac{m}{c\quad 2}$ / 2000s, (d) 10 $\frac{m}{c\quad 2}$ / 2000s and (e) 20 $\frac{m}{c\quad 2}$ / 2000s.

Table 1 shows overpotentials of the samples electrodeposited with various conditions. It can be seen that sample fabricated with 5 $\frac{m}{c\quad 2}$ current density during 2000s shows the least overpotential as compared with others.

[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
Time(s)	500	1000	2000	2000	2000
Overpotential *(mV)	0.5075	0.5178	0.4984	0.5160	0.5134

* Overpotential of the samples have been measured versus Ag/AgCl.

Conclusion

In summary, electrodeposition with high current densities led to nonefficient morphology while short time deposition also resulted in low surface density of cobalt nanoflakes. Hence it was found that electrodepositing cobalt nanoflakes with low current densities and long duration times obtains the best electrocatalyst performance.

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Enhanced electrocatalytic oxidation of methanol at rGO-NiO nanocomposite modified carbon ceramic electrode in alkaline medium

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Abstract

In this work enhanced electrocatalytic oxidation of methanol at reduced graphene oxide-nickel oxide nanocomposite modified carbon ceramic electrode (rGO-NiO/CCE) was studied by electrochemical techniques in alkaline medium. Due to some unique properties of carbon ceramic electrode (CCE) involving high porosity, renewable surface, good conductivity, and economy it was used as a substrate in this study (1). The composition of reduced graphene oxide with excellent conductivity and high surface to volume ratio, and NiO results a new nanocomposite with brilliant performance for electrocatalytic applications. The mechanism of electrocatalytic oxidation of methanol on rGO-NiO/CCE was investigated and proposed to be done by reaction with NiOOH and also direct electro-oxidation reaction. The effects of scan rate and methanol concentration on the anodic peak heights as well as current decay measurements were studied. Cyclic voltammetry studies demonstrated that the rGO-NiO/CCE exhibits much higher electrocatalytic activity and stability rather than CCE, rGO/CCE, NiO/CCE in methanol oxidation.

Keywords: *reduced graphene oxide, nickel oxide, methanol oxidation, carbon ceramic electrode*

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Preparation and Electrochemical Performance of Hematite (α-Fe_2O_3) Nanoparticles as Supercapacitor Electrode Material

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Abstract

As a new class of energy storage devices, supercapacitors display the desirable characteristics of high power density (ten times more than batteries), fast rates of charge–discharge (with seconds), excellent cycling stability, and low maintenance cost, which make them one of the most promising candidates for next-generation power devices [1–3]. Unfortunately, the energy storage density of existing supercapacitors is limited, generally one order of magnitude lower than that of batteries [4]. Currently, for practical applications, it is essential to increase the energy density of supercapacitors, without sacrificing the device power density and cycle life. Experimental evidence suggests that electrode materials play a key role in the development of high performance supercapacitors. Among various supercapacitor electrode materials, pseudo-capacitive transition-metal oxides and electronically conducting polymers based on faradic redox charges to rage have exhibited much higher energy density than that of electrochemical double-layer capacitive carbon materials [5–7]. Among various metal oxides, iron oxides has attracted great attention due to its low cost and environmentally benign nature [5].

In this work, we report on the electrochemical synthesis of α-Fe_2O_3 nanoparticles *via* cathodic electrodeposition route. The prepared nanoparticles were characterized by XRD, IR and SEM techniques. Their electrochemical properties was also evaluated by cyclic voltammetry, galvanostatic charge–discharge cycling and electrochemical impedance spectroscopy tests. Fig. 1 showed the CV and CP curves of the prepared α-Fe_2O_3 electrode in 0.5 M Na_2SO_3. The specific capacitance of the prepared α-Fe_2O_3 was calculated at a scan rate of 2 mV s^{-1}. Also, the capacitance retention after 1000 cycles is about 92 % of the initial capacitance at a current density of 1 A g^{-1}. The high capacitance as well as stability of α-Fe_2O_3 electrode is attributed to

its large surface area and fine particle morphology. As iron oxides are inexpensive, the synthetic route adopted for α-Fe_2O_3 in the present study is convenient and the SC is high with good cycling stability, the α-Fe_2O_3 nanoparticles have a potential material for supercapacitors.

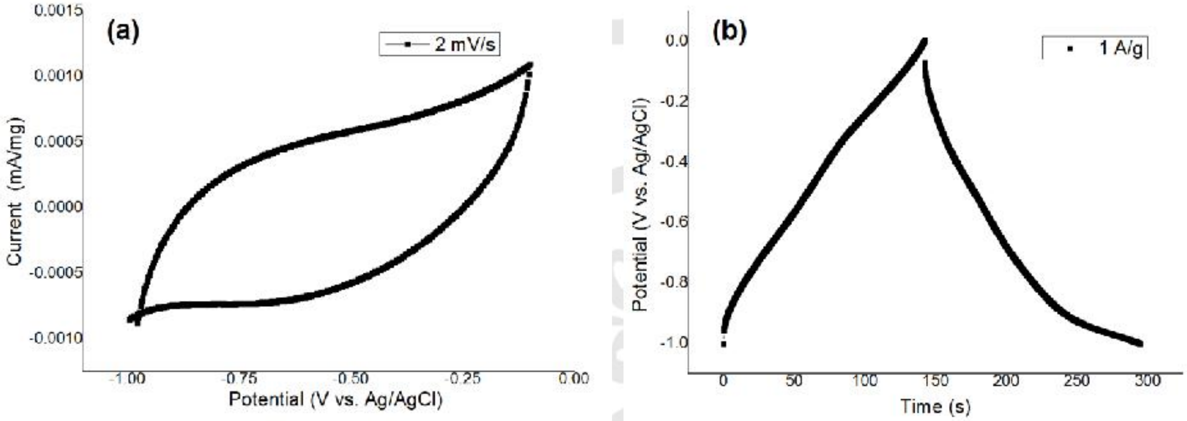

Fig. 1. (a) CV and (b) CP of α-Fe_2O_3 nanoparticles.

Keywords: *α-Fe_2O_3, Electrochemical synthesis, Nanoparticles, Supercapacitors*

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Electrodeposition of functionalized multiwalled carbon nanotubes and graphene oxide onto TiO_2 nanotubes for supercapacitor applications

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Abstract

The hybrid of graphene oxide (GO) and multiwalled carbon nanotubes (MWCNT) used as supercapacitor have recently attracted tremendous interest because of their unique thermal, mechanical, and electrical properties [1]. According to the previous literatures, the fabrication of GO/RGO-CNT hybrid for supercapacitor applications can be performed via the physical combing of CNTs, GO/RGO and a polymer binder in a solvent and then coating of the resulting composite on a suitable substrate [2, 3]. Based on this procedure not only the thickness and amount of the hybrid film deposited on substrate can not be better controlled but also the film does not have good mechanical properties and results the decrease of specific capacitance, cycle life and conductivity of the electrode might be expected. In the present work a new strategy to produce GO-MWCNT hybrid without any polymer binder for supercapacitor applications has been presented. The hybrid was prepared by simple co-electrochemical reduction of functionalized multiwalled carbon nanotubes (fMWCNTs) and GO onto the previously formed TiO_2 nanotubes fabricated by anodizing of titanium.

Fig. 1a shows the SEM image of bare TiO_2NTs/Ti electrode where distinct and well resolved nanotubes are visible. Fig. 1b demonstrates the successful formation of the 3D network structure of the fMWCNT-GO hybrid where RGO sheets and RfMWCNT particles deposited on the TiO_2 nanotubes are visible. Fig. 2 presents the galvanostatic charge–discharge curves of the electrodes examined in 1.0 M H_2SO_4 electrolyte at a constant current of 12 A g^{-1}. Using Equations (1), the specific capacitance of 600 F g^{-1} is obtained at a current density of 12.0A g^{-1} in 1.0 M H_2SO_4 electrolyte for R(fMWCNT-GO)/TiO_2NTs/Ti electrode, compared to 490 F g^{-1} and 400 F g^{-1} for RfMWCNT/TiO_2NTs/Ti and RGO/TiO_2NTs/Ti electrodes respectively.

$$C_{SP} = (I \times \Delta t)/(\Delta V \times m) \qquad (1)$$

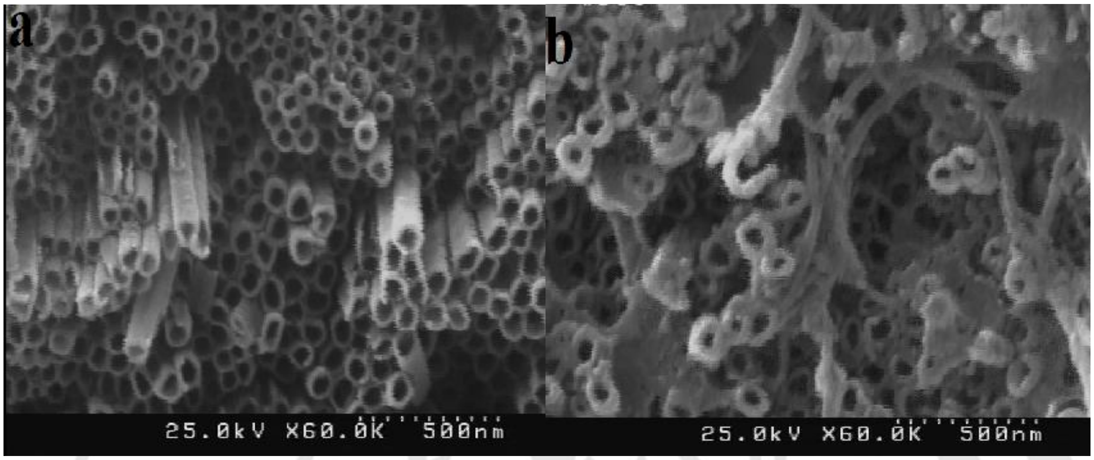

Figure 1

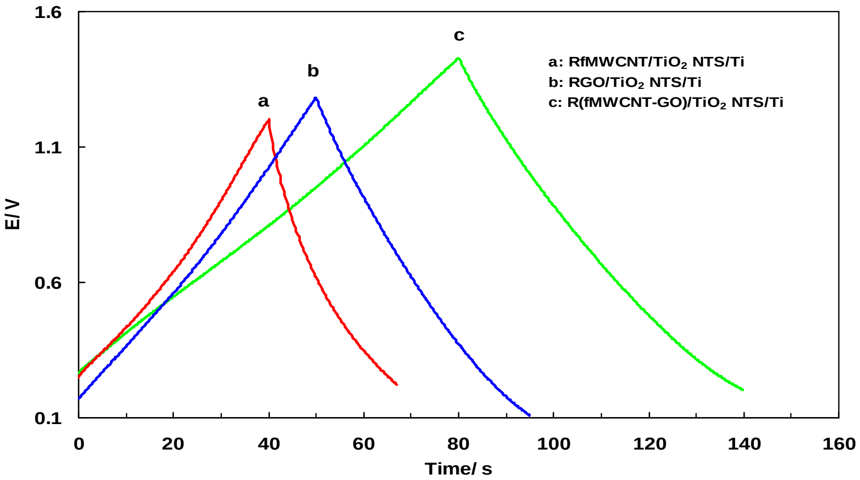

Figure 2

Keywords: *Supercapacitor, Multiwalled carbon nanotubes, Graphene oxide, TiO_2 nanotubes*

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In situ activation of Ni alloy with Mo for hydrogen evolution reaction

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Keywords: *Hydrogen evolution reaction, in situ activation, Tafel, Electrochemical impedance spectroscopy.*

Abstract

In this study Ni alloy have been activate during hydrogen evolution reaction by adding Mo ions into the alkaline electrolyte. After dissolving different amount of ammonium molybdate in the NaOH electrolyte, Ni alloy was used as cathode for hydrogen evolution reaction. Afterwards a comparison between hydrogen overpotential measured in Ni alloy with and without in situ activation has been made; the in situ activation shows an improvement of electro catalytic properties of Ni alloy for hydrogen evolution reaction. In order to increase the impact of in situ activation of Mo ions used of Ni structure, that extremely significant impact in improving the Ni catalyst activation during in situ activation The values of overpotential and Tafel slop for Ni alloy,with and without of Mo improved . In situ activation Ni showed a good stability for HER. In this study are used from chronopetentiometery (CP), chronoamperometric (CA), electrochemically impedance spectroscopy (EIS) and linear polarization (LP) techniques.

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Spontaneous Deposition of Pd Nanoparticles on Single Wall Carbon Nanotubes as an Electrocatalyst for Methanol Fuel Cell

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Abstract

Direct methanol fuel cell (DMFC) has attracted great attention in portable devices and transportation applications because of its high energy density, low cost, and easiness in transportation and storage [1]. A great deal of interest has been focused on the choice of Pd-based catalyst because it has a good electro activity for methanol oxidation in alkaline media [2]. Pd catalysts can overcome the CO-poisoning effect and thereby yield high performance in DMFCs. In order to improve catalytic properties of nanoparticles and minimize the overall cost of fuel cell, Pd nanoparticles (PdNPs) are deposited on several materials such as carbon supports. Functionalized carbon nanotubes (FCNTs) with many oxygen-containing functional groups (such as carboxyl and hydroxyl groups) are getting more attractive as a support material for Pd nanoparticles [3]. The immobilization of metal nanoparticles on nanotubes is of interest to obtain nanoparticles/nanotube hybrid materials with useful properties [4]. In this work, the nanocomposite of PdNPs on single wall carbon nanotube (SWCNT) was prepared by a facile spontaneous reduction method without using any reducing agent. SWCNT-supported Pd (PdNPs/SWCNT) was decorated on carbon ceramic electrode (PdNPs/SWCNT/CCE) and used as electrocatalyst for oxidation of methanol in alkaline media. PdNPs/SWCNT nanocomposite was characterized by scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD) and energy dispersive X-ray spectroscopy (EDX). Electrochemical studies including cyclic voltammetry and chronoamperometry were used to study electrochemical properties of obtained electrocatalyst. The effects of some experimental factors such as methanol concentration, scan rate, the upper limit of potential scanning region and long-term stability of electrode were investigated. It was found that PdNPs/SWCNT/CCE was catalytically more active than Pd nanoparticles decorated on CCE without any support. On the

other hand, the PdNPs/SWCNT/CCE catalyst has satisfactory stability and reproducibility for electrooxidation of methanol when stored in ambient conditions and improve catalytic activity in continues cycling makes it more attractive for fuel cell applications.

Keywords: *Electrocatalyst, Pd nanoparticle, SWCNT, Carbon-ceramic electrode, Methanol fuel cells*

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Electrochemical Supercapacitor Studies of GO – MWCNTs

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Abstract

over the past few years, considerable effort has been devoted to the development of alternative energy storage/conversion devices with high power and energy densities because of the ever-increasing environmental problems and the up-coming depletion of fossil fuels. Supercapacitors have attracted a great deal of attention owing to their higher power densities relative to secondary batteries and traditional electric double-layer capacitors[1-3]. Graphene and multiwalled carbon nanotubes (MWCNTs) have enjoyed significant recent attention. [2].

Herein we report physical mixing/dispersion method for preparing the electroactive material for supercapacitor electrode. GO was prepared by Hummer's method[4] and dispersed in distilled water and then MWCNTs were added to it by ultrasonication for 0.5h. The specific capacitance of GO-MWCNTs from the cyclic voltammetry (CV) curves of figure (1) was found to be 256 mF. cm^{-2} at scan rate of 10 mV.s^{-1} that was greater than of 12 mF.cm^{-2} obtained for MWCNT by Honda, et al [5]. MWCNTs tend to agglomerate while suspended in water, and surfactants are needed for uniform dispersion. The high dispersibility of graphene oxide (GO) in water and its π-π interaction with MWCNTs facilitates the dispersion of MWCNTs without use of surfactant [6].

High specific surface area of GO and MWCNTs and surface functionalization can cause an improvement in the specific capacitance of carbon materials.

Keywords: Supercapacitor, Graphene Oxide, MWCNTs, Capacitance

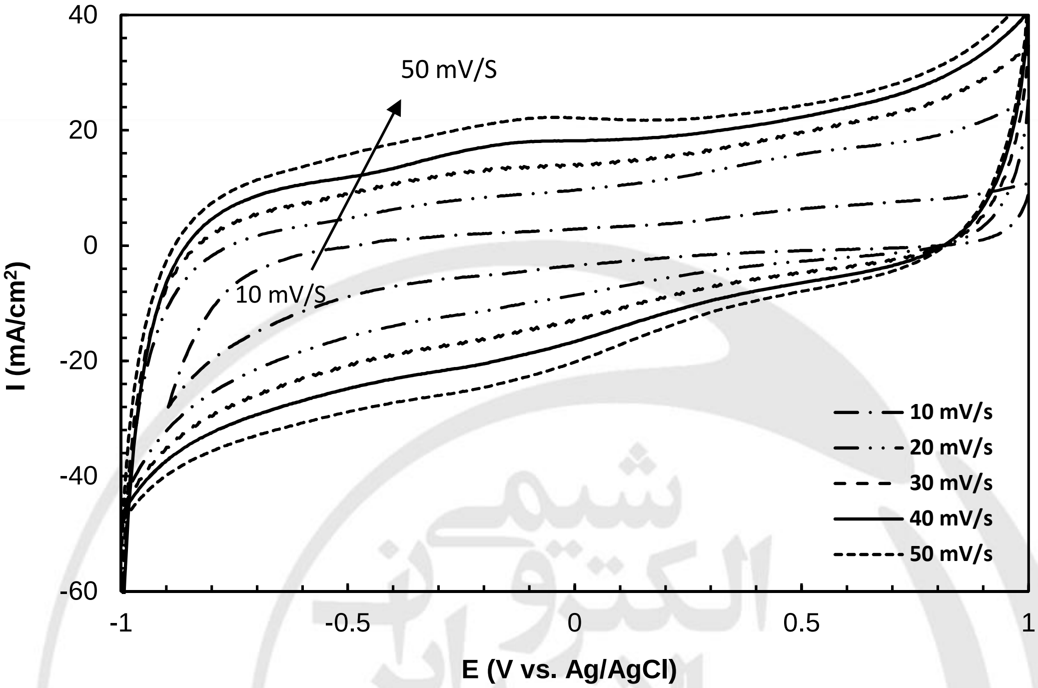

Figure. 3. CV curves of GO-MWCNTs at different scan rates in 0.5M Na_2SO_4 solution.

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Supercapacitive performance of NiO Nanospheres Prepared by Electrodeposition-Heat treatment method

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Abstract

Nanostructured nickel oxide (NiO) has received increased interest because of its potential applications in rechargeable alkaline batteries [1], supercapacitors [2] and solar cells [3]. As a result, different synthesis methods such as chemical precipitation, decomposition, hydrothermal, surfactant template, solid state, solvothermal and sol–gel have been developed for preparation of NiO nanostructures with various shapes and sizes. Furthermore, electrochemical methods (i.e. anodic and cathodic electrodeposition) have been applied for the preparation of nanostructured NiO and demonstrated that electrolytic NiO exhibits better supercapacitive behavior, which can be employed in electrochemical supercapacitors. In this letter, we report NiO ultrafine nanoparticles prepared by galvanostatic deposition ($i=0.5$ A dm^{-2}) from 0.005 M $Ni(NO_3)_2$ bath (T=40°C) followed by heat-treatment at 300ºC for 3h. The supercapacitive performance of the nanoparticles was evaluated by cyclic voltammetry (CV) and charge-discharge techniques.

Fig. 1a shows XRD pattern of the oxide product. The observed peaks in this XRD pattern are fully matched with the corresponding pure cubic-structured crystalline NiO (JCPDS 47-1049, solid lines in Fig. 1a). The SEM image (Fig. 1b) showed the smooth and uniform sphere shape morphology for NiO. In fact, NiO sample is composed of well–dispersed spheres with the size of about 50 nm (Fig. 1b). The galvanostatic charge-discharge cycling (1000 cycles) was recorded at a current density of 2 A g^{-1} which the first 20 cycles is presented in Fig. 2. Then, the specific capacitance was calculated to be 1108 F g^{-1}. As seen in Fig. 2, the specific capacitances of 500th and 1000th discharging cycles were calculated to be 1042 and 998 F g^{-1}, which revealed 94.1% and 90.2% capacity retentions after 500 and 1000 discharging. These results confirmed an excellent cycling stability of NiO nanospheres.

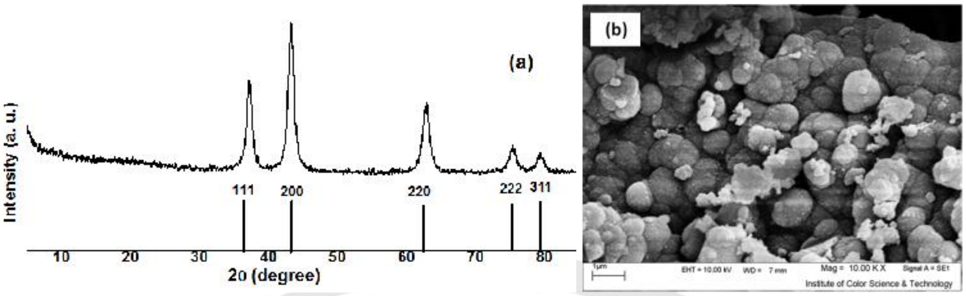

Fig. 1. (a) XRD pattern and (b) SEM image of NiO nanospheres.

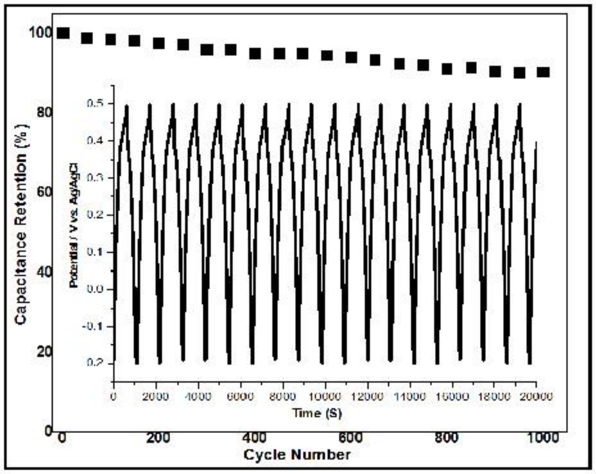

Fig. 2. Cycling performance of NiO nanospheres at the applied current density of 2 A/g

Keywords: *NiO, Electrosynthesis, Nanospheres, Supercapacitors*

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Electrocatalytic oxidation of formaldehyde on novel composite of nickel/ triton-x100/poly(o-aminophenol-co-aniline) modified carbon paste electrode

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Abstract

In recent years, many reports have been published on the oxidation of formaldehyde under a wide range of conditions and on various electrodes [1-4]. Although Pt is one of the most efficient metal catalysts for oxidation of formaldehyde, it is easily poisoned by the CO-like intermediate produced from incomplete oxidation of the fuel. Another problem intrinsic to Pt is its high cost. One approach to solving these problems is the development of a cheaper, non poison able catalyst while maintaining high activity for the oxidation process. In this approach several reports have already been published on the surfaces of catalysts such as Cu [2], Ni [3], and Ag [4].

It is well known that conducting polymers (CPs) with porous structures and high surface areas have been proved to be suitable host materials for dispersion of metallic particles [5-6]. In the family of conductive polymers, aniline is a molecule used to modify electrode surfaces, forming the polyaniline polymer (PANI). The electropolymerization of aniline by continuous potential scanning allows the study of the redox properties of the electrogenerated films and their growth. Additionally, in recent years a wide variety of copolymers have been studied for many different applications. Copolymerization can be used as a technique to improve the properties of a material. The characteristics of electrochemical copolymerization are highly dependent on the synthesis conditions, in particular, the mole fraction of each of the monomers involved in the reaction [7-9].

This paper deals with electrochemical oxidation of formaldehyde in alkaline solution with a new electrocatalytic system composed of Ni(II)/Ni(III) redox ions incorporated in poly(o-aminophenol-co-aniline)/Triton-X100 film modified carbon paste electrode. At first, copolymeric film on the surface of carbon paste electrode was formed by successive potential cycling in solution containing o-aminophenol and aniline as monomer and Triton X-100 as a surfactant.

Ni(II) ions were incorporated into the electrode by immersion of the copolymeric modified electrode having amine groups in 0.1 M Ni(II) ion solution.

The influences of some parameters such as mol ratio of monomers in copolymer formation, the number of potential cycling for copolymer formation, and formaldehyde concentration on its oxidation current have been investigated. The rate constant (*k*) for the chemical reaction between the formaldehyde and nickel hydroxide has been evaluated by chronoamperometry method.

Keywords**:** *Electropolymerization, Copolymer, Triton-X100, Electrocatalytic Oxidation, Nickel, Formaldehyde*

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Electro-oxidation of formaldehyde on nickel oxide nanoparticle-modified glassy carbon electrode as a promising electrode material to enhance the performance of a fuel cell anode

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Abstract

In this work, prepared nickel oxide nanoparticle-modified glassy carbon electrode (NiO-NPs@GCE) was successfully employed for electrocatalytic oxidation of formaldehyde (HCHO) in alkaline media. Scanning electron microscopy (SEM), cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and chronoamperometry was employed.

Keywords: *Formaldehyde electro-oxidation, Nickeloxide nanoparticle, fuel cell, cyclic voltammetry*

Introduction

Finding alternative metals (Ni, Cu, etc.) as low-priced materials is attended to used in anodes for HCHO oxidation, instead of Pt or Pd. In this work, GC electrode was modified with NiO-NPs for electro-oxidation of formaldehyde.

Methods

The preparation method of NiO-NPs@GC electrode was previously described (1). The nickel solution composition was a 10 mM nickel nitrate and 1 M sodium chloride in ammonia buffer (pH=8.5). Electrodeposition process was performed at a potential of -1.3 V vs. Ag/AgCl, on a GC disc electrode with apparent surface area of 0.0314 cm^2. CV, chronoamperometry and EIS techniques were applied using potentiostat/galvanostat apparatus. SEM analysis was applied using a Philips model X30 instrument. All cases of electro-oxidation of HCHO were done in a solution of 0.1 M HCHO and 0.1 M KOH.

Results and discussion:

SEM image of NiO-NPs on the surface of GCE, shows the size of particles is between 40 to 60 nm (Figure 1). Electrocatalytic activity of prepared electrode toward electro-oxidation of formaldehyde at a scan rate of 10 mVs^{-1} is investigated by CV techniques (typically shown as Figure 2).

Table 1.Shows the parameters that explain the electrocatalytic activity of modified electrode towards formaldehyde oxidation. Figure 3 Suggests that the electrocatalytic oxidation of formaldehyde on NiO-NPs electrode is a diffusion controlled process. Moreover, Figure 4 Indicates that the electro-oxidation process on NiO-NPs electrode is irreversible. EIS image shows that the increase in the cathodic potential, results in increasing rate of the electron-transfer procedure.

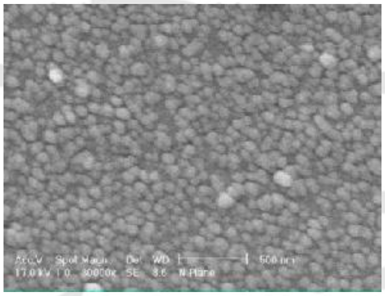

Fig. 1. SEM image of electrodeposited NiO-NPs on GCE.

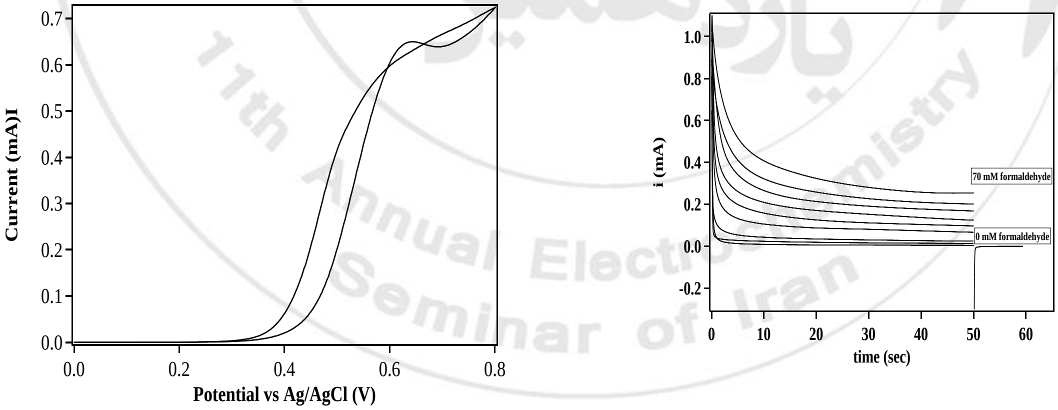

Fig. 2. CV for modified electrode at 10 mVs^{-1}

Table 1.CV parameters for formaldehyde oxidation.

Onset E / V	E_p / V	j / mA/cm^2	A_f/A_b ratio

0.41	0.63	21.33	0.86

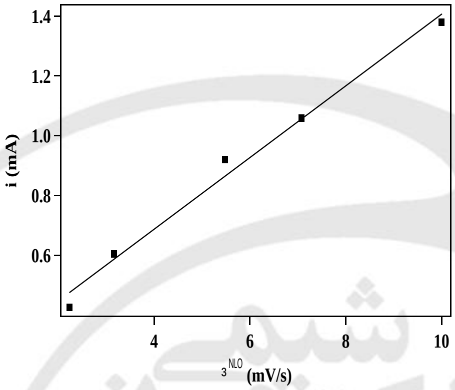

Fig. 3.Peak currents vs. the square root of scan rates.

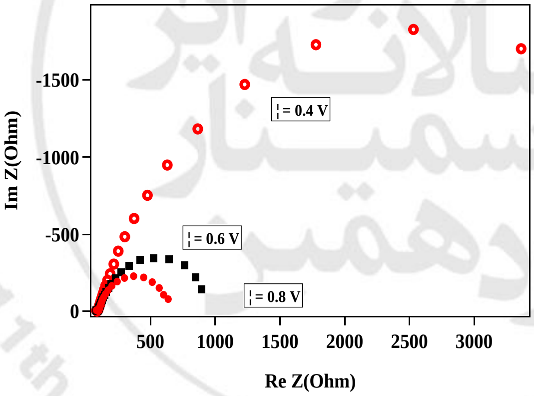

Fig. 4. Chronoamperograms recorded for electro-oxidations of 0 to 70 mM of formaldehyde.

Fig. 5. Nyquist plots for electrocatalytic behavior of NiO-NPs electrode towards formaldehyde between -400 to -800 mV.

Conclusions

This work demonstrated that NiO-NPs@GCE has excellent catalytic activity, thus it suggests as high performance and low price anode for fuel cell purposes.

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Effect of different dicarboxylic acid additives on electrochemical behavior of Vanadium Redox Flow Batteries

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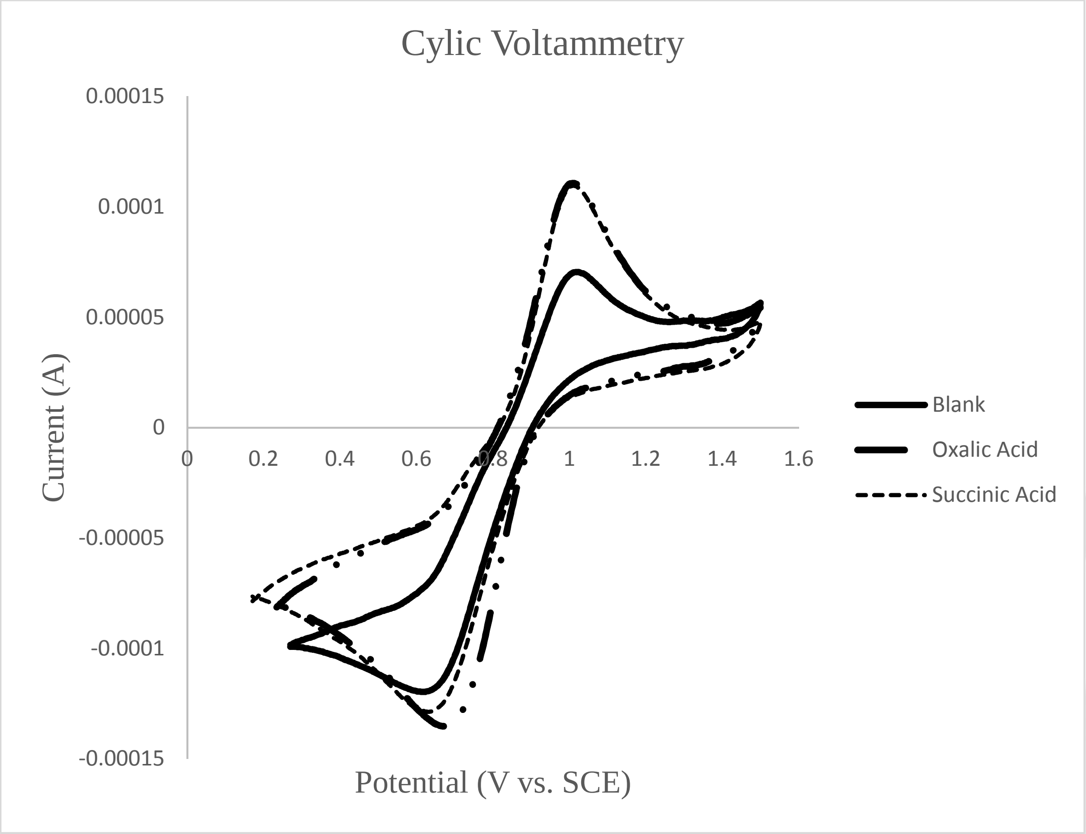
Abstract

The vanadium redox flow battery (VRB) is one of the most promising electrochemical energy storage systems deemed suitable for a wide range of renewable energy applications that are emerging rapidly to reduce the carbon footprint of electricity generation. Typically, each cell comprises of an anode, a cathode and an ion exchange membrane separator that allows diffusion of ions across the membrane while preventing the cross-mixing of the electrolyte solutions from these two reservoirs. Redox flow batteries have many technical benefits over other energy storage systems; they represent an excellent combination of energy efficiency, capital cost and life cycle costs when compared to other technologies.

In this work some of short chain dicarboxylic acids were added to catholyte of VRFB to improve the electrochemical behavior of V(V)/V(IV) redox couples. These additives were Oxalic acid and succinic acid. Cylic Voltammetry, Electrochemical Impedance Spectroscopy techniques were used to investigate the effect of these additives. According to the results of experiments Oxalic acid and succinic acid had better performance in comparison with the blank electrolyte, respectively.



Keywords: *Vanadium Redox Flow Batteries, Carbon Felt, Electrolyte additive, Dicarboxylic acid*

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Sn-Ni alloy nanoparticles as anode of lithium ion battery

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Abstract

Sn-Ni alloy nanoparticles are synthesized readily by pulse electrodeposition method for their applications in Li-ion batteries. It is found Nickel not only affects the phase structure and morphology of the alloy, but also impacts Li-Sn alloying and dealloying behaviors. In lithium ion batteries, the Sn-alloying electrodes deliver stronger cycling stability than the pure Sn anode. The prepared Sn-Ni alloy is characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The electrochemical tests of the alloying electrode shows the first discharge capacity 715 mA.h.g^{-1} and the reversible discharge capacity 591 mA.hg^{-1} over 25 cycles.

Keywords: *Li ion battery, Anode, Alloying electrode, Tin, cyclability*

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Preparation of Cu-Pd bimetallic nanoporous carbon composite and its application as electrocatalyst for hydrogen evolution reaction

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Abstract

Nowadays, fuel cell become promising power sources due to owing to its low pollutant emission, renewable energy, and high-energy conversion efficiency [1]. Hydrogen, H_2, is being considered as an energy carrier and one of the most important fuel in the fuel cell technology. Therefore, there are many attempts to use different electrodes (with the minimum of Pt content) for the hydrogen evolution reaction (HER). For this purpose, variety of porous materials are used as electrocatalyst towards HER. The metal-organic framework-derived nanoporous carbon (MDNPC) due to high surface area, good conductivity and easy synthesis method are applied as a support for preparation of electrocatalyst. The MDNPC is synthesized by indirect and direct carbonization of different metal organic frameworks (MOFs). In this article, MOF-199 are used as template to synthesis of Cu/nanoporous carbon composite (Cu/NPCC) by direct carbonization under N_2 atmosphere at 900 °C. There are different methods to preparation of MOFs, such as: hydrothermal, microwave-assisted, mechanochemical, sonochemical and recently, electrochemical techniques [2-4]. Among these methods, electrochemical techniques have several advantages, such as: mild synthesis conditions, shorter synthesis times, and the possibility to control the reaction conditions directly during the synthesis process and higher conductivity by the addition of an electrolyte and thus, a lower ohmic drop, results in a higher yield and production rate of MOFs. In this method, an electrode is used as the source of metal ions. The electrode is placed in a solution of the linker, often also containing an electrolyte. Upon applying an appropriate voltage or current, the metal dissolves and the metal ions required for the MOF formation are released near the electrode surface. Also, Anodic dissolution eliminates the use of metal salts, preventing their entrapment in the MOF pores. However, the use of conducting salts can result in entrapment and care must be taken to remove them. In this

article, the MOF-199 are synthesized by hydrothermal and electrochemical synthesis methods and the effect of synthesis producers are investigated on its catalytic performance for HER electrocatalysis. The Cu-Pd/nanoporous carbon composite-electrochemical (Cu-Pd/NPCC-electro) and Pd/nanoporous carbon composite-hydrothermal (Cu-Pd/NPCC-hydro) were synthesized by utilization of Cu/NPCC-electro and Cu/NPCC-hydro as a precursor for galvanic replacement reaction (GRR) of its Cu atoms by Pd (IV) ions, upon immersion in a palladium chloride solution. The synthesized materials was characterized by XRD, SEM, FT-IR, and BET technique. Electrochemical characterization was performed in a conventional three-electrode cell. An Ag|AgCl|KCl (3M) and a platinum wire served as reference and counter electrodes, respectively. To prepare of working electrode, 7 µL of suspended Cu-Pd/NPCC-electro and Cu-Pd/NPCC-hydro in ethanol (without adding any binder and conductive agents) were deposited onto glassy carbon electrode. The electrocatalytic activity of the as-fabricated electrodes for HER was investigated by LSV technique over the potential range from 0 to -1.0 V vs. Ag|AgCl|KCl (3M), and results were shown in Figure 1. The results showed that the Cu-Pd/NPCC-electro has a more positive effect on the reduction of hydrogen ions in H_2SO_4 solution. This behavior can be related to high conductivity of Cu-Pd/NPCC-electro due to high electron transfer site in electrochemical synthesized MOF-199 and lower charge transfer resistance that demonstrated in electrochemical impedance spectroscopy (EIS) studies.

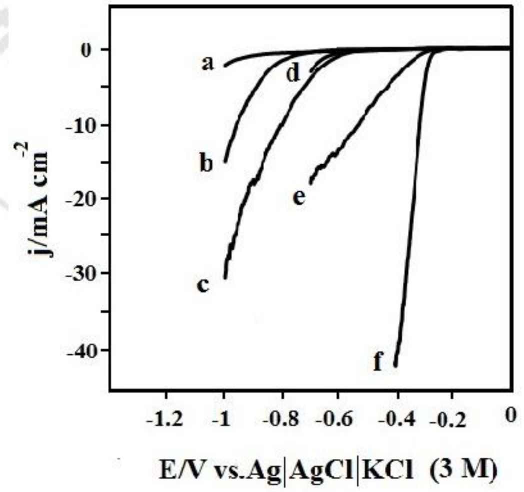

Figure 1. LSV signal for the HER on (a) bare GCE, (b) Cu/NPCC-hydro/GCE (c) Cu/NPCC-electro/GCE, (d) Pd/GCE, (e) Cu-Pd/NPCC-hydro/GCE and (f) Cu-Pd/NPCC-electro/GCE in 0.5 M H_2SO_4 solution at ¬ = 5 mV s^{-1}.

Keywords: *MOF- 199, Electrosynthesis, MOF-derived nanoporous carbon, Cu-Pd bimetallic nanocomposite, Galvanic replacement, Hydrogen evolution reaction*

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بهبود ریزساختار و مورفولوژی نانوپودرهای اکسیدسریم، سنتز شده به روش ژل احتراقی به منظور استفاده در پیل‌های سوختی حالت جامد

نویسنده: حجیه بسطامی*
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چکیده:

استفاده از پودرهای با اندازه‌ی نانو امکان رسیدن به چگالی نسبی بالا و ریزساختار ریزتر را در دماهای نسبتاً پایین‌تر در مقایسه با پودرهای معمولی فراهم می‌کند. در پژوهش حاضر از روش ژل احتراقی جهت سنتز نانوپودر اکسید سریا، به منظور استفاده در پیل‌های سوختی حالت جامد استفاده شده است. آنالیز پراش پرتو ایکس، فاز اکسید سریم را تأیید کرد. آنالیز میکروسکوپ الکترونی(SEM) حضور ذرات کروی در محدوده‌ی بین 50-70nm را آشکار کرد. نقش اکسید کمیاب خاکی در کاهش اندازه‌ی بلورک‌های اکسید سریم مطرح شده است.

واژگان کلیدی: پیل سوختی حالت جامد؛ اکسید سریم؛ نانوپودر؛ ژل احتراقی؛ اکسید کمیاب خاکی

Study of Platinum Electrodeposition with Cyclic Voltammetery Method for Using as Electrocatalyst in Methanol Oxidation Reaction

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Abstract

Direct methanol fuel cell is an attractive power source for portable power applications and in electrical vehicles [1]. The use of methanol as fuel has several advantages in comparison to hydrogen: it is a cheap liquid fuel, easily handled, transported, and stored, and with a high theoretical energy density [2–4]. Although a lot of progress has been made in the development of DMFC, its performance is still limited by the poor kinetics of the anode reaction[4–6]. Platinum-based nanomaterials supported on carbon (e.g., Pt/C) are commonly employed electrocatalyst in DMFCs [7]. The electrodeposition method for preparing platinum electrocatalyst is rapid and facile, allowing easy control of the nucleation and growth of metal nanoparticles [8-9].

In this work, cyclic voltammetry (CV) method (voltage range: -0.25 to 0.65 V versus Ag/AgCl and 50 mVs^{-1} scan rate) was used for platinum electrodeposition on carbon Vulcan XC-72 paste on carbon paper sheet. The effect of scan number of CV method on performance of prepared platinum electrocatalyst was studied. For doing that, the scan numbers were varied 10 up to 50. The cyclic voltammetry and linear sweep voltammetry (LSV) methods was used to estimate the behavior of the fabricated electrodes in 1 M KOH aqueous solution at a scan rate 100 mVs^{-1} in presence of 1 M methanol at room temperature.

As it was shown in figure 1 & 2, the scan number of CV affects on efficiency of fabricated electrodes. According our results, the 30 scan number is optimized condition. Also, optimized electrode has good open circuit voltage and high current density for methanol oxidation reaction.

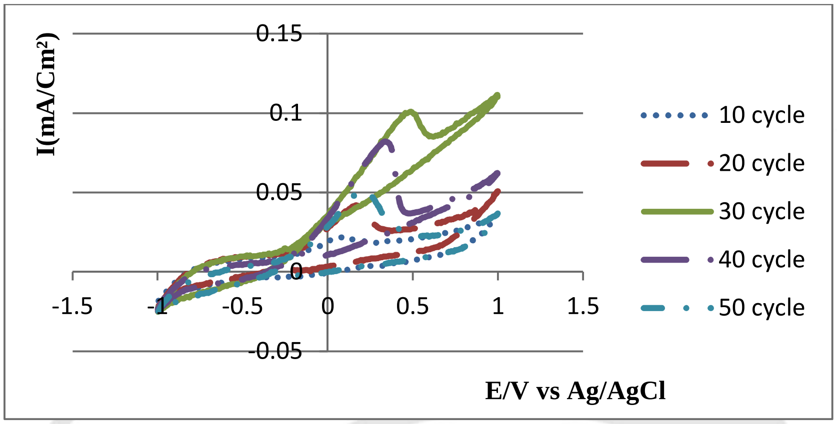

Figure 1 CV diagram of methanol oxidation in alkali solution

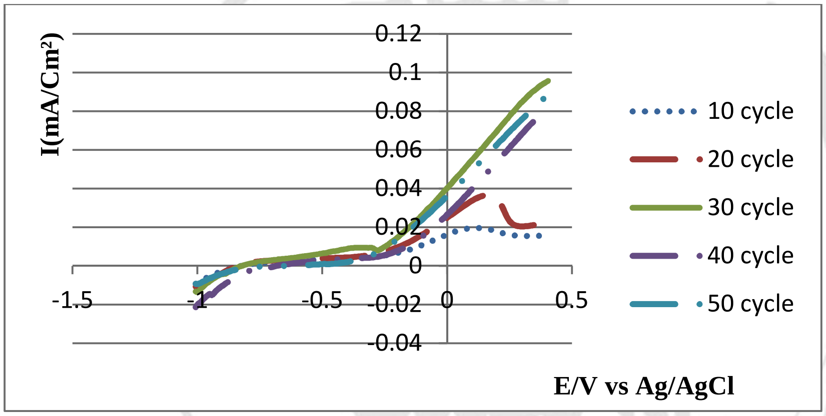

Figure 2 LSV diagram of methanol oxidation in alkali solution

Keywords: Direct methanol fuel cell (DMFC), Nano electro catalyst, Platinum, Carbon paper, Electro oxidation reaction, Electro chemical deposition

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Effect of constant potential on the electrodeposition of platinum on the oxygen reduction reaction in PEM Fuel cell

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Abstract

A PEMFC is a device that converts the chemical energy of a fuel directly into electrical energy by electrochemical reactions. When hydrogen is used as the source of the fuel the byproduct is essentially the pure water, thus making it an efficient and clean technology [1]. The oxygen reduction reaction (ORR) is also the most important reaction in life processes such as biological respiration, and in energy converting systems such as fuel cells. ORR in aqueous solutions occurs mainly by two pathways: the direct 4-electron reduction pathway from O_2 to H_2O, and the 2-electron reduction pathway from O_2 to hydrogen peroxide (H_2O_2). In non-aqueous aprotic solvents and/or in alkaline solutions, the 1-electron reduction pathway from O_2 to superoxide (O^{2-}) can also occur. In proton exchange membrane (PEM) fuel cells, ORR is the reaction occurring at the cathode [2&3]. Platinum is used as electrocatalyst in low temperature fuel cell systems to fast sluggish ORR. Many methods was used for preparation this catalyst. For this purpose, at this work electrochemical deposition method was applied. For doing that, the Platinum is deposited on the carbon Vulcan XC-72 paste on carbon paper. Electrochemical deposition method was carried out in two steps, the electrodeposition 30 cycle number in 0.5mM H_2PtCl_6 using the cyclic voltammetry technique which sweeps between -0.25V to 0.65 V vs. a Ag/AgCl reference electrode and 100 mVs^{-1} scan rate, then 18 seconds in constant potential at various values -0.15 , -0.05 , 0.05 and 0.15 V versus Ag/AgCl reference electrode. For evaluating fabricated electrodes from mentioned method for ORR, linear sweep voltammetry (LSV) method was used. Exchange current density at low and high current region ($i_{0\ LCD}$ and $i_{0\ HCD}$) were determined. It was shown in table 1, applying the constant potential in preparation electrocatalyst processes influence on exchange current density. In optimized condition, this potential is -0.05 V versus Ag/AgCl electrode.

Table 1- $i_{0\ LCD}$ and $i_{0\ HCD}$ values of the fabricated electrodes calculated from LSV

$i_{0\ LCD}$ Low Current(mA)	$i_{0\ HCD}$ High Current(mA)	Constant potential V versus Ag/AgCl
0. 379	11.7	-0.15
1.81	26.1	-0.05
0. 569	15.7	0.05
1.34	24.2	0.15

Keywords: *PEM Fuel Cell, oxygen reduction reaction (ORR), electrochemical deposition, exchange current density*

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The synthesis and ionic characteristic of hydroxide conductive polymer membrane for solid alkaline fuel cell

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Abstract

Anion exchange membrane is one of the most important parts of solid alkaline fuel cell. In this study the anion exchange membrane were prepared via chloromethylation, amination and alkalization. For this membrane trimethylamine and 1,6-tetra hexanediamine were used as amination agents that provided anion exchange sites on polysulfone backbone. The anion exchange membrane characterizations were performed with the hydroxide conductivity at different temperatures, ion exchange capacity and activation energy for hydroxide ion transport.

Keywords: *Hydroxide Exchange Membrane, Polysulfone, Amine Group, Ionic Conductivity, Solid Alkaline Fuel Cell.*

Introduction

Solid alkaline fuel cells (SAFCs) with anion exchange membranes (AEMs) as solid electrolyte have some advantages such as: employing non-expensive metal catalysts, effective reduction of oxygen in cathode, using various liquid fuels and reducing fuel crossovering due to the counter-current migration of fuel and hydroxide ion.….[1] . In the SAFCs, AEM is one of the most important components that improve fuel cell performance. In this research anion exchange membrane were prepared based on polysulfone with ammonium cation groups. Trimethylamine (TMA) and N, N, N', N'-tetramethyl-1,6-hexanediamine (TMHDA) were used as amination agents. The hydroxide conductivity at different temperatures, ion exchange capacity (IEC) and activation energy for hydroxide transport (E_a) were measured to characterize the membrane performance. The final results show that this membrane can be good candidate for applying in membrane electrode assembly in solid alkaline fuel cell system.

Methods

All chemicals used for membrane preparation were supplied from Merck and Sigma Aldrich companies. The chloromethylation step was performed as discussed in other reference [2] at 55°C for 72 hr and the chloromethylated polysulfone (CMPSf) was obtained. In amination step, the CMPSf was dissolved in N-methyl-2-pyrrolidone (NMP). Then TMHDA and TMA were added to the solution and the reaction continued for 24 hr at 80°C. The resulted solution was casted and the anion exchange membrane in chloride form was obtained. In alkalization step, the membrane was soaked in 1 molar KOH solution to provide the membrane in hydroxide form. The IEC of the membranes was determined by titration method as discussed in other work [3]. The hydroxide conductivity was calculated by electrochemical impedance spectroscopy (EIS) and E_a was obtained by Arrhenius form equation as reported in elsewhere [4].

Results and Discussion

Figure 1 illustrates the ionic conductivity increment with temperature for prepared AEM. As the temperature increases, the polymer free volume enlarges which enhances overall mobility of ions and polymer chains and consequently the ionic conductivity increases.

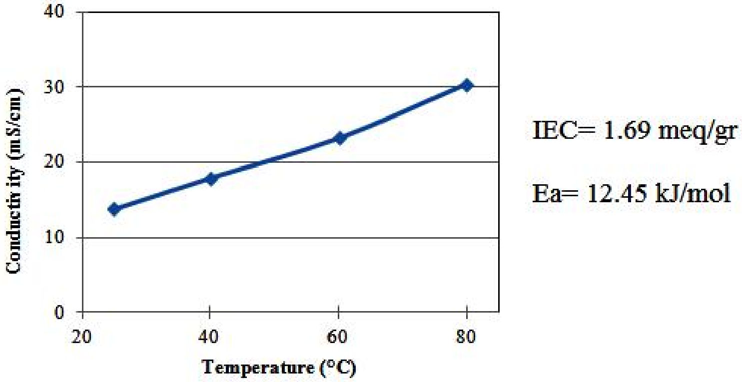

Figure 1- Temperature dependency of ionic conductivity for prepared AEM

Conclusions

The AEM was prepared via chloromethylation, amination and alkalization. The ion transport properties were measured for this membrane. The results show that increasing temperature, improves hydroxide conductivity and this membrane can be good candidate for solid alkaline fuel cell systems.

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Study of water content properties in anion exchange membranes for fuel cell applications

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Abstract

In current study, anion exchange membranes were synthesized by chloromethylation, amination and alkalization. These membranes are based on polysulfone and functionalized with amine groups (trimethylammonium and 1,6-tetra hexanediamine). 1,6-tetra hexanediamine not only has been used as amination agent, but also acts as crosslinker in membrane structure. The water content properties such as swelling ratio, water uptake and hydration number were determined for the prepared membranes. The membrane with crosslinked structure shows enhanced water content properties and better stability. Therefore this membrane can be good candidate for solid alkaline fuel cell applications.

Keywords: *Anion Exchange Membrane, Ammonium Moieties, Polysulfone, Solid Alkaline Fuel Cell, Swelling Ratio.*

Introduction

In recent years, solid alkaline fuel cells (SAFCs) with anion exchange membranes (AEMs) attract much attention because of their many important advantages such as the use of metal catalysts on the electrodes with reasonable price, fast oxygen reduction reaction and ….[1] . In the SAFCs, AEM is one of the most important components that improve fuel cell performance. In this study trimethylamine (TMA) and 1,6-tetra hexanediamine (TMHDA) were used as amination and crosslinking agents that provided anion exchange sites on polysulfone (PSF) backbone. The water content properties (swelling ratio, water uptake and hydration number) were measured to characterize the membrane dimensional stability. The ex-situ results show that the membrane with crosslinked structure can be good candidate for SAFC applications.

Methods

All chemicals used for membrane preparation were supplied from Merck and Sigma Aldrich companies. AEMs were prepared via chloromethylation, amination and alkalization.The chloromethylation step was performed as discussed in other reference [2] at 55°C for 24 hr and the chloromethylated polysulfone (CMPSf) was obtained. In amination step, the CMPSf was dissolved in N-methyl-2-pyrrolidone (NMP). Then TMA and TMHDA (in the membrane with crosslinked structure) were added to the solution and the reaction continued for 12 hr at 60°C. The resulted solution was casted and the anion exchange membrane in chloride form was obtained. In alkalization step, the membrane was soaked in 1 molar KOH solution to provide the membrane in hydroxide form. The water content properties measurements (swelling ratio, water uptake and hydration number) were performed in deionized water (at room temperature for 48hr) and calculated as reported in elsewhere [3].

Results and Discussion

Figure 1 shows the ^{1}HNMR spectra for CMPSF that confirms successful chloromethylation reaction on PSF. Table 1 reports the swelling ratio, water uptake and hydration number for two anion exchange membranes (PSF-1 with only TMA agent and PSF-2 with both TMA and TMHDA agents). As seen, PSF-2 with crosslinked structure has enhanced properties.

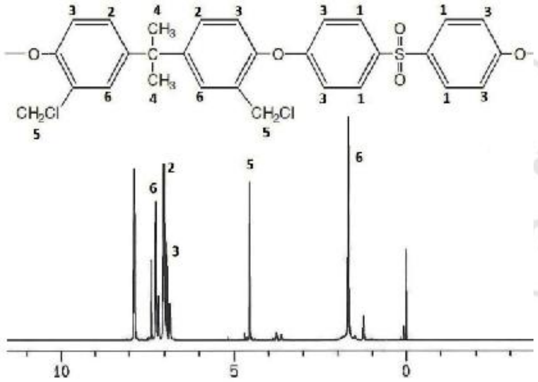

Figure 1- ^{1}HNMR spectra for CMPSF

Table 1- Swelling ratio, water uptake and hydration number for the prepared AEMs

membrane	PSF-1	PSF-2
swelling ratio (%)	9.67	4.76
water uptake (%)	33.33	12.22
hydration number	20	8.5

Conclusions

The anion exchange membrane with TMA and TMHDA (both amination and crosslinking agents) shows improved water content properties and better dimensional stability. Therefore, it can be good candidate for applying in solid alkaline fuel cell system.

Reference

(1) Wang, Y. J.; Qiao, J.; Baker, R.; Zhang, J., Chem. Soc. Rev. **2013**, 42, 5768.
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Optimization of grid configuration by investigating its effect on positive plate of lead-acid batteries via numerical modeling

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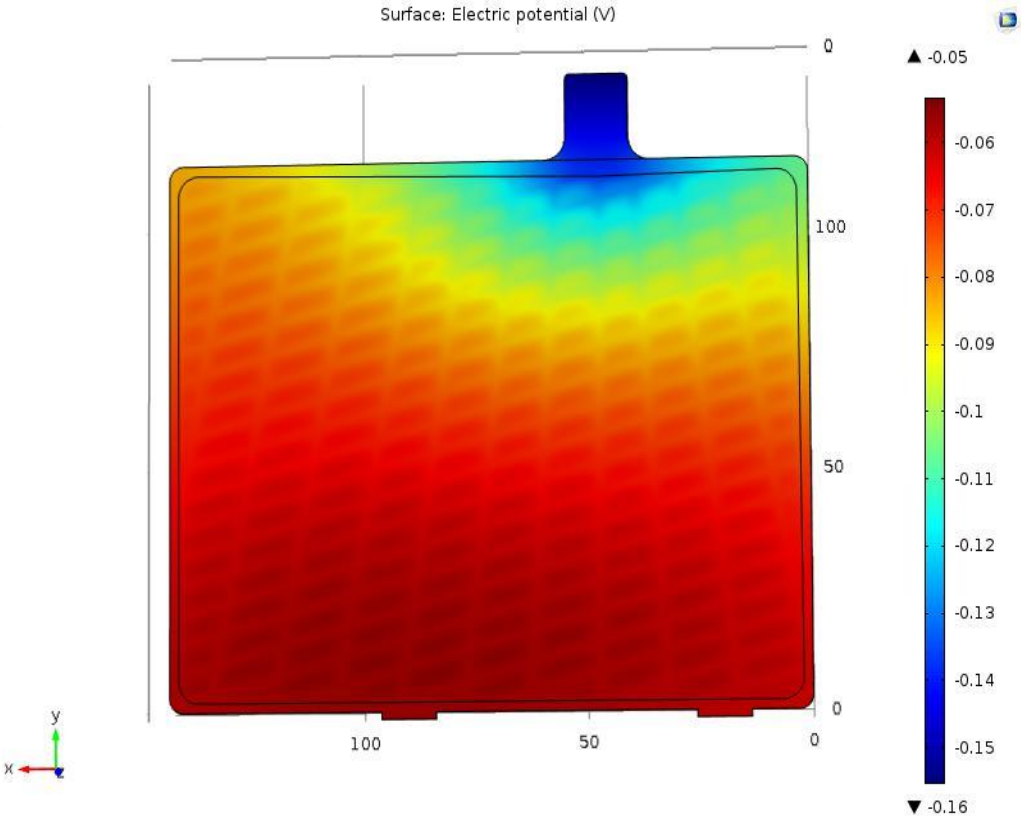
Abstract

Regarding the increasing application of lead-acid batteries, huge efforts have been exerted to enhance efficiency and cycle life as well as improving charge acceptance and capacity of these batteries [1]. The configuration of grid wires plays an important role in minimizing ohmic drop and more uniform potential and current density distribution through grid wires and therefore improves current collecting ability and may reduce corrosion especially near the lug.

In this study, numerical methods have been employed to investigate the effect of grid configuration on the performance of positive electrode of lead-acid batteries via modeling the current and potential distribution through gird wires, active material and adjacent electrolyte to the surface of each grid. The distinct trait of this work is that in addition to modeling the myriad of different configurations which are in literature or are recommended by authentic and well-known companies, some novel and unique designs are proposed and modeled as well.

It can clearly be perceived from the result of the modeling that optimized tow-side radial, middle-lug design offers the best performance and current collecting ability for the positive electrode of lead-acid batteries and simultaneously provides the lowest total grid weight and the best tensile strength which is of utmost importance in mass production and gives rise to more cost-effective and competitive products.



In the end it is worthwhile to say that this grid is going to be manufactured and used as an R&D project in NirouGostaran Khorasan Company and the same project is in the process for negative electrode as well.

Keywords*: *Lead-acid batteries, Grid configuration, Grid design, Positive electrode, Numerical modeling

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A Facile Electrochemical Synthesis of $NiCo_2O_4$ Nanosheets for High Performance Supercapacitor Applications

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Abstract

Electrochemical energy storage devices comprising batteries, fuel cells and supercapacitors play an important practical role in future energy applications. This is due to the growing demand for renewable clean energies with discrete nature. Supercapacitors are receiving increasing consideration due to a combination of high power and high energy density, long cycle life and fast charge/discharge processes. Supercapacitors are generally classified into electrical double-layer capacitors (EDLCs) and faradaic pseudocapacitors. The latter can provide much higher specific capacitance and energy density. In this work, spinel $NiCo_2O_4$ nanostructures have been prepared by cathodic electrodeposition of mixed Ni/Co hydroxides and subsequent heating of the deposited layer. The electrodeposition step has been carried out galvanostatically at different current densities ranging from 0.15 mA cm^{-2} to 0.65 mA cm^{-2} from a nitrate bath containing Ni and Co at an initial Ni/Co ratio of 0.5. In the second step, the obtained mixed hydroxide layer has been calcined to prepare spinel $NiCo_2O_4$. The whole process has been monitored by a variety of characterization methods including X-Ray diffraction (XRD), Scanning electron microscopy (SEM) and Energy dispersive X-Ray spectrometry (EDS). The XRD patterns showed that the obtained final product is composed of spinel $NiCo_2O_4$ regardless of the variation in the applied current density. The SEM micrographs revealed that the obtained nanocrystals are composed of interlocked nanosheets but the morphological properties of the nanosheets are influenced by the current density. The EDS analysis showed that the applied current density has a detrimental effect on the stoichiometry and Ni/Co ratio of the final product. It was found that, due to kinetic effects, the Ni/Co ratio changes from 0.43 to 0.53 by increasing the current density from 0.15 mA cm^{-2} to 0.55 mA cm^{-2}. The storage ability of the samples was investigated by cyclic voltammetry in 1M KOH aqueous solution at different scan rates ranging from 1 to 50 mVs^{-1}.

The results showed that the storage ability is a complex function of various structural parameters including morphology, stoichiometry and Ni/Co ratio of the obtained nanosheets. The maximum of the achieved storage ability was found to be 305 F g^{-1} for the sample prepared at a current density of 5 mV s^{-1}. The proposed method provides a facile, cost effective and high performance strategy for the synthesis of spinel $NiCo_2O_4$ for supercapacitor applications.

Key words: Supercapacitor, $NiCo_2O_4$*, Nanosheets, electrosynthesis*

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Study of Atomic Structure and Composition of intermetallic “Pt$_3$Co” Nanoparticles on MWCNT in Enhanced Elrctroactivity of Methanol Oxidation

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Abstract

Pt and Pt–Co supported on MWCNTs were synthesized by the impregnation method to enhance and optimize nanocatalyst performance and durability for the methanol oxidation reaction in fuel-cell applications, Pt–metal disordered alloys and describe a new class of Pt–Co nanocatalysts composed of ordered Pt$_3$Co intermetallic with atomic-layer in platinum crystal lattic. The particle size, morphology and chemical composition of Pt$_3$Co/MWCNTs was characterized by XRD and SEM. It was found that the PtCo/MWCNTs catalyst exhibited a fcc nanostructure. A homogeneous distribution of Pt–Co nanodeposits with particle size of 7-12 nm was attained in SEM images at Pt$_3$Co/MWCNTs powder. EDX analysis confirmed the reduction of Co in Pt$_3$Co/MWCNTs electrocatalyst. These nanocatalysts exhibited increase electroactivity when compared with the disordered Pt/MWCNT nanoparticles as well as Pt/C. So far, this activity for the methanol oxidation reaction is the highest among the Pt–Co systems reported in the literature under similar testing conditions. The high activity and stability are attributed to the Pt-rich shell and the stable intermetallic Pt$_3$Co core arrangement. These ordered nanoparticles provide a new direction for catalyst performance optimization for next-generation fuel cells.

Keywords: *Platinum–cobalt , Methanol oxidation , Fuel cells, MWCNTs, Electrocatalyst*

Synthesis and electrochemical performance lithium cobalt oxide as cathode materials of lithium-ion battery

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Abstract

In an attempt to understand the effect of synthesis concentration upon electrochemical performance of $LiCoO_2$, the compound was synthesized at three different molar ratio of lithium: cobalt, viz., 1:1, 1.3:1 and 1.7:1 using a novel flame spray pyrolysis method. Charge-discharge curves and cyclic voltammetry studies evidence that $LiCoO_2$ synthesized at ratio of 1.7:1 exhibits better electrochemical cycling behavior. It is found that $LiCoO_2$ nanoparticles, shows a high capacity of 126 mAh g^{-1} at 0.1 C in the first cycle and a reversible capacity of 103 mAh g^{-1} at 0.1 C in the 3th cycle. Based on our experimental observations and conjecture on the particle formation, the properties of nanoparticles such as particle size and crystalline phase can be controlled by the gas flow rates and precursor concentration. In the present study, we synthesized the crystalline $LiCoO_2$ nanoparticles, which is favorable for the application to the cathode material.

Keywords: *Electrochemistry, Lithium ion battery, Flame spray pyrolysis, Lithium cobalt oxide.*

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Nanoporous graphene/CuO composite as high-performance supercapacitor electrode material

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Abstract

With development of portable electronics, demands for low cost, and high performance energy storage devices with enhanced energy/power density have increased. Because of intriguing features, supercapacitors have attracted great interesting to complement or replace batteries in various electronic devices. Herein, we report a high performance supercapacitor based on nanoporous graphene/CuO composite synthesized with low cost hydrothermal method. The synergic effects of graphene/CuO composition with its nanoporous structure have a key role in providing highly conductive surface for uniform growth of CuO nanoparticles, faster electron transfer, prevention of restacking/agglomeration, simultaneous EDLC and pseudocapacitance contribution, facile mass transport and large accessible surface area. The nanoporous graphene/CuO electrode exhibits excellent electrochemical performance including a specific capacitance of 575 F g^{-1} at 1 A g^{-1} and 82% retention at an ultrafast rate of 50 A g^{-1} and excellent cycle life (6% loss after 5000 cycles).

Nanoporous structure with a high internal porosity and homogenous nanosized metal oxides would effectively prevent the restacking and aggregation of graphene nanosheets (GNS) and consequently maintain their ion-accessible surface area.[1, 2] Among the various metal oxides, CuO has attracted great interest because of its low cost and elemental abundance, easy preparation at the nanoscale, and nontoxicity.[3] Graphene oxide (GO) was synthesized via chemical exfoliation (modified Hummers' method) as reported previously.[4] Nanoporous graphene/CuO was prepared as follow: 200 mg GO was ultrasonicated in 80 mL distilled water for 1 h, then the homogeneous solution was heated to 95 ˚C and 2 mL of cupric acetate aqueous solution (223 mg mL^{-1}) was added into it under ultrasonication. After several minutes, 5 mL of ammonia solution (25%) was added to the above solution. After, 3 mL of 1% H_2O_2 aqueous solution was added and the mixture was transferred into a sealed Teflon-lined stainless steel autoclave and heated at 180 ˚C for 8 h.

XRD, SEM and TEM images confirm the preparation of CuO nanoparticles on graphene nanosheets. Also, BET and BJH isotherms confirm nanoporous structure of sample. The half-cell electrochemical performance of the electrode was investigated in a 3 M KOH solution. The nanoporous graphene/CuO electrode exhibits excellent electrochemical performance including a specific capacitance of 575 F g^{-1} at 1 A g^{-1} and 82% retention at an ultrafast rate of 50 A g^{-1} and excellent cycle life (6 % loss after 5000 cycles).

This remarkable performance contrasts with nanoporous graphene/CuO made by low cost hydrothermal method, giving some insights into the design of high-performance composite electrode materials for supercapacitor applications. We envision these electrodes to be useful in a broad range of applications such as supercapacitors, lithium ion batteries, fuel cells, gas sensors, biosensors, catalysis, and other electronic devices.

Keywords: *Supercapacitor, Nanoporous, Graphene/CuO, Composite.*

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A Facile Preparation of Palladium nanoparticles Supported on polypyrrole functionalized CNTs with enhanced electrocatalytic performance for ethanol electrooxidation

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Abstract

Due to the rapidly growing global energy needs and the quickly decreasing fossil fuel resources, it is essential to seek renewable, high performance, cost-effective and enviromentally beneficial green energy sources. In recent years, direct ethanol fuel cells (DEFCs) are attracting increasing attention owing to their wide applications [1]. Pd and Pd based catalysts have good electrocatalytic activity and excellent anti-CO toxic ability in comparison with Pt[2]. on the other hand the choice of a suitable support with large surface area, good conductivity and strong adsorption of metals is another key factor affecting the electrocatalytic performance of the catalysts, because it can affect the size and dispersion of the metal nanoparticles[3]. Polypyrrole (PPy) with low dimensional nanostructures has been used as a promising support material because of its high electrical conductivity and feasibility to anchor metal nanoparticles onto the surface [4]. In this study, a facile and reproducible method for synthesis of Pd nanoparticles (Pd NPs) and conducting polymer as a supporting material was demonstrated. Pd NPs were synthesized using chemical reduction process with $NaBH_4$ under certain conditions. Polypyrrole@carbon nanotubes (PPy@CNT) nanocomposite was fabricated through in-situ emulsion polymerization using sodium dodecyl sulfate (SDS) as an emulsifier and ammonium persulfate (APS) as an oxidant. Field Emission SEM (FE-SEM) images of Pd NPs and PPY@CNT are shown in Fig. 1. CNTs are distributed in the form of an extended network over a large area. The surface morphology was found to be uniform and tubular walls are sufficiently decorated with nanoparticles. Ethanol electrooxidation on the as-synthesized Pd/PPy@CNT/GCE and Pd/GCE was then investigated and compared in alkaline media by cyclic voltammetry and chronoamperometry studies at room temperature. these measurements

showed higher current density and longer term stability in ethanol oxidation with the Pd/PPy@CNT nanocatalyst. The facile synthetic process and excellent catalytic performance of the as-prepared catalysts demonstrate that they can be used as a promising catalyst for DEFCs.

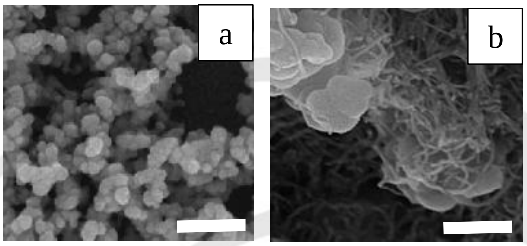

Fig. 4. FE-SEM images of (a) Pd NPs (b) PPy@CNT (scale bar for images is 100 nm).

Keywords: *Ethanol electrooxidation, Conducting polymer, Palladium nanoparticles, cyclic voltammetry*

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Molecular Dynamic Study of $[EMIM]^+[PF_6]^-$ Ionic Liquid near a Monolayer Graphene Surface

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Introduction

One of the important applications of ionic liquids is energy storage as an electric double-layer (EDL) supercapacitor. Several theoretical studies have been reported on the mechanism of EDL supercapacitors [1, 2, 3]; however, understanding molecular structure of ILs near an electrode surface is missing. In this study, detailed molecular dynamics (MD) simulation results of the structure of $[EMIM]^+[PF_6]^-$ IL near a neutral monolayer graphene electrode have been investigated.

Method and Simulation Details

All MD simulations were carried out by DL_POLY_2.17 package. An NVT ensemble at 873 K using Nose-Hoover thermostat was accomplished. To be ensured that system reaches equilibrium a three-step 1.5 ns cooling procedure, was applied on the target system. Finally, 2 ns production run was performed at 373 K and atmospheric pressure, with 1 fs time step, and 12 Å cutoff distance.

Results and Discussion

The results of MD simulation have shown accumulation of IL ions near the surface as Fig. 1 demonstrates. This aggregation has a solid like behavior over 19 Å distance away from electrode showing a layer-by-layer structure as Vatamanu et al. [2] mentioned. Number density profile of $[EMIM]^+$ cation, $[PF_6]^-$ anion, and IL shows layering structure accurately.

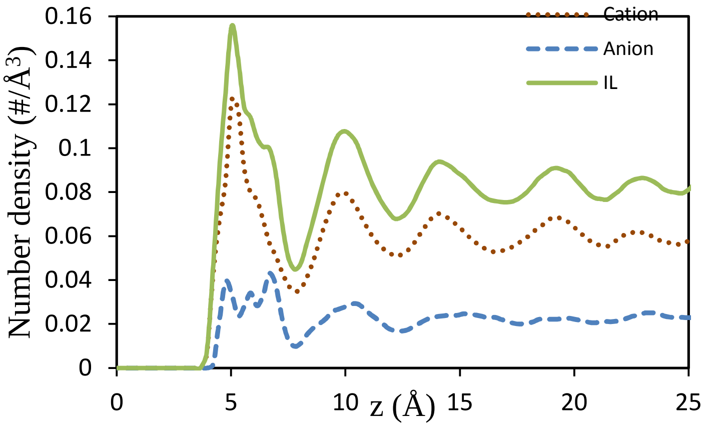

Figure 5: Number density of sum of atoms from the surface to the bulk of IL

$[EMIM]^+[PF_6]^-$ angle distribution of the first layer of imidazolium ring in Fig. 2 illustrates the cations with lower distance and more distance to the surface, were parallel and perpendicular, respectively.

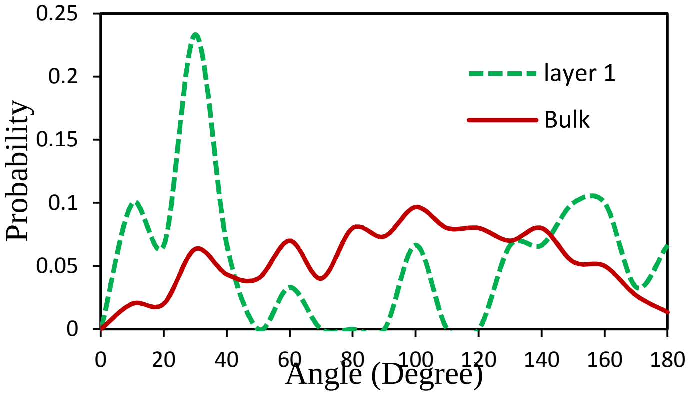

Figure 6: Angle distribution of first layer and the bulk of IL

Imidazolium charge distribution of ions was considered as a candidate of potential zero charge (PZC), to understand the charge behavior

of IL near the surface, (Fig. 3). The sharp peaks of total charge distribution tend to negative values because of the higher charge density of anions than the cations.

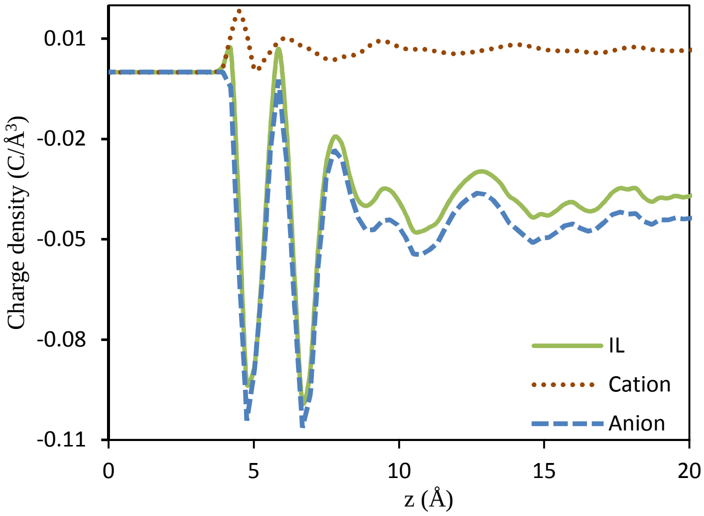

Figure 7: Charge density of cation, anion, and IL near the surface to the bulk

Conclusion

The layering behavior of $[EMIm]^+[PF_6]^-$ and total charge distribution of ions near the surface were shown the promising application of IL as supercapacitor electrolyte. It was resulted from the low charge distribution of the first layer due to its low potential zero charge.

Keywords: *Molecular Dynamics, Double Layer, Supercapacitor*

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Preparation of GrapheneNanosheets/CarbonNanotube/Pt/Polyaniline Nanocomposite with high specific capacitance as Electrode Material for Supercapacitors

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Abstract

GrapheneNanosheets/Carbon Nanotube/Pt/Polyaniline Nanocomposite (GNS/CNT/Pt/PANI) is synthesized via in situ polymerization. The PANI nanofibers was homogeneously coating on the surface of GNS greatly improve the charge transfer reaction. CNTs as conductive wires interconnected among GNS/PANI particles and also Pt nanoparticles as an extender surface area. Electrochemical properties were characterized by cyclicvoltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvanostatic charge/discharge. This analysis showed that the GNS/CNT/Pt/PANI composites exhibit remarkable specific capacitance than the pure individual components.

Fabrication of MEA on carbon supported $PtSnO_2$ and Pt for ethanol oxidation in DEFC

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Abstract

A remarkable alternative to H2-fueled PEMFC for portable and mobile application is the use of ethanol as a fuel [1]. Direct ethanol fuel cells (DEFCs) appear as a good choice for producing sustainable energy for portable applications. However, they are still far from attaining acceptable levels of power output, since their performance is affected by the slow electrochemical ethanol oxidation and water and ethanol crossover [2].

In the present work, an experimental study on the performance of a passive DEFC is described. The PtSnO2/C (3:1) and Pt/C are used for anode and commercial Pt/C is used for anode material. A maximum power density of 1.78 mW cm^{-2}, was obtained using a Nafion 115 membrane, 4 mg cm^{-2} of PtSnO2 and 3 mg cm^{-2} of Pt on the anode and cathode catalyst layer. The carbon supported $PtSnO_2$ catalyst showed higher OCV and power density for ethanol compared with Pt/C as anode catalyst. In addition, the EOR was investigated in different concentrations of ethanol and the 1M solution was the optimum concentration has been reported by other groups. This feature has been related to the ethanol crossover to the cathode side reducing the power density by increase in concentration of ethanol.

Keywords: *Tin Oxide, DEFC*

Title area
Direct Ethanol Fuel Cell

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Silver salts effects on the TiO_2 Photoanodes in the Water splitting system under visible irradiations

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Abstract

The photocatalytic splitting of water into H_2 and O_2 has attracted considerable attention because the process presents an avenue for direct generation of an energy carrier that is easily stored and transformed into electric energy. [1]

In this paper different silver salts were deposited on a conducting support of TiO_2/ FTO electrodes through the deposition-precipitation method and have been used as visible light induced photoanode in water splitting reaction. PhotoElectrochemical measurements such as Current-Voltage and Chronoamperometry diagrams demonstrated that the Silver salts loading enhanced the visible spectral absorption of TiO_2 and consequently a higher O_2 and H_2 production, were observed.

Via some characterization techniques such as XRD, EDX and SEM, it is obvious that the thin layer of silver salts is nanostructured materials. Plus, it is obvious that the light sensitivity in the visible part of the spectrum for the prepared photoanodes is due to self-sensitization caused by reduced silver species. [2]

Keywords: *Silver salts, TiO_2, Photoanode, Photoelectrochemical measurements, Visible light spectrum, Water splitting*

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Synthesis of Nanocomposite with Carbon-SnO_2-Ga_2O_3 on TiO_2 Nanotubes and Application in Lithium Ion Batteries

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Abstract

Currently, demands for rechargeable batteries are increasing for applications in mobile devices, electric-powered transportation, and stationary energy storage. For these applications, lithium ion batteries (LIBs) have been the most promising system due to their long cycle life, high energy density, safety, and so on [1]. In the present work, we have employed a simple process of anodizing Ti foils to prepare TiO_2 nanotube arrays which show enhanced electrochemical properties for applications as Li-ion battery electrode materials [2]. Through the introduction of well-distributed tin oxide nanocrystals on the surface of pre-prepared TiO_2 nanotubes and followed by carbon coating, a novel TiO_2/SnO_2- Ga_2O_3-C. As an anode material of Li-ion batteries (LIBs), NTs exhibit excellent long-term cycling stability and satisfactory rate capability, which are ascribed to the synergetic effects of a unique combination of material properties in the well-designed conductive matrix [3]. Electrode performance was tested by charge/discharge galvanostatic and cyclic voltammetry experiments. The structure of nanotube titanium oxide will be studied by scanning electron microscope (SEM).

Keywords: electrochemical synthesis, energy storage, nanostructure

Title area
Lithium Ion Batteries

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Impact of process parameters of positive paste on Charge-Acceptance of SLI batteries

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Abstract

Due to importance of quality and life span, Charge-Acceptance (C.A) is a vital factor in battery production. It was established that paste preparation and formation conditions had a significant impact on battery C.A. In this study the effects of paste density, acid/oxide ratio, time and maximum temperature in mixing stage have been investigated.

The current research was performed by X-Ray Diffraction for phase identification, Scanning Electron Microscope for microstructure analysis and battery acceptance testing. Results have been shown that both increasing in paste density, mixing time and acid/oxide ratio plus decreasing in maximum temperature led the improvement of C.A factor.

Keywords: *Charge acceptance*, *Lead-Acid battery*, *Positive paste*, *Paste density*, *Mixing time and temperature*, *Acid/Oxide ratio*

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Verification upon the Rechargeable Batteries, The Pulse-Current Electrodeposition , for Platinum Electrodes

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Abstract

The chemical pasting of a mixture of active material on a support conductor is used to repare the positive electrodes of alkaline batteries. This kind of electrode is used in the batteries of mobile phones, mp3s, emergency lights, and electric vehicles.

Keywords: *battery, electrodeposition, pulse-current, SEM micrograph*

Introduction

Platinum hydroxide should have a homogeneous particle size and bulk distribution. Two methods are commonly used to obtain this kind of platinum hydroxide: indirect chemical precipitation and direct chemical precipitation. In both cases platinum hydroxide is obtained as a powder that then must be properly prepared to build the electrodes. For the manufacture of platinum hydroxide electrodes for use in high-performance batteries, such as platinum hydrogen batteries used as power source in space satellites, the impregnation technique used consists of the cathodic electrodeposition of sintered platinum plates[1,2].

Experimental Methods

Continuous current was applied using 64 $mAcm^{-2}$ amplitude for 3 h. The parameters of intermittent pulse trains were 64 $mAcm^{-2}$ amplitude; time ON: OFF is existed.and total time was 3 h. The pulses were generated by GED-M1LYP digital generator. All electrochemical experiments were performed in a conventional glass cell in 6M KOH solution that was prepared from AnalaR grade potassium hydroxide and twice-distilled water. The counterelectrode was a nickel mesh.

Results and Discussion

After impregnation, the electrodes were rinsed in deionized water and formed using the Eagle-Picher formation procedure. The procedure consisted of 5 1/2 cycles beginning and ending with the discharge. Each cycle was 40 min long in 20% potassium hydroxide. For the first 4 cycles, the current was at a 3.4 C rate. The current was reduced to 0.75 C for cycle five and again reduced to 0.5 C for the final half cycle. After that, the electrodes were cycled many times. Moreover, having greater capacity than CC, the plateau for CP_3 is better defined and is shifted by about 25 to 50 mV in the potential positive direction. This difference indicates that when the loading is high, the particles are not able to absorb the proton quickly; therefore, mass transport is the limitation. The higher the amount of active material is, the lower the active surface of the material results. Therefore, it is proton diffusion within the solid one that limits the speed of the reaction. For this reason, it has a greater ohmic drop. The morphology of the deposited material is shown in Figure 1.The deposits made by applying a continuous current Figure 1,cover the total platinum mesh and are more compact than those deposited through a train of pulses. Also, figure 1 shows that the material is compact and its composition corresponds to the active material. The loading (gcm^{-3}) from sample CC (continuous current) was 10% larger than that of sample CP_3 (pulse current). The surface morphology of the deposited material in the first sample is homogeneous and compact. In the case of pulse-current deposition, the active material is deposited along the shape of the porous substrate and leaves visible gaps or pores.

Conclusions

All electrodes that were electrochemically impregnated with pulse current showed optimum capacity, similar to loading values found in the literature, with the active material producing a larger active surface area. When the impregnation current is continuous, the active material forms a homogeneous and compact surface with optimum loading but poor performance during discharge. Furthermore, the electrodes that were impregnated with different pulse currents produce loading similar to that of the electrodes impregnated with continuous current, although their active material is deposited following the shape of the porous substrate. This type of deposition produces a larger active surface area that has the highest utilization percentage. The particle size influences the electrochemical performance. When the particle size decreases, the amount of adsorbed water molecules on the surface of the particles increases. This surface water is thought to improve platinum hydroxide particle wettability, thus resulting in an enhanced proton transport within the active mass during the charge-discharge process and a better utilization of the electrode material.

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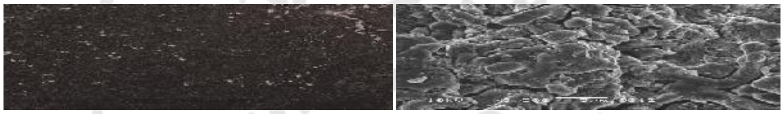

(a) *(b)*

Figure 1: SEM micrographs of the electrode surface (CC), with platinum hydroxide as the active material; (a) 120x and (b) 3500x

A comparison of different carbon used as the positive electrode (cathode) in Lithium/Thionyl Chloride (Li/$SOCl_2$) cells

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Abstract

The Li/$SOCl_2$ battery system consists of a Li anode, a carbon cathode, and the $LiAlCl_4$/$SOCl_2$ electrolyte solution. Different varieties of carbon can be used to construct the cathode. According to the literature [1] colloidal Teflon is used as the binding material for fabricating the carbon electrode. The composition of the paste is given as: carbon; 80% by weight; Teflon binder; 20% by weight. The procedure entails rolling the carbon/PTFE mix onto the syringe. The pretreatment of carbon cathodes with acetone has led to an increase in cell voltage and capacity for Li/$SOC1_2$ cells [2]. This treatment is thought to work by removing impurities from the carbon and increasing the total pore volume and average pore diameters. During cell discharge $SOC1_2$ reduction takes place at such a cathode, resulting in the precipitation of reaction products, mainly LiCl, within the pores of the substrate. This leads to eventual passivation of the cathode surface and, hence, cell failure. Most of the Li/$SOC1_2$ cell research under taken is to improve the performance of this positive electrode. For this reason, we studied the reduction reaction of $SOCl_2$ on different carbons in a three-electrode cell by cyclic voltammetry. Carbons that used for this purpose are acetylene black (AB), Vulcan, Multiwalled carbon nanotube (MWCNT), activated carbon and refined carbon from SAFT Li/$SOCl_2$ battery. The cathode substrate in Li/$SOC1_2$ cells provides a conductive surface on which $SOC1_2$ is depolarized. Fig.1 is a comparative cyclic voltammograms (CVs) of the Li/$SOCl_2$ cell with different carbons as cathode in 1 M $LiAlCl_4$/$SOCl_2$. The results of electrochemical techniques show that the reduction rate of $SOCl_2$ on surface of Acetylene black, which consists of submicron sized particles and high surface area is better and like as refined carbons from SAFT Li/$SOCl_2$ battery. The reduction rate of $SOCl_2$ on surface of activated carbon and glassy carbon is the worst of all due to the low conductivity.

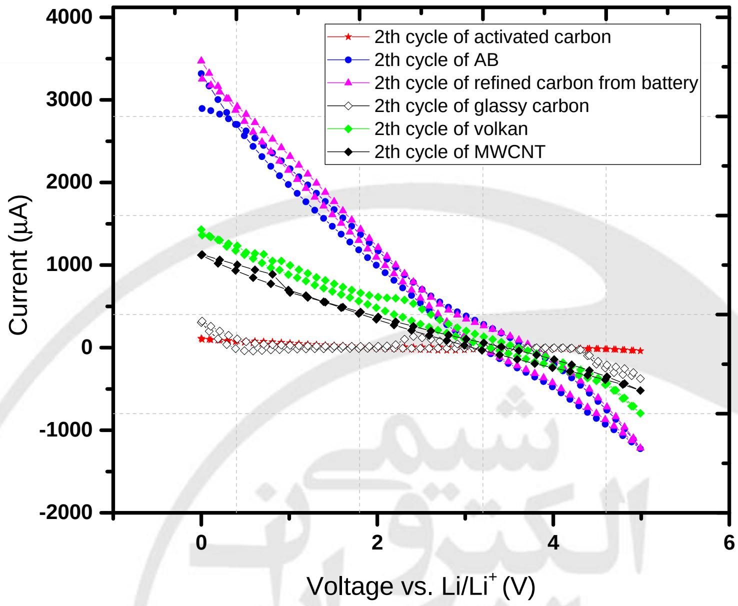

Fig 1.the CVs of 1 M $LiAlCl_4/SOCl_2$ and different carbons as a cathode at 80 mV s^{-1} .

Keywords: *Lithium thionyl chloride cell, Glassy carbon, Activated carbon, Acetylene black, Multiwalled carbon nanotube, Vulcan*

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The use of Polyvinylpyrrolidone (PVP) as Electrocatalyst in Lithium/Thionyl Chloride (Li/SOCl2) cells

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Abstract

Lithium/thionyl chloride (Li/SOCl2) battery, which is high energy density, high operation voltage, long storage life, and wide operation temperature range (−55~85°C), has been widely used to power various electronic devices for industrial and military applications [1,2]. During the discharge of the $Li/SOCl_2$ battery, the electrode reaction of battery is as follows:

$Li \rightarrow Li^+ + e$

$2SOCl_2 + 4e \rightarrow 4Cl^- + SO_2 + S$

In the above reaction, the Li^+ ions around the lithium electrode migrate to the carbon electrode surface and react with the Cl^- anion:

$Li^+ + Cl^- \rightarrow LiCl$

Due to the low solubility of lithium chloride crystallite in $SOCl_2$ electrolyte, as the discharge goes on, the amount of lithium chloride crystallites deposited on the carbon electrode is increased. It can affect the performance of the battery. One possible approach to enhance the cell performance is the addition of catalyst molecules which must be readily oxidizable/ reducible and accelerate the rate of electron transfer. In our report, the high energy of $Li/SOCl_2$ battery may due to the rate enhancement of $SOCl_2$ reduction reaction and the retardation deposition of lithium chloride crystallite by adding a polymer called Polyvinylpyrrolidone. Polyvinylpyrrolidone (PVP), also commonly called polyvidone or povidone, is a polymer made from the monomer *N*-vinylpyrrolidone [3], PVP have been used as catalysts to catalyze lithium/thionyl chloride ($Li/SOCl_2$) cell. The catalytic activity of PVP derivatives to $Li/SOCl_2$ cell is evaluated by the electrochemical techniques of the cell whose electrolyte contains the PVP. The catalytic effects of PVP polymer on the reduction of thionyl chloride at carbon electrode have been evaluated in three electrode system by cyclic voltammetric techniques[4].

A two-step electron transfer process, mechanism is proposed and proved by the cyclic voltammetry. Fig.1 is a comparative cyclic voltammograms (CVs) of the Li/$SOCl_2$ cell with/without 2 mg PVP in 1 M $LiAlCl_4/SOCl_2$. The results of cyclic voltammetry show that the adding of PVP improves the reduction rate of $SOCl_2$, This maybe due to the reason that the Li^+ ion is easily to coordinate with PVP.

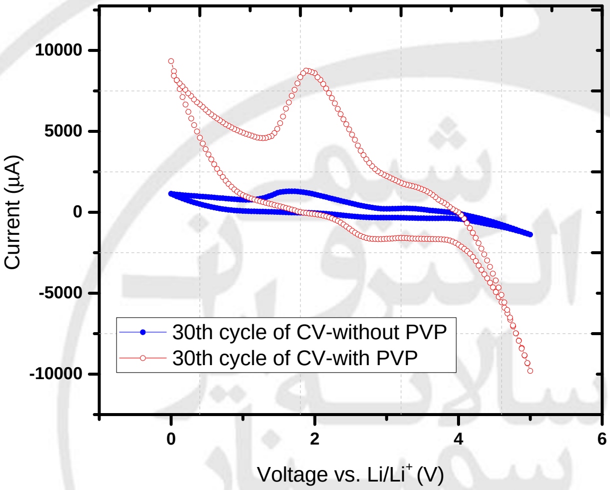

Fig 1. The cyclic voltammetry curves of 1 M $LiAlCl_4/SOCl_2$ with/without PVP at 80 mV s^{-1} .

Keywords: Polyvinylpyrrolidone, Lithium thionyl chloride cell, Catalyst, Cyclic voltammetry

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Manufacturing of a new nanocomposite bipolar plate by graphite powder from proton exchange fuel cells

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Abstract

The bipolar plates are responsible of two thirds of the weight and 80% of volume of PEM fuel cells stacks. Also, they contribute to the high cost of fuel cells stack. The bipolar plate has a key role in increasing power density and reducing cost. The bipolar plates in a fuel cell stack serve a number of functions including the electrical connection, structural support, and physical separation between successive fuel cells, and enable reactant gases to access the anode and cathode electrodes via flow fields. Desirable properties of a bipolar plate include high electronic and thermal conductivity, low contact resistance, corrosion resistance in the harsh cell environment, mechanical toughness, and low cost. Preparation and study of the conducting composites of epoxy/graphite with varied composition were carried out for fuel cells application. The electrical and thermal conductivity, permeability and tensile properties of epoxy/graphite composite were investigated.SEM and optic microscopes were used to microstructure investigation. this material selection is conducted by using simple additive weighting method(SAWM). Thus, in this paper, shows mechanical properties that is suitable for fuel cell application.

Key words: *Bipolar plate, nanocomposite, polymer exchange fuel cell, graphite powder.*

Electrochemical synthesis and characterization of graphene /polyaniline nanofibers composites as electrode for supercapacitors

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Abstract

Graphene, polyaniline and graphene nanosheets(GNS)/polyaniline(PANI) nanocomposite are fabricated on steel by constant current electrochemical method in aniline monomer and SDS surfactant.The characterization of synthesized catalysts have been investigation by FT-IR,SEM techniques.The GNS/PANI composites exhibit better electrochemical performances than the pure individual components. A remarkable specific capacitance of 1100 F g−1 (based on GNS/PANI composites) is obtained at a scan rate of 5 mV s−1 in 0.5 M H2SO4 solution compared to 380 F g−1 for pure PANI and 200 F g−1 for GNS. The excellent performance is not only due to the GNS which can provide good electrical conductivity and high specific surface area. The resulting composites are promising electrode materials for high-performance electrical energy storage devices.

Keywords: *Electrochemical synthesis, Graphene, Polyaniline, Composite, Supercapacitor*

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Investigation of metal free electro-catalysts based on halogen doped RGO for oxygen reduction reaction

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Abstract

metal free electro-catalysts based on halogen doped reduced graphene oxide (X-RGO) have shown promising oxygen reduction reaction (ORR) activity in alkaline media. In this study, we report a facil method to synthesis of RGO from graphite electrodes using ionic liquid-assisted electrochemical exfoliation and Cl-RGO and Br-RGO in solution phase. The characterization of synthesized catalysts have been investigation by FT-IR, Raman and XRD techniques. We have evaluated the effectiveness of doping and performed electrochemical measurements (involving chronoamprometry, cyclic voltammetry, and linear sweep voltammetry and impedance spectroscopy) of the ORR activity in 0.5 M KOH solution. The resulting kinetic of ORR process by X-RGO electro-catalysts becomes improve more than RGO.

Keywords: *electro-catalyst, Metal free, Oxygen reduction reaction, Halogen, Graphene.*

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A comparison of three $Li/SOCl_2$ batteries with Different duration of using which used as the power source in gas meters

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Abstract

Lithium/thionyl chloride ($Li/SOCl_2$) battery are considered promising power sources because of their high energy density, high operation voltage, long storage life and wide operation temperature range [1]. With these advantages, $Li/SOCl_2$ primary battery, as one of the most important primary batteries, has been widely used with low power consumption applications in civil, military areas and electronic meters such as gas meters and water meters [2]. The $Li/SOCl_2$ battery system consists of a Li anode, a carbon cathode, and the $LiAlCl_4/SOCl_2$ electrolyte solution. During the discharge of the $Li/SOCl_2$ battery, Li^+ ions around the lithium electrode migrate to the carbon electrode surface and react with the Cl^- anion thereupon LiCl film is formed on the cathode. deposition of LiCl clogged the porous carbon cathode and This film on the surface of the carbon electrode appears to be an important factor influencing the cathodic process and cell performance.

In this paper three commercial SAFT $Li/SOCl_2$, “D” size battery used to investigate and evaluated by electrochemical techniques. three candidate batteries and the codes used for each battery types are listed in table.1. voltage of each battery measured before I-V test. Fig.1 is a comparative I-V curves of three candidate batteries. S_3 candidate battery was used as a power source in a gas meter for longer time compared with S_1 that used for less time. S_1 which have low resistance and high voltage is better in performance because of low amount of lithium chloride crystals on the surface of carbon. S_3 which have high resistance and low voltage is worst in performance because of high amount of lithium chloride crystals on the surface of carbon cathode. There is no I-V curve for S_1 battery because of very low voltage.

code	Voltage (V)
S_1	3.680
S_2	3.677
S_3	0.005

Table 1. voltage of three candidate SAFT Li/$SOCl_2$, “D” size batteries with Different duration of using, before I-V test .

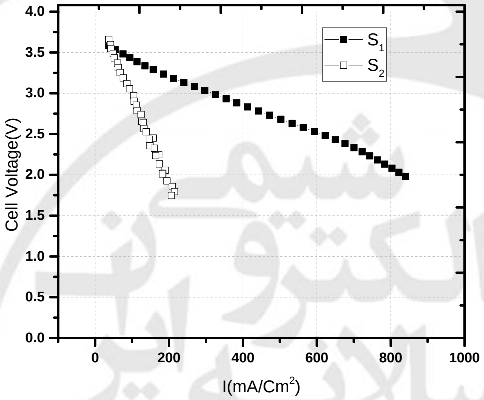

Fig 1. I-V curves of three candidate SAFT Li/$SOCl_2$ batteries at Scan rate: 5 mv/S and voltage range : OCV – 2V

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Keywords: *Discharge time, Power source, Gas meter, SAFT Li/$SOCl_2$ battery, Electrochemical techniques*

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PdNi electrocatalysts with enhanced catalytic activity for oxygen reduction in acid media

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Abstract

Carbon-supported Palladium-Nickel (PdNi) alloyed electrocatalysts with different Pd/Ni atomic ratios was used for oxygen reduction reaction (ORR), in acid media. This bimetallic catalyst was synthesized via the metallic reductive precipitations of the nitrate precursors with Ethylene Glycol (EG). The characterization of the electrocatalysts using X-ray diffraction (XRD) showed bimetallic nanoparticles having a narrow size ranged 5-3 nm with face-centered cubic (fcc) hexagonal structure. Cyclic voltammograms and polarization curves from rotating-disk electrode measurements showed significantly higher activity on PdNi than observed on Pd catalyst, with a mechanism involving four electrons transfer to water formation. The PdNi/C alloy electrocatalysts are inactive for the adsorption and oxidation of methanol. Therefore, bimetallic alloyed Pd-Ni catalysts can act as a promising methanol-tolerant ORR catalyst in a direct methanol fuel cell (DMFC).

Keywords: Palladium-Nickel alloy, electrocatalysts, Oxygen reduction reaction, Acid Media, Direct methanol fuel cell.

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Pd-Ni and Pd-Co nanoparticles supported on carbon as an effective catalyst for oxygen reduction

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Abstract

Alloying is a strategy that has been used to find non-Pt electrocatalysts that are effective and less expensive for the oxygen reduction reaction (ORR) [1]. Mixing two or more metals can result in a catalyst that has distinct properties from its monometallic components. For example, it has been found that the addition of metals that bind oxygen strongly (Co, Ni, etc.) can lower oxygen binding to more noble metals (Pt or Pd) and improve their ORR activity [2]. In this work, we investigate the effect of alloy composition in Pd-Ni and Pd-Co nanoparticles on the ORR activity. Nickel (II) chloride ($NiCl_2$), palladium (II) chloride ($PdCl_2$) and sodium borohydride ($NaBH_4$, 99.99%) were purchased from Sigma-Aldrich. Carbon (Vulcan XC-72 R) was provided by the Cabot Corporation. 50 mg of carbon was ultrasonically dispersed in de-ionized water. $PdCl_2$ and $NiCl_2$ (1:1) or $PdCl_2$ and $CoCl_2.6H_2O$ (1:1) was added and the total metal content was 20 wt%. Then 10 mL of $NaBH_4$ solution in excess was added. The solid particles were separated by filtration, washed and dried. The catalyst inks were prepared by mixing 30 mg of catalysts with 2-propanole, de-ionized water and 5wt% nafion solution. After the painting of catalyst inks on the carbon felt, the final electrodes were dried at 120 ^{o}C for 1 h. The electrochemical measurements were carried out using three-electrode compartment. An Ag/AgCl electrode was used as the reference electrode and platinum as the counter electrode. Cyclic voltammetry (CV) was applying a scan rate of 20 mV s^{-1} between 1 and +1 V vs. Ag/AgCl in the O_2 and N_2 saturated NaOH solution. EIS measurements were performed over a frequency range of 100 KHz to 0.01 Hz. The CV plots of Pd-Ni/C and Pd-Co/ C are shown in Fig. 1. The ORR peaks of Pd-Ni/C and Pd-Co/C are achieved at 0.3 and 0 V vs. Ag/AgCl, respectively. In the oxygen saturated solution, the water reduction is happened in more positive potential for both electrodes, in the comparison of nitrogen saturated one. Polarization curves are produced at a scan rate of 1 mV s^{-1} and the kinetic parameters were extracted by the Tafel equation (Fig. 2). The Tafel slopes

and current densities of Pd-Ni/C and Pd-Co/C electrodes were 128 and 131 mV/decade and 6.2 × 10^{-3} and 5.6 mA cm^{-2}, respectively. A Tafel slope of 120 mV per decade shows that the first electron transfer is rds. The EIS measurement is done at ORR potentials of electrodes based on CV plots. The charge transfer resistance of Pd-Ni/C and Pd-Co/C electrodes are 8 and 14 Ω cm^2. These results lead us to conclude that Pd-Ni/C alloy catalysts acts more powerful than Pd-Co/C one. According to Volcano plots the ORR activities of Ni particles are higher than Co one. So, by alloying Pd with Ni, the ORR activity is enhanced.

Keywords: *Palladium, Alloy, Electrocatalysts, Oxygen reduction reaction*

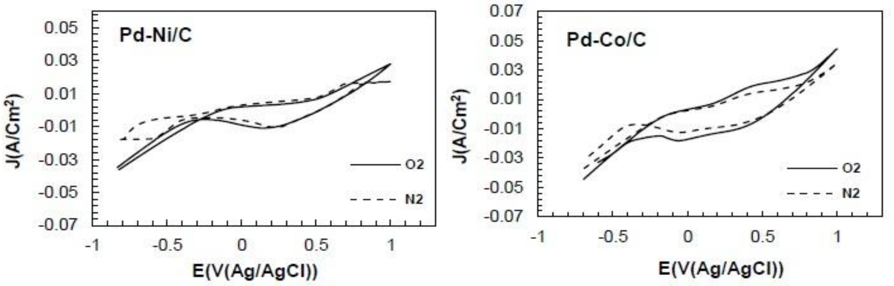

Fig. 1. Cyclic voltammograms of Pd-Ni/C and Pd-Co/C electrodes in O_2 and N_2 saturated 0.1 M NaOH solution with 20 mV s^{-1} scan rate.

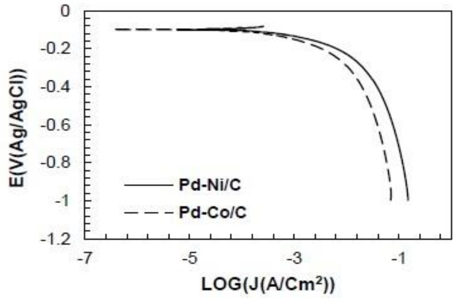

Fig. 2. Tafel polarization curves of Pd-Ni/C and Pd-Co/C electrodes in O_2 saturated 0.1 M NaOH solution with 1 mV s^{-1} sweep rate

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Membrane Electrode Assembly health detection in a 4 cells stack using linear sweep voltammetery

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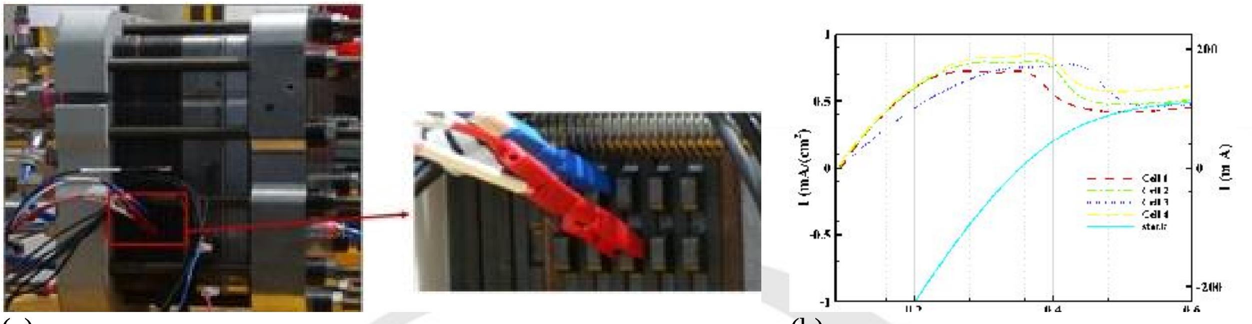
Abstract

Fuel cell technology has undergone significant development in the past 15 years, spurred in part by its unique energy conversion characteristics; directly converting chemical energy to electrical energy. Of the six different fuel cell types pursued commercially, the proton exchange membrane fuel cell (PEMFC) has received the greatest amount of research and development investment due to its suitability in a variety of applications. PEMFC electrolyte permeability to reactants and electrons is considered as a critical factor which reduces FC performances and lifetime (1). Linear sweep voltammetery (LSV) is a powerful tool allowing the estimation of hydrogen crossover and the detection of any internal electronic short between anode and cathode. A scan rate between 1 and 4mVs^{-1} is adopted. In order to prevent platinum oxidation, the scan potential range is limited from 0 to 0.8V [2]. In LSV experiments, the anode is usually fed with hydrogen while the cathode is supplied with nitrogen. At this value all crossover H_2 is instantaneously oxidized due to the high overpotential applied. Based on the limiting current, one can, ultimately, calculate the flux of H_2 gas (J_{xover}) using Faraday's law (2).

$$J_x \qquad = \frac{i_{li}}{n} \tag{1}$$

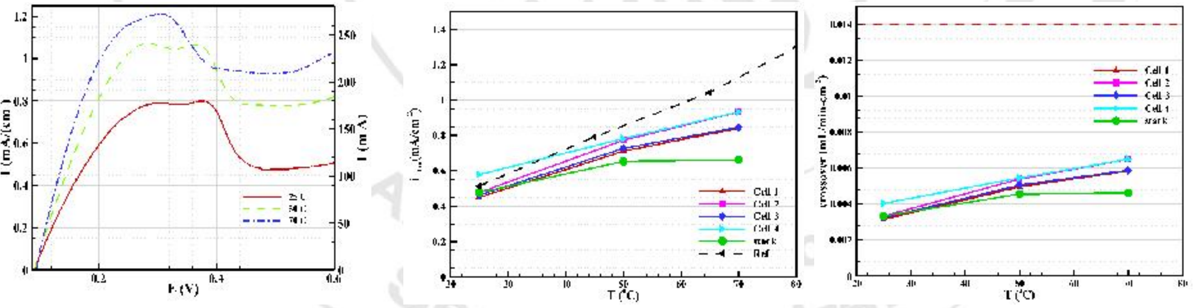
Where i_{lim} (Acm^{-2}) is the transport limiting current density; n is the number of electrons required per reaction (HOR = 2), and F is the Faraday's constant (96,485 Cmole^{-1}).



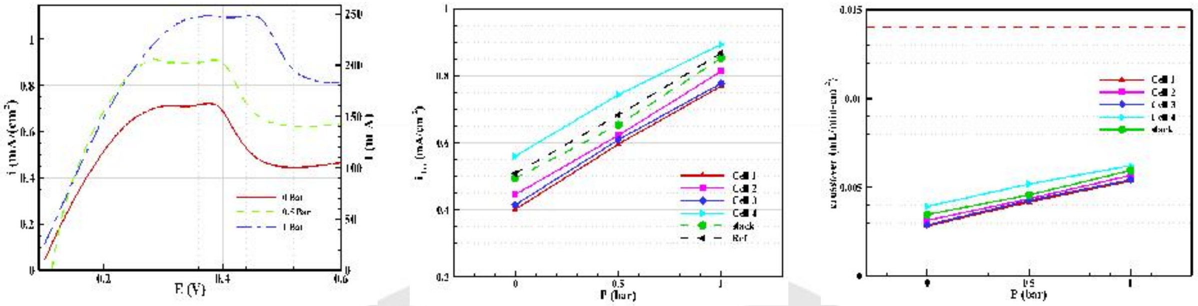
(a) (b)

Fig. 1: (a) Connection of single cell anode and cathode to potentiostate/galvanostate device for LSV test (b) Linear sweep voltammograms of cells 1, 2, 3, 4 and stack at T=25 ^{o}C, P=0 barg, scan rate= 2 mV/s

The purpose of this test is to verify the device (Biologic sp150) performance (when it working with fuel cell 4 cells stack) and the MEAs health assessment within the stack. As shown in Fig.1, the working electrode should connect to cathode and reference and counter electrode should connect to anode of single cell. Fig.1 (b) shows single cells and stack LSV. To verify the device performance, linear sweep voltammograms of single cells and stack at different temperatures and pressures were recorded (Fig 2 a,b) and compared with values in the literature (3). As shown in Fig 2 (c,d) the demeanor of single cells and stack are similar to literature and illustrate the verification of potentiostate/galvanostate in LSV test.



(a) (c) (e)



(b) (d) (f)

Fig. 2: LSV data of cell 2 at (a) different cell temperatures (b) different pressure; comparison of hydrogen crossover of single cells and stack with literature at (c) different cell temperatures (d) different pressure; (e),(f) assessment of single cells and DOE hydrogen crossover detection limit; scan rate = 2 mV/s, 4/2 L/min (H_2/N_2), T_{cell} = 25, 50, 75 ºC, P_{cell} = 0.0, 0.5, 1.0 barg, working electrode = cathode, counter/reference = anode.

To assess the MEAs health, the amount of hydrogen (mL/min-cm^2) was calculated using equ.1 and compared with the DOE limit values (3).

Keywords: *Polymer electrolyte membrane fuel cell, 4 cells stack, Hydrogen crossover, Linear sweep voltammetry*

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The Effect of Anodic Reactant Relative Humidity on the Performance and EIS Response of PEM Fuel Cell

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Abstract

The effect of relative humidity of the anode (RH_a) on proton exchange membrane (PEM) fuel cells has been studied focusing on fully humidified cathode operation condition. The amount of humidity in the fuel stream affected the cell performance, which could in turn be reflected by EIS spectra measurements. Results indicated that high power density was achieved at high relative humidity of the fuel gas. Anode relative humidity were shown to have significant effects on the AC impedance of cell. Based on the impedance spectra, charge transfer resistance, mass transfer resistance, and solution resistance can be extracted using the equivalent circuits set up. The Nyquist plots were fitted by Zview software. When anode relative humidity decreased, high ohmic and charge transfer resistances could be observed. Also the capacitance parameters increase with enhancing relative humidity. With increasing of the gases pressure, solution resistance was increased. While increasing the operating pressure led to a water flooding in electrode, resulting high mass transfer resistance.

Keywords: *Relative humidity, Operation condition, Polarization curve, Electrochemical impedance spectroscopy, PEM fuel cell.*

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Sonochemical synthesis of graphene-manganese oxide nanohybrid as an electrode material for supercapacitor

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Introduction

Supercapacitors represent a new class of energy storage devices that have been attracted many researchers in last few years. Graphene with unique properties such as superior electrical conductivity and large specific surface area is one of the most suitable materials in supercapacitor applications [1]. Therefore graphene, especially chemically modified graphene is one of the most promising carbon materials to be applied to energy storage systems [2]. Besides, metal oxides are being used as active compounds in supercapacitors due to their role in redox reactions. In this research, sonochemical synthesis and characterization of a novel manganese oxide (MnO_2)/reduced graphene oxide (RGO) nanohybrid that coated onto stainless steel (SS) was studied. The electrochemical performance of the MnO_2/SS and MnO_2/RGO/SS electrodes were compared by electrochemical methods.

Experimental methods

Graphene oxide (GO) was synthesized from graphite flakes (GF) by the modified Hummers method followed by exfoliation using sonication [3]. The MnO_2 samples were prepared by a chemical oxidation technique using different concentrations of aqueous solutions of $MnSO_4$ and $KBrO_3$ in the presence of ultrasonic vibration. MnO_2 nanoparticles anchor on GO sheets through an electrostatic coprecipitation method. Then, the prepared nanohybrid was pressed on SS. All electrochemical measurements were done in a three-electrode system: a MnO_2/RGO/SS was used as the working electrode; a platinum foil and an Ag/AgCl were served as counter and reference electrodes, respectively. The measurements carried out in a 0.5 M Na_2SO_4 aqueous electrolyte by cyclic voltammetry (CV) between 0.0 and 1.0 V at different scan rates. Also, charge/discharge technique was used to investigate the elecrtrochemical behavior of prepared electrode.

Results and discussion

Fig. 1 shows a comparison between the CV curves of the MnO_2/SS and MnO_2/RGO/SS at 20mVs^{-1}. From CV, it is obvious that the MnO_2/SS exhibits lower specific capacitance than MnO_2/RGO/SS. The electrochemical performance of MnO_2/RGO/SS was studied in 0.5 M Na_2SO_4 at different scan rates (Fig 2). As it can be seen, with the increase of scan rate, all the CV curves do not obviously change and stay nearly rectangular. Also, MnO_2/RGO/SS film shows a near ideal rectangular behavior. Specific capacitance of MnO_2/ERGO/SS calculated from the CV curves at the scan rate of 20 mVs^{-1} is 361 Fg^{-1}, which was higher than 147 Fg^{-1} for ERGO/SS.

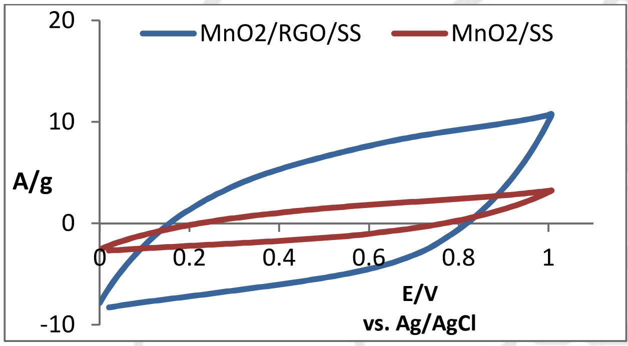

Fig. 1 shows the CV curves of the MnO_2/SS and MnO_2/RGO/SS electrode at scan rate 20 mVs^{-1}.

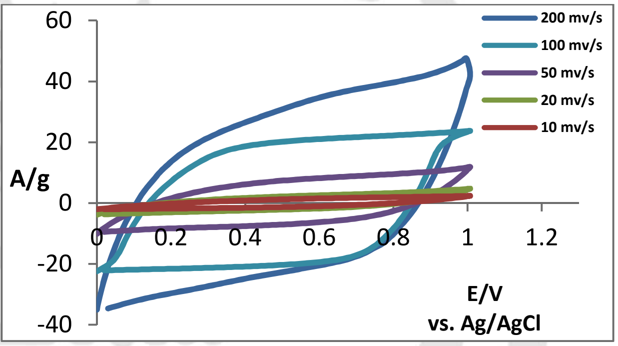

Fig. 2 CV curves of MnO_2/RGO/SS electrode at different scan rates from 10 to 200 mVs^{-1}.

Conclusions

The electrochemical studies demonstrate that the MnO_2/RGO/SS electrode exhibits reasonably good specific capacitance and MnO_2 nanoparticles are effective for improving the electrochemical properties of RGO.

Keywords: *Sonochemical, Supercapacitor, Nanohybrid, Graphene, Manganese oxide*

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Increased cycle life of lithium ion battery anode assisted by metal oxide nanoparticles

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Abstract

Nowadays, lithium ion batteries (LIBs) are one of the most popular rechargeable batteries. To increase cycle life of these batteries, many strategies have been adopted, among which incorporation of metal oxide nanostructures, either as nanofilm or nanoparticle, into electrodes seems to be an effective method. Here, this strategy have been examined on the LIB anode using commercially available Al_2O_3, SiO_2, TiO_2, ZnO and Fe_2O_3 nanoparticles as modifier, and mesocarbon microbead (MCMB) as the active material. Nanoparticle-incorporated anodes were fabricated as follows: specified amounts of MCMB, polyvinylidene fluoride, N-Methyl-2-pyrrolidone, and respective nanoparticle were thoroughly mixing and coated on copper foil by using a micrometer adjustable film applicator. After drying in oven, the electrodes were roll-pressed and cut into disks where served as working electrode. A lithium metal disk and a microporous polyolefine film were used as counter and reference electrodes, and separator, respectively. A 1 M solution of $LiPF_6$ in 1:1 (v/v) ethylene carbonate: diethyl carbonate used as electrolyte. Electrochemical cycle life experiments were conducted on a battery tester using a two-electrode battery test cell. Among the tested nanoparticles, Al_2O_3 showed the best performance in improving cycling stability of the MCMB-based anode.

Keywords: *Lithium ion battery, anode, MCMB, Metal oxide nanoparticle, Al_2O_3.*

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Synthesis and electrochemical performance lithium cobalt oxide as cathode materials of lithium-ion battery

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Abstract

Liquid-feed flame spray pyrolysis (LF-FSP) has emerged as a promising technique for producing wide range of single or multicomponent nanomaterials. Using this technique, several nanostructured lithium ion battery (LIB) materials have been produced. Herein, we report LF-FSP synthesis of nanostructured $LiCoO_2$ as LIB cathode active material. Molar ratios of lithium: cobalt in the precursor solution was altered at three different levels, viz., 1:1, 1.3:1 and 1.7:1. Charge-discharge and cyclic voltammetric studies showed that performance of the $LiCoO_2$ sample synthesized at ratio of 1.7:1 was superior based on a high capacity of 126 mAh g^{-1} at 0.1 C in the first cycle and a reversible capacity of 103 mAh g^{-1} at 0.1 C in the 3th cycle.

Keywords: *Lithium ion battery, Flame sprays pyrolysis, Lithium cobalt oxide.*

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Effect of Surfactants on Electrocatalytic Performance of Copper Nanoparticles for Hydrogen Evolution Reaction

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Abstract

In this work, effect of different types of surfactants on hydrogen evolution reaction (HER) onto copper nanoparticles modified carbon paste electrode (nano-Cu/CPE) was studied. In this way, SDS, CTAB, and TX-100 were used as anionic, cationic and non-ionic surfactants, respectively. Among these surfactants, SDS had the best efficiency with the lowest over-potential for hydrogen evolution in 0.5 M H_2SO_4 solution.

Keywords: *Surfactant, Electrocatalysis, Copper nanoparticle; Hydrogen evolution reaction*

Introduction

Hydrogen, as a high-quality clean and renewable energy resource, is considered as one of the most promising candidates for the fuel of the future [1]. Hydrogen produced by water electrolysis has been identified as one such renewable energy carrier. The most widely used electrode material for hydrogen electrolysers is platinum. However, the commercial use of this material is limited due to its low abundance and high cost. Hence, it is imperatives to reduce the amount of loaded Pt [2] or replacing it with modified electrodes. On the other hand, surfactants can give rise to adsorbed layers of varying thickness monolayers, bilayers or multilayers of a very complex structure, thus affecting the rate of electrode reaction [3]. In this paper, nano-sized Cu is investigated as electrocatalyst for electrochemical production of hydrogen from water in the presence of different surfactants.

Experimental

After preparation of the carbon paste electrode, for nano-Cu electrodeposition, the electrode was dipped into 0.1 M H_2SO_4 solution containing $CuSO_4$ and a fixed potential during a given period of time was applied.

Surface morphology

In order to surface characterization, the micrograph of the nano-Cu/CPE has been investigated by SEM. Fig.1 shows morphology of the electrode consisting of spherical nano-Cu with average sizes about 55 nm.

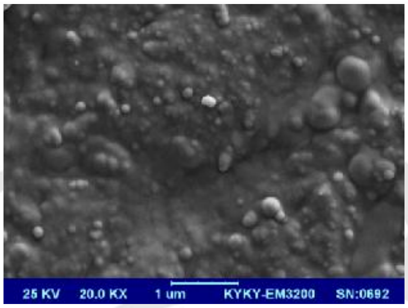

Fig. 1. SEM image of the nano-Cu/CPE.

HER study

The electrocatalytic activity of the nano-Cu/CPE in 0.5 M H_2SO_4 solution containing different surfactants was measured. At the nano-Cu/CPE, while is not too active in CTAB media, it shows high electrocatalytic activity in SDS and TX-100 as it is clear in Fig. 2. It can be seen that the electrocatalytic activity of nano-Cu/CPE increased in the order: SDS>TX-100>CTAB.

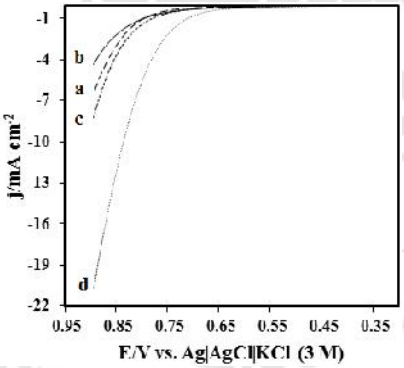

Fig. 2. 10th CV of the nano-Cu/CPE in 0.5 M H_2SO_4 solution containing different surfactants at $\upsilon = 50$ mV s^{-1}: (a) without surfactants; (b) CTAB; (c) TX-100 and (d) SDS (only the forward sweep was illustrated).

Conclusion

The nano-Cu/CPE exhibited the best catalytic performance in H_2SO_4 solution containing SDS. The enhanced action of SDS results from physical (electrostatic) adsorption of the negatively charged DS^- to the positively charged copper surface, forming a layer on the copper surface.

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Synthesis of Graphene/Metal Nanoparticle Composite via Quasi-Two-Step Reduction at Room Temperature for Electro-Oxidation of Ethanol in Alkaline Medium

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Abstract

Recently, renewable green energies such as fuel cells are increasingly considered due to depletion of fossil fuels and environmental pollution. Providing efficient and cost-effective catalysts is one of the most important programs in the development of fuel cells. One of the ways for improving the electrocatalytic activity of the fuel cell catalysts is to introduce a support material with an appropriate electrical conductivity and capability of dispersing and carrying the catalyst particles effectively [1,2]. Among the various carbon materials for loading the catalyst nanoparticles, graphene, is one of the excellent candidate due to mechanical flexibility, chemical stability, thermal conductivity, high surface area and its two-dimensional single or several atomic layers [3].

In this work, we use a quasi-two-step reduction method at room temperature to produce a non noble effective metal nanoparticle-graphene composite for the electro oxidation of ethanol in order of application in direct alcohol fuel cells.

Graphite oxide was synthesized from natural graphite powder using a modified Hummers' method. After the bath sonication (Struers Metason) and then centrifuging and removing unexfoliated materials, a suspension of graphene oxide (GO) was obtained.

Nickel nanoparticles synthesized using a little amount of a diluted aqueous solution of $NaBH_4$ as the reductant agent at room temperature.

A suspension of GO (1 $mg.ml^{-1}$) and an appropriate amount of polyvinylpyrrolidone were prepared and followed by bath ultrasonication for 30 min. then GO colloidal dispersion added to the suspension of nickel nanoparticles and followed by stirring. A little amount of a diluted aqueous solution of $NaBH_4$ added to the suspension gradually. After completion the reaction, the homogeneous suspension stirred for 12 h. All experimental steps were conducted at room

temperature (25 °C). Finally, the black product was collected by centrifugation and then washed several times with ethanol and DI water. The resultant product was dried at 45 °C in air-oven and used for the following experiments. A catalyst ink of rGO/NiNP composite and FEP in IPA were prepared and dropped on the glassy carbon electrode at the loading of 0.034 mg.cm^{-2}.

The effect of temperature on the ethanol oxidation for rGO/NiNP composite catalyst was investigated by performing voltammograms at scan rate of 100 mVs^{-1} at the temperatures of 25 and 60 °C (Fig. 1). Current density increased significantly with the higher temperature, i.e. peak current density was greater, indicating an increase in reaction kinetics.

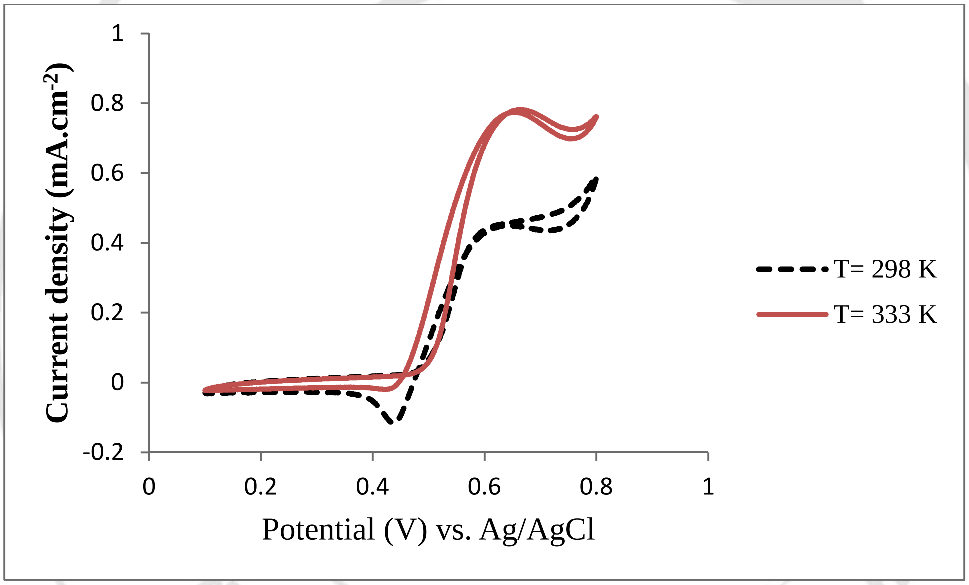

Fig. 1. CVs of rGO/NiNP composite electrode in 0.1M KOH/0.1M C_2H_5OH solution with a scan rate of 100mVs^{-1}at 25°C and 60 °C.

Keywords: *Quasi-Two-Step Reduction, Nickel Nanoparticles, Polyvinylpyrrolidone, Ethanol Oxidation*

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Highly active metal organic framework composite for oxygen reduction reaction in alkaline medium

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Abstract

Developing economical and commercially available materials to replace precious and nondurable platinum based catalysts is a very important issue in contemporary fuel cell technology [1]. Nanostructured carbon materials have the potential to reduce the costs, improve the fuel tolerance and scalability; however, they are limited presently by their relatively low catalytic activity [2]. Herein, we have synthesized a new electrocatalyst for the oxygen reduction reaction derived from in situ growth of metal–organic frameworks on carbon nanotubes, followed by pyrolysis. The most efficient catalyst yielded comparable catalytic activity than commercial platinum-based catalysts. The electrochemical measurements were carried out in alkaline medium. The synthesized MOF/CNT composite showed a comparable activity with Pt/C.

Keywords*: *MOF, Oxygen reduction reaction

Title area
Feul cell

Reference

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Nanocomposite membranes based sulfonated poly (ether ether ketone) for proton exchange membrane fuel cell application

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Abstract

Novel nanocomposite membranes based on sulfonated poly (ether ether ketone) (SPEEK) and $BaZrO_3$ nanoparticles were prepared with solution casting method. The morphology, thermal properties, proton conductivity and fuel cell performance of the nanocomposite membranes were investigated. The nanocomposite membrane with 1 wt.% of $BaZrO_3$ nanoparticles showed the highest proton conductivity of 70 mS/cm at 80 °C. The outstanding proton conductivity of the nanocomposite membranes can be attributed to presence of $BaZrO_3$ nanoparticles which can perform as pathways for proton transport. Moreover, the nanocomposite membranes also showed elevated thermal stabilities. The SPEEK/$BaZrO_3$ (1 wt.%) nanocomposite membrane showed a peak power density of 130 mW/cm^2 at 80 °C. The new SPEEK/$BaZrO_3$ nanocomposite membranes with the well-defined proton transport channels can be the potential alternative materials to Nafion for PEMFC.

Keywords: *Sulfonated poly (ether ether ketone), nanocomposite membrane, proton conductivity.*

Results and Discussion

Nafion, is the most commonly studied membrane in PEMFC which has high hydrolytic and oxidative stability and excellent proton conductivity in its hydrated state. However, reduction in its proton conductivity and mechanical stability at temperatures above 80 °C and its high cost limit its usage for PEMFC [1]. In recent years, several kinds of proton exchange membranes such as, sulfonated poly (ether sulfone)s (SPES), sulfonated poly(arylene ether sulfone), sulfonated polyimides (SPI), sulfonated polybenzimidazoles (SPBI) and sulfonated poly(ether ether ketone)s (SPEEK) [2] have been investigated. Among them, SPEEK has been greatly considered due to its low cost, high thermal/chemical stability and good proton conductivity. The protons can be transported in the hydrogen-bonded ionic network within fully water-swollen membranes. SPEEK/$BaZrO_3$ nanocomposite membranes demonstrated higher proton conductivity compared with SPEEK based membrane (Figure 1). $BaZrO_3$ with considerable levels of protonic conductivity has an enormous potential for use in fuel cells. $BaZrO_3$ has concerned much consideration for its applications in PEM fuel cells such as: simple cubic perovskite structure, excellent mechanical and structural integrity under extreme thermal excursions and high chemical stability [3]. $BaZrO_3$ is the best proton conductors with perovskite structure and exhibit small activation energies for proton migration. It was revealed that SPEEK/$BaZrO_3$ nanocomposite membranes (1 wt %) demonstrated high proton conductivity (70 mS/cm) compared with other SPEEK/$BaZrO_3$ nanocomposite membranes in different temperatures. As shown in Figure 1, the proton conductivity of the nanocomposite membranes was increased with increase in temperature.

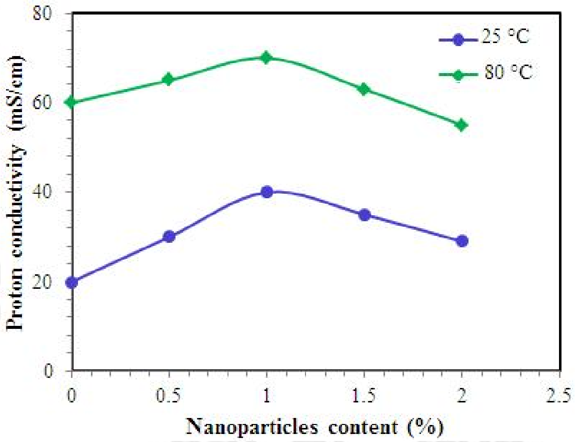

Figure. 1. Proton conductivity of nanocomposite membranes at different temperatures.

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Preparation of Electrode Material for Supercapacitor based on Electropolymerized Poly (*ortho*-Methoxyaniline)/MWCNT Composite Film

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Abstract

In this work, ortho-Methoxyaniline (OMA) was electropolymerized onto multi-walled carbon nanotubes (MWCNTs) modified glassy carbon electrode (GCE) in 0.5 M H_2SO_4 solution. The electrochemical response of the POMA/MWCNT film was higher than pure POMA. The galvanostatic charge-discharge and electrochemical impedance spectroscopy experiments showed that the POMA/MWCNT composites possess good capacitive characteristics. Stability of the nanocomposite was also investigated.

Keywords: *Supercapacitor, Multi-walled carbon nanotube, Poly (ortho-Methoxyaniline), Composite*

Introduction

Supercapacitors or ultra-capacitors due to their superior properties such as rapid charge/discharge process, high power density, long cycle life, and low cost are unique types of energy storage devices being developed for a wide range of applications. Generally, supercapacitors are divided into three classes; electrochemical double layer capacitors, pseudo-capacitors, and hybrid capacitors [1]. Among them, hybrid supercapacitors combine the advantages of both double layer capacitors and pseudo-capacitors [2]. Composites composed of multi-walled carbon nanotubes (MWCNTs) and conducting polymers as hybrid supercapacitor materials have exhibited great promise due to the two charge/discharge storage mechanisms [3]. In this work, application of electropolymerized POMA/MWCNT composite film as an electrode material for hybrid supercapacitor was investigated.

Experimental details

An ethanol/MWCNT suspension was cast on the electrode surface and dried at room temperature to form the MWCNT film modified GCE (MWCNT/GCE). The MWCNT/GCE was immersed in 0.5 M H_2SO_4 solution containing 0.10 M OMA and polymerization was carried out by using consecutive CVs at $\upsilon = 50$ mV s^{-1}). After this, the POMA/MWCNT/GCE was thoroughly rinsed with H_2SO_4 solution and 10 cycles were employed until stable voltammograms were attained.

Results

The POMA films were synthesized electrochemically at the GCE surface in the absence and presence of MWCNT (Fig. 1). The current density of the POMA/MWCNT is higher than pure POMA, indicating that the polymerization rate is improved by presence of the CNT, possibly due to its high surface area.

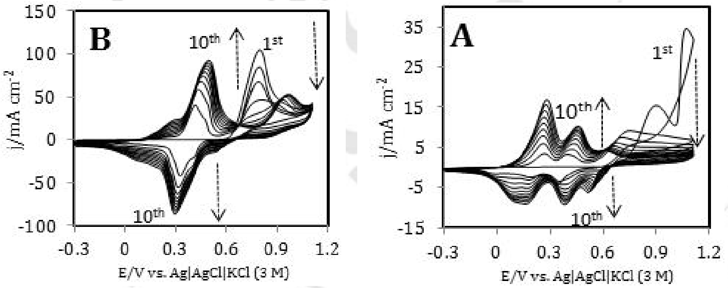

Fig. 1. Electropolymerization pattern of 0.10 M OMA at the surface of bare GCE (A) and MWCNT/GCE (B).

Surface morphology

The surface morphology of the MWCNT (a) and POMA/MWCNT (b) was characterized with SEM (Fig. 2). As shown in trace (b), POMA film has a rough surface with many small cavities and/or holes with no uniformity on the electrode surface.

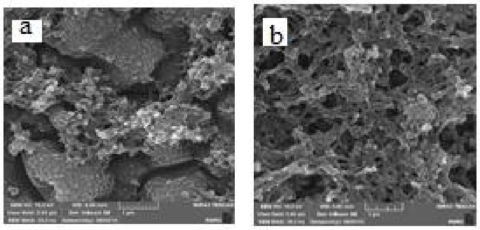

Fig. 2. SEM images of the POMA (a) and POMA/MWCNT (b).

Conclusion

The presence of MWCNT may promotes the polymerization rate and results in a highly porous composite with electrical conductivity. The results showed that the POMA/MWCNT composites possess very good capacitive characteristics, which are better than those of pure POMA and MWCNT.

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Study of electrochemical performance of $LiFePO_4$ and graphite electrodes with EC/DMC electrolyte in Li-ion batteries

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Abstract

The demand for reachargeable batteries with longer cycle-lives and higher performance for modern electrical devices has been increasingly developed. For many years, these needs have been met by variants of the lithium-ion battery that has been first commercialized by Sony [1]. Recently, $LiFePO_4$ has been investigated intensively as a potential cathode material for rechargeable Li-ion batteries because of its low cost and improved safety [2-5]. The performance of industrial electrodes, lithium iron (II) phosphate, $LiFePO_4$, as a cathode material and graphite as an anode in a lithium secondary battery was evaluated using conventional electrochemical analyses such as cyclic voltammetry, charge-discharge profile, and Electrochemical Impedance Spectroscopy (EIS). Both anode and cathode materials were tested in half cell separately versus Li/Li^+ as reference electrode. A conventional solvent such as ethylene carbonate and dimethyl carbonate (EC/DMC; 1:1 v/v %) with 1M $LiPF_6$ were used in all tests. The EIS measurements showed an eligible resistance value for both anode and cathode electrodes. CV studies of these system were also done in which the peak current was not noticeably changed during first cycles. Half wave potential and the intensity of peaks confirmed the mechanism of insertion/deletion of lithium into working electrode as redox mechanism in LIB's. The specific capacity and cyclic stability were also investigated at 0.1 C-rates, at room temperature. The discharge capacity at 1^{st} cycle and the cycleability during 25 cycles were studied. The discharge capacity and cycleability were comparable with current values of $LiFePO_4$ and graphite based electrodes.

Keywords: Lithium-ion batteries, $LiFePO_4$, Graphite, discharge capacity, and cycleability

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Physical and electrochemical investigation of SPEEK/ZrO_2 nanocomposite membrane for PEMFC applications

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Abstract

In this study sulfonated poly (ether ether ketone) nanocomposite membrane containing 2.5 wt% zirconium oxide was fabricated by solution casting method. The sulfonation degree was evaluated by H-NMR and titration method. Water uptake, proton conductivity and ion exchange capacity (IEC) of the prepared membrane were determined. Proton conductivity of pristine and nanocomposite membrane is increased with temperature up to 80°C, suggesting proton conductivity is a thermally activated process. All results show addition of hygroscopic zirconia to SPEEK membrane exhibit increased water retention with good proton conductivity at different temperatures. These features make this nanocomposite membrane attractive for fuel cell applications.

Keywords: Nanocomposite membrane, PEMFC, SPEEK membrane, Zirconia nanoparticles, Proton conductivity.

1. Introduction

In recent years most of attempts concentrated on replacing Nafion by low cost non-perfluorinated polymers for PEMFC applications because of several undesirable aspects of Nafion membranes. Among hydrocarbon membranes sulfonated poly ether ether ketone (SPEEK) is the most alternative [1]. Its properties related on degree of sulfonation (DS). A DS about 60-70% is suitable according to the reasonable swelling, water uptake and proton conductivity of membrane in this range of sulfonation [2]. For higher temperatures applications of a PEMFC with SPEEK (80-120°C), the main problem is membrane drying that causes water uptake and proton conductivity decreasing. Zirconia as a hygroscopic metal oxide may be suitable for improving SPEEK properties as its desirable effects on Nafion membrane [3, 4]. In this study, nanocomposite membrane based on SPEEK with 2.5 wt% zirconia was prepared.

Physicochemical and electrochemical properties of membrane were investigated by H-NMR, IEC, WU and proton conductivity test.

2. Methods

2.1. Preparation

At first for polymer sulfonation 5 g degassed PEEK (Aldrich Co.) was dissolved in 100 ml sulfuric acid 95-97% (Merck Co.) under nitrogen atmosphere in a three neck flask at 50°C following procedures described in the literatures [1]. Finally polymer fibers were dried at 60°C for 12 h followed by drying at 110°C in a vacuum oven. The sulfonation degree was determined by H-NMR and IEC. For membrane preparation sulfonated polymer was dissolved in N, N-dimethyl acetamide (DMAc) (Merck Co.) at 45°C. Zirconium oxide nanoparticles were synthesized by solution combustion method. Then prepared zirconia powder was added into the polymeric solution and stirring to 24 h. After ultrasonication, the solution was casted onto a clean glass plate and dried at 60°C for 16 h. Then membrane was peeled off by immersing in DI water and dried at 120°C in a vacuum oven. SPEEK plain membrane was prepared as the same method. The thickness of dried membranes was 100-120µm. Before IEC and proton conductivity measuring, membranes were pretreated in 0.5M H_2SO_4 at 80°C for 1h and DI water for 1h.

2.2. Characterizations

The H-NMR analysis spectra was recorded on a Bruker Spectrospin 400 (Ultrashield TM) spectrometer. The X-ray power diffraction (XRD) pattern of zirconia nanoparticles was recorded with a PHILIPS PW-1800 diffractometer with Cu-Kα radiation source (λ=1.5418A°). For IEC measuring the prepared membranes were immersed in 2M NaCl for 48 h. After removing membranes, solution was titrated with 0.1M NaOH, in the presence of phenolphthalein as an indicator. Water uptake of membranes were measured by weight difference between dried membranes at 100°C in a vacuum oven for 24 h and wet membranes after immersing in DI water for 24 h at room temperature. Proton conductivity was measured by a two probe AC impedance spectroscopy with a potentiostat/galvanostat (Biologic, SP-150).

3. Results and Discussion

Figure 1 shows H-NMR spectrum of SPEEK. Each sulfonic acid group SO_3H results in a singlet at 7.5 ppm. The ratio between peak area of 7.5 ppm and the integrated peak area of other signals gives DS [5] that is 65.04 for this experiment.

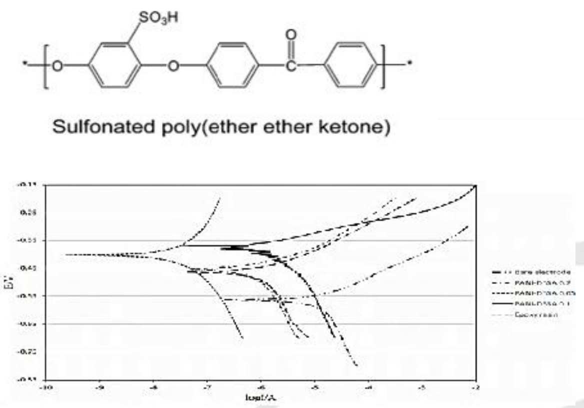

Fig.1 H-NMR spectra of SPEEK

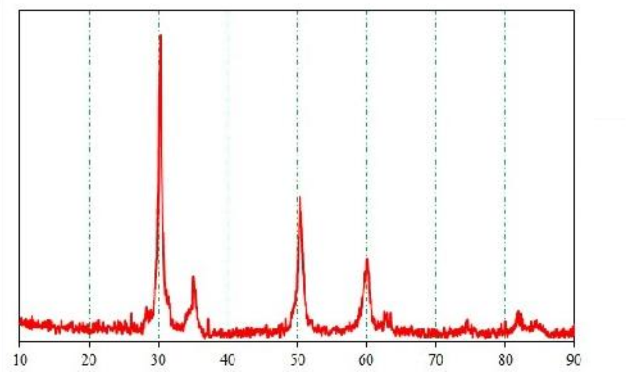

Fig.2 XRD pattern of zirconia powder

Figure 2 shows XRD of zirconia. The average size of zirconia by using Scherrer equation is about 13.1 nm. Water uptake, ion exchange capacity and proton conductivity of the plain and nanocomposite membranes are reported in Table.1.

Table.1 IEC, water uptake and proton conductivity of the plain and nanocomposite membranes

	IEC	**WU (%)**	**σ-30°C**	**σ-40°C**	**σ-60°C**	**σ-80°C**
SPEEK	1.78	18.6	25.14	26.82	32.11	33.57
SPEEK-2.5%Z	1.72	28.01	23.6	26.46	30.03	30.78

Water uptake increases in presence of zirconia because of hydrophilic nature of these nanoparticles. Degree of sulfonation using IEC is 62.92% that is in good agreement with H-NMR. Proton conductivity (σ) of the plain and composite membrane increased with temperature up to 80°C, suggesting proton conductivity is a thermally activated process. As shown up to 80°C, proton conductivity of composite membrane is lower than plain because of nonconductive nanoparticles.

4. Conclusions

In this work plain and nanocomposite membranes with a loading 2.5% zirconia nanoparticles based on SPEEK with 65.04% sulfonation were prepared. As shown nanocomposite membrane has better water uptake with lower IEC. This nancomposite has a good proton conductivity at different temperatures because of zirconia hygroscopicity. Based on results zirconia additive donates desirable properties to SPEEK. So this nanocomposite may be suitable for PEMFC applications at high temperatures.

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Preparation and comparison of physical and electrochemical properties of Nafion and Nafion/ZrO_2 nanocomposite membranes

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Abstract

Nafion nanocomposite membrane containing 5wt% zirconium oxide was fabricated. Nanocomposite and pristine Nafion membrane were prepared by casting method. The effect of zirconium oxide nanoparticles is evaluated by comparing the properties of Nafion nanocomposite and filler-free membranes. Zirconium oxide nanoparticles were characterized with XRD. Physical and electrochemical properties of membranes, water uptake, proton conductivity and ion exchange capacity (IEC), were determined. Proton conductivity of pristine and nanocomposite membranes increased with temperature. Zirconium oxide causes hydrophilicity of the nanocomposite membrane is higher than that of pristine Nafion membrane and this allowed increasing the nanocomposite membrane's conductivity at high temperature.

Keywords: Nafion, PEMFC, Nanocomposite membrane, Zirconia, Proton conductivity.

1. Introduction

A PEM fuel cell uses a polymer membrane as an electrolyte, which conducts protons to the cathode side. The most commonly used membrane is Nafion [1]. In spite of various favorable properties of Nafion membranes, such as high chemical stability and good proton conductivity, these membranes are still open to improvements. One of the major drawbacks of Nafion-type membranes is the limited thermal stability. Various methods have been investigated for solving this issue [2]. A promising method is the dispersion of certain fillers in the Nafion matrix such as TiO_2 [3], CeO_2 [4] and graphene [5], etc. In the current study zirconium oxide nanpoparticles are added to the Nafion membrane and properties of the prepared membranes are investigated.

2. Methods

2.1. Preparation

Nanocomposite membrane was prepared by casting method. 5 wt% Nafion solution (purchased from Ion Power) was evaporated at 60ºC and re-dissolved in N, N-Dimethylacetamide (DMAc, purchased from Merck) at 60ºC. Temperature of solution gradually increases to 90ºC. The resulting solution was kept under stirring until the concentration of polymer in solution reaches to 20 %. After ultrasonication for 60 min and degassing for 60 min in a vacuum oven at room temperature this solution was casted onto a glass plate and dried at 60°C for 16 h. The prepared membranes was peeled off by immersing in di-ionized water and dried at 120°C in a vacuum oven. The thickness of dried membranes was 120-140 µm. Before IEC and proton conductivity measuring, membranes underwent the following standard treatment; 1 h in 3% H_2O_2 at 80ºC, 1 h in H_2O at 80ºC, 1 h in 0.5 M H_2SO_4 at 80ºC and finally 1 h in H_2O at 80ºC. Then membranes were kept in DI water to the test. For comparison purposes, pristine Nafion membrane was also prepared.

2.2. Characterizations

The X-ray power diffraction (XRD) pattern of zirconia nanoparticles was recorded with a PHILIPS PW-1800 diffractometer with Cu-Kα radiation source (λ = 1.4518A°). For IEC measuring the prepared membranes were immersed in 2M NaCl for 48 h. After removing membranes, solution was titrated with 0.1M NaOH, in the presence of phenolphthalein as an indicator. Water uptake of membranes were measured by weight difference between dried membranes at 100°C in a vacuum oven for 24 h and wet membranes after immersing in DI water for 24 h at 60°C. Proton conductivity was measured by a two probe AC impedance spectroscopy with a potentiostat/galvanostat (Biologic, SP-150).

3. Results and discussion

Figure 1 shows XRD of zirconia nanoparticles. The average size of zirconia by using Debey-Scherrer equation, $d=K\lambda/\beta\cos(\theta)$, is about 13 nm. Ion exchange capacity (IEC), Water uptake and Proton conductivity of pristine and nanocomposite membranes are summarized in Table.1.

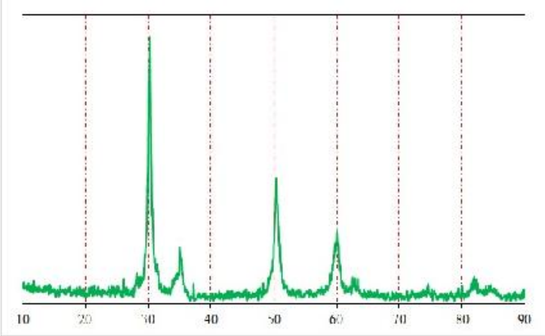

Fig. 1. XRD pattern of zirconia nanoparticles

Table.1 IEC, water uptake and Proton conductivity (mS/cm) of plain and nanocomposite membranes

		Water uptake		**Proton Conductivity at RH=100%**		
	IEC (meq/gr)	**Room Temperature**	**60°C**	**Room Temperature**	**60°C**	**80°C**
Nafion-ZrO_2	0.88	9.5	18.8	29.9	32.1	34.3
Pristine Nafion	0.92	8.6	11.3	40.1	43.5	46.3

Water uptake is a key property for PEMs which should be seriously considered, because the loss of water would cause decreased proton conductivity. The results in Table 1, confirm the improved hygroscopic property of nanocomposite membrane. Membranes in 60°C show more water uptake compared with the ambient temperature. This is due to more swellings of Nafion in high temperatures which results in more water uptakes. The reduced proton conductivity of Nafion/ZrO_2 membrane in comparison with pristine Nafion at RH=100% condition was due to the non-proton-conducting property of ZrO_2. The zirconia nanoparticles inhibits the free proton conduction in the membrane and hence, membrane's proton conductivity decreases.

4. Conclusions

In this study the effect of zirconium oxide nanoparticles is evaluated by comparing the properties of Nafion nanocomposite and filler-free membranes. Nafion-ZrO_2 nanocomposite membrane show enhanced water retention compared to pristine Nafion. Therefore, addition of hygroscopic zirconia to Nafion would slow down the proton conductivity decrease rate at higher temperatures. As a result, the operating temperature range can be extended to higher temperatures.

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Characterization of Sn/Graphene composite as anode in lithium ion batteries

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Abstract

Developing anode materials with high capacity and cycling stability is one of the researches of highest interest in lithium ion battery (LIB). Sn or Sn-based anode materials have been widely considered as one of the most promising anode candidates for its relatively high conductivity and noticeable theoretical capacity (994 mAh g^{-1}) [1]. Drastic volume change of Sn occurring during lithium insertion/deletion in charging/discharging process leads to cracking and pulverization of the electrodes and eventually quick fading of capacity. To address this problem, fabricating carbonaceous composite material such as Sn/C [2]anodes and Sn/CNTs[3] anodes seems to be an applicable strategy. Graphene (G) has recently been investigated as the functional matrix support for Sn-based nanostructures due to its intrinsic properties of flexible two-dimensional (2D) structure, high surface area, and excellent electrical conductivity, which not only facilitate the transfer of electrons, but also diminish the stress of the collective electrode upon battery cycling[4-5]. The discharge capacity at 1st and 2nd cycles and the cyleability during 25 cycles were evaluated as two most important criteria in LIBs. Physical characterizations such as SEM and XRD have been done to study the morphology of the system as working electrode. The electrolyte role has been studied since it affects both potential window and diffusion of lithium ions determining the impedance of electrolyte. Also, Electrochemical Impedance Spectroscopy (EIS) was analyzed to study the resistance behavior of the system. The Sn/graphene composite was produced through co-electrodeposition of components in aqueous medium under the constant and pulsed current applied on current collector substrate. The findings indicated that the composite produced has comparable discharge capacity in 1st and 2nd cycles while noticeably higher cycleability during 25 cycles. Additionally, EIS studies indicated that the graphene improves the resistance behavior of the system.

Keywords: *Lithium ion battery, Sn/ Graphene composite, discharge capacity, cycleability , cyclic voltammetry*

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Effect of sintering temperature on the lithium storage performance of $LiFePO_4$-C nanocomposite powders synthesized by ultrasonic spray pyrolysis technique

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Abstract

Research on the high rate, safe, durable, and cheap electrode materials in the field of lithium ion batteries (LIBs) is one of the hot topics in the field. In this regards, some anodic and cathodic materials having the foregoing merits were introduced, among which $LiFePO_4$ is one of the promising cathodic materials. In this study, $LiFePO_4$-C nanocomposite was synthesized by ultrasonic spray pyrolysis technique. A precursor solution composed of $LiNO_3$, $Fe(NO_3)_3.9H_2O$, H_3PO_4 and sucrose dissolved in distilled water was ultrasonically sprayed into an inert atmosphere tube furnace at 600 °C, and the synthesized powders were collected and sintered at 600 to 800 °C in N_2 +5%H_2 atmosphere. The electrochemical performances of the synthesized samples were examined with charge-discharge, cyclic voltammetry and electrochemical impedance spectroscopy tests. The sample sintered at 700°C showed the best electrochemical performance as follows: The initial discharge capacity of 136 mAh/g at 0.1 C rate and 104 mAh/g at 100mAg^{-1} rate, keeping a capacity retention ratio of 90% after 50 cycles. While, without sintering process, the initial discharge capacity was 65 mAh/g at 0.1C rate and 32 mAh/g at 100mAg^{-1} rate, and capacity retention ratio of 84% was observed after 50 cycles.

Keywords: *Spray pyrolysis, $LiFePO_4$, Lithim-ion battery, Cathode*

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Enhance electrochemical performance of $LiFePO_4$-C nanocomposite with V_2O_5 addition in lithium-ion battery cathode

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Abstract

Olivine structured $LiFePO_4$ is one of the promising materials of lithium ion battery cathode, in terms of price, safety, rate, and cycle life. In this study, $LiFePO_4$-C was synthesized by spray pyrolysis technique to apply as lithium ion battery cathode. Spray pyrolysis is a simple, continuous, and easily controllable technique for synthesis of nanomaterials. V_2O_5 powder was also added to cathode to further promote the electrochemical performance towards lithium ion storage. The electrochemical performance was evaluated by galvanostatic charge-discharge, cyclic voltammetry, and electrochemical impedance spectroscopy in a two-electrode cell. The results showed the beneficial role of the addition of V_2O_5 in terms of improving the specific capacity, rate capability, and cycling stability and lithium ion diffusion rate of the $LiFePO_4$-C-based cathode. The obtained electrochemical performance metrics was as follows: The initial discharge capacity of 154 $mAhg^{-1}$ at 0.1C and 110 $mAhg^{-1}$at 100 $mAhg^{-1}$ rate, and keeping a capacity retention ratio of 93% after 50 cycles.

Keywords: *Electrochemical properties, V_2O_5 particle, $LiFePO_4$, Lithium- Ion battery*

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Multiwalled Carbon Nanotube Supported PtRuPd as a Electrocatalyst for Ethylene glycol oxidation reaction in Fuel Cells

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Abstract

The activity of the Ethylene glycol (EG) oxidation reaction of a multiwalled carbon nanotube (MWCNT)-supported PtRuPd catalyst was investigated by Cyclicvoltammetry, X-ray diffraction (XRD), Scanning Electron Microscope (SEM) and Energy Dispersive Spectrometer (EDS). The PtRuPd nanoparticles with 1:1:1 and 1:2:1 and 1:1:2 atomic ratios (with same morphological structures) were deposited on the MWCNTs .Cyclicvoltammetry results demonstrated that the MWCNT supported PtRuPd(1:1:2) catalyst exhibited a higher mass activity (mA mg-1 of PtRuPd) for the Ethylene glycol oxidation reaction than other ratios.

Keywords: *Multiwalled Carbon Nanotube ¤Fuel Cells ¤Ethylene glycol*

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Ionic conductivity of $Li_{1.3}Al0_{.3}Ti_{1.7}(PO_4)_3$ solid electrolyte synthesized by solution-based method

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Abstract

LiTi2(PO4)3 based compounds with nasicon type structures are known as low temperature solid electrolytes with fast Li^+ ion transport. Substitution of $Ti^{4+}\rightarrow M^{3+}+Li^+$ in the system Li_{1+x}MxTi2−x(PO4)3 (where M=Fe, Sc, Al, Y, B, In, Ga) leads to higher conductivities by several orders higher than those of host compounds. $Li_{1.3}Al0_{.3}Ti_{1.7}(PO_4)_3$ (LATP) is one of the most highly conductive, air stable, lithium ceramic electrolytes that have been used in li-air batteries recently as solid electrolyre interface . The significant advantage of ceramic based artificial SEI in li air batteries is that it protects the lithium metal from all atmospheric contamination.Most studies on LATP have adopted solid state reaction and melting–quenching methods for the LATP preparation .These methods cannot be easily applied to the mass production due to high energy consumption and contamination of impurities in the final products. On the other hand solution based synthesis method favors the preparation of powder with controlled composition and metallurgy. In this study we have prepared LATP powders by a solution based synthesis method continued by sintering to obtain the highest ionic conductivity.

50 mL of NH4OH and 25 mL of Ti(OC3H8)4 was used as precursor producing a white gelatinous precipitate.The precipitate was washed with 500 mL of deionized water to remove the excess base and placed in 100 mL of deionized water. To this solution was added 200 mL of a 1 M solution of anhydrous oxalic acid. Al(NO3)3·9H2O, (NH4)2HPO4, and 5% excess LiNO3 were added under stirring with stoichiometric ratios to the solution. The final solution was then heated on a hot plate until all the water was evaporated, which produces a white precipitate of well mixed precursors for annealing.

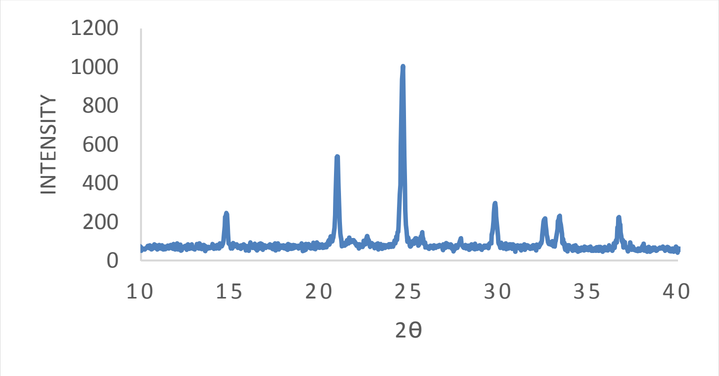

Figure 8. X-ray diffraction patterns for Li1.3Al0.3Ti1.7 (PO4)3 powders

The dried mixture was heated at 850°C for 5 hours to obtain crytalline structure. The Xrd patterns of grounded powder were depicted in fig.1. As seen diffraction peaks were well matched with the standard pattern of LTP, and no impurity phase was observed. The peak intensities shows high crystallinity of grownded powders. The milled powder was used to form the pellet, which was then calcined at 650 and 850 $°C$ for 3 hours. Li ion conductivity of the LATP pellet was measured by AC impedance method. Prior to measure, Au was sputtered on both side of the pellet to ensure electrical contact. Data was obtained at 10 mV voltage signal in a frequency range of 1Hz to 1MHz at room temperature. The density of the pellets was determined via Archimede's method. Sample properties and obtained value for conductivity and density was depicted in Table 1.

sample	Sintering temperature (℃)	total conductivity(S/cm)	Density(gr/cm^2)
Sample 1	650	1.12×10^{-4}	2.64
Sample 2	850	2.84×10^{-5}	2.09

SEM micrographs (fig.2) of pulished surfaces shows two different areas . More well sintered areas with higher density was observed in sample 1 as a result of higher sintering temperature . The measured densities are in agreement with SEM micrographs. Furthermore higher total conductivity of sample 1 in comparsion with sample 2 is a result of its lower porosity.

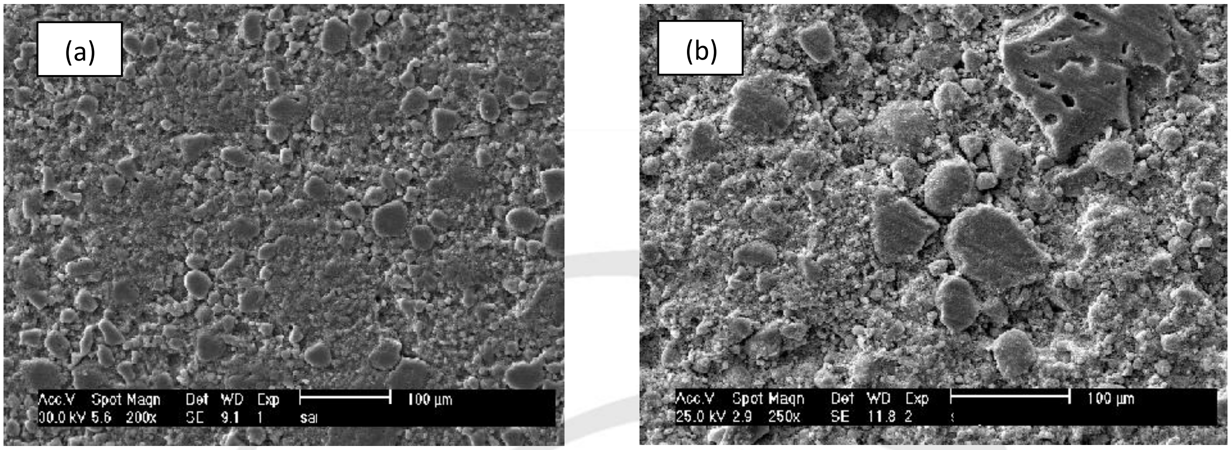

Figure2. SEM micrograph of sintered pellets at a) 850°C b) 650°C

According to this total conductivity LATP pellets could be used as solid electrolyte in a Li-air battery.

Keywords: NASICON, Solid electrolyte, Ionic conductivity, LATP

Effect of caustic treatment of reduced graphene oxide on its structure and performance toward ORR

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Abstract

Oxygen reduction reaction (ORR) plays an important role in electrochemical devices such as fuel cells, metal-air batteries, and advanced chlor-alkali cells [1]. Currently due to sluggish kinetics of ORR, notable studies for achievement of active and durable electrocatalysts were done [2]. During last decade, graphene-based electrocatalysts demonstrated remarkable performance toward ORR [3]. In synthesis of graphene-based electrocatalysts, corrosive chemicals have been used for pH control or as treatment agents. In the present work, the effect of caustic on the structure and performance of reduced graphene oxide was investigated by using Raman, FTIR, XRD, and voltammetry techniques. The results revealed that caustic treatment introduced some defects in the graphene planes. These defects might play as active sites to promote ORR activity.

Keywords: Fuel cells, Electrocatalyst, Oxygen Reduction Reaction, Graphene, Caustic Treatment

Title area

Fuel cell, Oxygen reduction reaction

Reference

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A review for fundamental aspects, electrosynthesis, characterisation and physioelectrochemical properties of highly efficient hybrid supercapacitors

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Abstract

Electrochemical capacitors (ECs), known as supercapacitors, are charge-storage devices that capable of very fast charges and discharges, with a unique combination of high power, high energy and long lifetime. ECs with these unique properties can bridge the gap between batteries and capacitors, offering great potentials in applications such as starting automotives and regenerating of brake energy. To date, carbon, transition metal oxides and conducting polymers (CPs) [1, 2] have been identified as most promising materials for ECs. Each material has its own unique advantages and disadvantages for supercapacitor applications. One of the attempts to obtain the better performance of supercapacitor electrode was to use pervoskite like SrRuO$_3$ containing one of element ruthenium. It is expected that the combined Graphen oxide and different metal oxides, a pervoskite i.e. BiFeO$_3$ has to show the similar or perhaps better performance. The bismuth iron oxide in five crystallite phases i.e. BiFeO$_3$, Bi$_2$ Fe$_4$O$_9$ and Bi3 Fe$_5$O$_{12}$ is well known. That means this material may sustain the charges in its phases during the electrochemical changes.

In the presented review, different metal oxide, ceramic material and graphen oxide/ conductive polymer as a composite materials were deposited on working electrode by cyclic voltammetry (CV) method and fundamental physielectrochemical aspects, electrochemical performance were evaluated in an aqueous redox super capacitor in acidic medium. Different electrochemical methods including galvanostatic charge–discharge (CD) experiments, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were carried out in order to investigate the applicability of the system as a hybrid supercapacitor in detail.

Keywords: *electrosynthesis, impedance, nanocomposite, supercapacitor*

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Potential application of nitrogen-doped graphene nanosheets as an efficient cathode electrocatalyst in alkaline PDMFC

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Abstract

The passive direct methanol fuel cell (PDMFC) are promising option for powering advanced electronic devices in the future due to the high power densities, easy fuel storage, low operating temperature, low noise level and simple design [1]. Fuel crossover is one of the major problems in the fuel cell performance which causes reduction in fuel utilization and occurrence of mixed potential in cathode compartment [2]. Using non-reactive catalyst to fuel in cathode is one of the interesting methods to decrease fuel crossover effect.

The aim of the present work is to investigate the performance of a PDMFC with application of nitrogen-doped graphene (NG) as cathode electrocatalyst which is highly selective to oxygen in presence of methanol. The results demonstrated that the PDMFC with NG has better performance compared to commercial Pt/C as cathode electrocatalyst.

Keywords: Direct Methanol Fuel Cell, Metal-free Electrocatalyst, Nitrogen-doped Graphene

Title area
Direct Methanol Fuel Cell

Reference

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Synthesis of cobalt catalyst supported on nitrogen doped graphene for oxygen reduction reaction

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Abstract

In this work, nitrogen-doped graphene was synthesized by a low temperature solvothermal process to use as catalyst supports for oxygen reduction reactions. Firstly NG was synthesized by solvothermal method, then Co nanoparticles were precipitated on NG using a polyol method and electrocatalytic properties of synthesized catalyst towards oxygen reduction reaction in 0.1 M KOH were investigated. Electrochemical measurements showed that Co/NG exhibited suitable electrocatalytic activity. The synthesized electrocatalyst was characterized using X-ray photoelectron spectroscopy (XPS).

Keywords: *Oxygen reduction reaction, Fuel cell, Nitrogen doped graphene, Co/NG catalyst*

1. Introduction

The sluggish kinetic rate of oxygen reduction reaction (ORR) at cathode is the main challenge for commercial applications of FCs [1]. Platinum remains impractical due to its high cost and sensitivity to poisoning [2]. Therefore, developing cost-effective and durable non-platinum catalysts for ORR has aroused extensive research interests. Several metal based catalyst, i.e. cobalt, manganese, iron, copper, nickel, have been found to catalyze the ORR and used as new cathode catalysts in FCs. Among these metals, cobalt is appealing because of its high catalytic ORR activities [3]. Nitrogen-doped carbon materials exhibit excellent cost, CO tolerance and rather good stability [4]. In current study Co/NG electrocatalyst are used as a catalyst for ORR.

2. Methods

2.1. Synthesis of N-doped graphene and Co/NG catalyst

Typically 1 gr of pentachloropyridine was placed in 25 ml stainless steel autoclave then 1 gr metallic potassium rapidly added to the autoclave. The autoclave was sealed and heated to the desired temperature naturally. The salty-dark precipitate products were filtered and washed out with acetone, absolute ethanol and water in sequence and then were dried in a vacuum at 80°C for 4 h. In second step, cobalt nanoparticles were precipitated on synthesized NG. Required amount of cobalt salt solution were added to NG. dispersion drop-wise and total metal loading was 40% wt. After stirring for 1 h to mixture was adjusted to pH 7 by drop-wise addition of 2.5 M NaOH and heat treated at 60°C for 1 h to ensure that the entire Co were completely reduced. Finally the catalyst slurry was centrifuged and washed 3-4 times with DI water and dried at 70°C for 8 h in vacuum oven.

2.2. Characterizations

X-ray photoelectron spectroscopy (XPS) was conducted to study of the surface species of synthesized Co/NG. Cyclic voltammograms were performed in a conventional three electrode system using Pt plate and Ag/AgCl electrode as counter electrode and reference electrode respectively and modified GCE (2mm diameter) as working electrode. The electrolyte was 0.1 M KOH solution, which was purged with oxygen 20 min prior to the electrochemical test. ORR activity can be evaluated by cyclic voltammetry (CV) and linear sweep voltammetry (LSV).

3. Results and Discussion

Fig. 1 depicts the XPS result of Co/NG catalyst. It shows a C1s peak at about 284 eV, an O1s peak at about 530 eV, N1s peak at about 400 eV and a Co2p peak at about 790 eV for Co/NG catalyst.

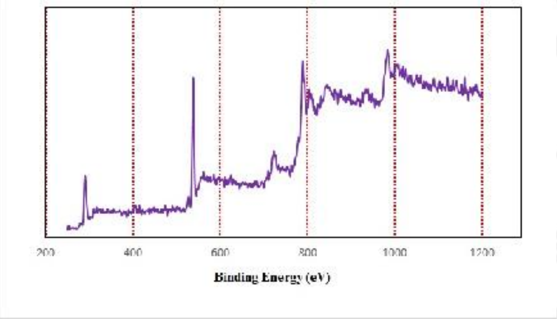

Fig. 1. XPS spectrum of Co/NG

The electrocatalylic activity of Co/NG was determined in a convectional three-electrode system in alkaline solution. In oxygen-saturated KOH solution, a prominent cathodic current appeared with a peak centered at ≈-0.7 V vs. Ag/AgCl/KCl (sat’d) indicating the pronounced catalytic activity of synthesized Co/NG for ORR (Fig. 2).

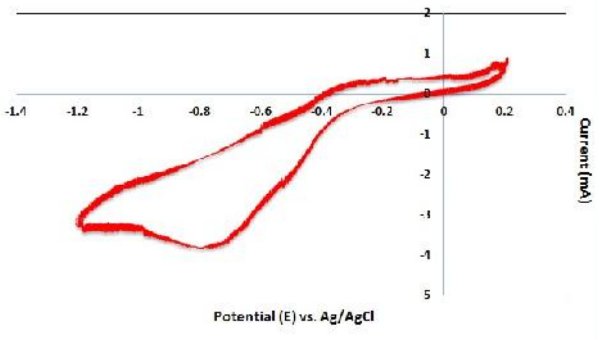

Fig. 2. CV in O_2-saturated 0.1 M KOH solution for Co/NG at a scanning rate of 100 mV/s.

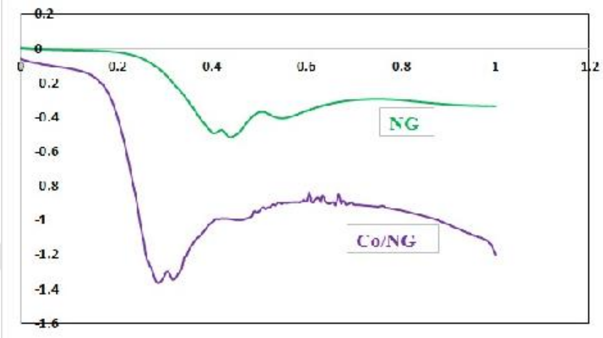

Fig. 3. LSVs for NG and Co/NG electrodes in O_2-saturated 0.1 M KOH solution at a scanning rate of 10 mV/s

Co/NG showed good performance and its LSV curve is compared with those for NG alone in Fig. 3. It is clear that the value of reduction current density for Co/NG improved compared with NG alone. Fig. 3 shows a general increase in the activity of synthesized catalysts for ORR after metal precipitation. Transitional metal nanoparticles can be considered to be electroactive sites for ORR.

4. Conclusions

In this study, an easily synthetic approach for large-scale preparation of NG via a simple solvothermal process was used. Electron accepting ability of nitrogen atoms create net positive charge on adjacent carbon atoms in hexagonal carbon plane of graphene, these carbon atoms can readily attract electrons from anode. Metal nanoparticles and nitrogen species have significant effects on improving the ORR catalytic activity observed in Co/NG catalyst.

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Synthesis and studying of active and durable support based on graphene for PEMFC

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Abstract

In this work,we have developedanefficientapproachto prepare the nitrogen doped graphene supported Pt nanocomposites (Pt/N-G). Nitrogen-doped graphene (N-G) was prepared by pyrolysis of graphene oxide with cyanamide as nitrogen containing precursor at different temperatures, which led to high and controllable nitrogen contents. Subsequently, the Pt nanoparticles were dispersed over N-G surface by modified chemical polyol reduction process..X-ray powder diffraction, FTIR spectroscopy, Raman spectroscopy, X-ray photoelectron Spectroscopy, and Transmission and scanning electron microscopy (TEM&SEM) were used to characterize the morphology and microstructure of the prepared catalysts. The TEM and elemental mapping images indicate that metal nanoparticles are more uniformly dispersed on the surface of N-doped graphene than other supports; and Pt nanoparticles dispersed without any aggregation. The catalytic activity and durability of the catalysts was evaluated by various electrochemical techniques. Compared to the undoped Pt/rGO and commercial Pt/C catalysts, an enhanced electro catalytic activity was obtained in the case of the Pt/N-rGO with optimized composition and nanostructure. The maximum power density of MEA for Pt/N-rGO was 1.4 times more than that of MEA fabricated by commercial Pt/C 20%.

Keywords: *PEMFC, graphene, N-doped, Pt nano particle*

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Synthesis of Nano Composite TiO_2 Nanotube/C as Anode Materials for Li Ion Batteries

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Abstract

Lithium rechargeable batteries are now well established as power sources for portable equipment. The C-doped TiO_2-NTAs are fabricated by rapid annealing of as-anodized TiO_2-NTAs in argon. The residual Ethylene glycol absorbed on the nanotube wall acts as the carbon source and no foreign carbon precursor is thus needed. The TNT/C composite as anode materials in li ion battery was tested by charge/discharge galvanostatic and electrochemical impedance spectroscopy electrochemical experiments. This component of TiO_2/Carbon was characterized by XRD and the morphology of titanium oxide nanotube/C was studied by scanning electron microscope (SEM).

***Keywords**: Li Ion Battery, Anode, Carbone, Titanium oxide Nanotube, Anodizing*

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Parametric Analysis of Proton Exchange Membrane Fuel Cell Performance under Different Operation Condition by Using a Neural Network

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Abstract

The neural network can construct relationships between the control factors and responses in the PEMFC. This study proposes a feed forward neural network modeling for parametric analysis of proton exchange membrane fuel cell (PEMFC) performance. The neural network trained with Lederberg-Marquardt algorithm. Numerous parameters affecting the maximum power density of PEMFC are analyzed, such as fuel cell operating temperatures, cathode and anode humidification temperatures and operating pressures. Experimental results are presented for identifying the proposed approach, which is useful to get deep knowledge of PEMFC behavior.

Keywords: PEM fuel cell, Maximum Power density, Operating condition, Artificial neural network.

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Effect of support on activity and stability of Pt–Pd catalyst for oxygen reduction reaction in proton exchange membrane fuel cells

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Abstract

Nowadays, the physical and chemical synthesis of Pt and Pd based nanocatalysts is of interest because they are very highly active electrocatalysts towards oxygen reduction reactions (ORR). The enhancement of the activity for Pt in the presence of Pd originates from the weakening of the O-O bond on Pd-modified Pt nanoparticles. On the other hand, the enhancements of the carbon support properties have been also pursued and are considered to be crucial. Sulfonation of carbon materials and its use as a support for catalysts as mixed electronic and protonic conductors has been demonstrated to be an efficient way to improve the structure of the triple-phase boundaries. In the present work, the Pt-Pd nanoparticles were loaded on the mixture of Vulcan XC-72 and MWCNT (1:3), which were functionalized in the mixture of 96% sulfuric acid and 4-aminobenzenesulfonic acid using sodium nitrite to produce intermediate diazonium salts from substituted anilines. The electrocatalytic activity of Pt_2Pd/C was investigated with regard to the oxygen reduction reaction (ORR). The maximum power density of MEA The maximum power density of MEA with Pt_2Pd /C catalyst is about 564 $mWcm^{-2}$.

Keywords: Polymer electrolyte fuel cell, Phenyl sulfonic acid, Pt-Pd nanoparticles, Electrocatalysis, Membrane Electrode Assembly (MEA).

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Synthesis of the LiFePO$_4$/graphene composite and its enhanced properties as cathode materials for lithium ion batteries

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Abstract

LiFePO$_4$ is the most promising cathode materials for lithium-ion batteries (LIBs). the bare LiFePO$_4$ shows poor rate capability because of its intrinsically low electronic conductivity. Incredible efforts have been devoted to improve the electron conductivities by coating physically and/ or chemically a thin layer of conductive carbon or derivatives on it [1-3]. Graphene have been demonstrated as one of optimal materials to modify the electrode materials, including LiFePO$_4$ [4].

In the work, we designed and fabricated a composite of LiFePO$_4$ modified with graphene. Fig. 1 shows the SEM images of as-prepared LiFePO$_4$/graphene composite. To get insight into the graphene coating effect on the electrodynamics of LiFePO$_4$, EIS measurements were carried out on the cells with LiFePO$_4$/graphene as cathode. The as-measured Nyquist plot is shown in Fig. 2. The plot was a combination of a depressed semicircle in the high frequency region and a spike in the low frequency region. Previous explanation on the impedance spectra is that the high frequency semicircle is related to the migration of the Li$^+$ ions at the electrode/electrolyte interface and charge transfer process. The spike is attributed to the Warburg impedance of long-range Li-ion diffusion [5]. Compared with that LiFePO$_4$, a smaller depressed semicircle has been shown for composite, indicating much lower interface impedance between the metal current collector and electrode materials, which may be beneficial to the rate performance of composite.

Cyclic voltammetry was performed in order to investigate the effect of graphene on the electrochemical properties of LiFePO$_4$ by using a scanning rate of 0.1 mV s^{-1}. The CV of LiFePO$_4$ /graphene composite show more symmetrical and sharper shape of the anodic/cathodic peaks, which indicates the better electrochemical activity.

Keywords: lithium ion battery, LiFePO$_4$, graphene

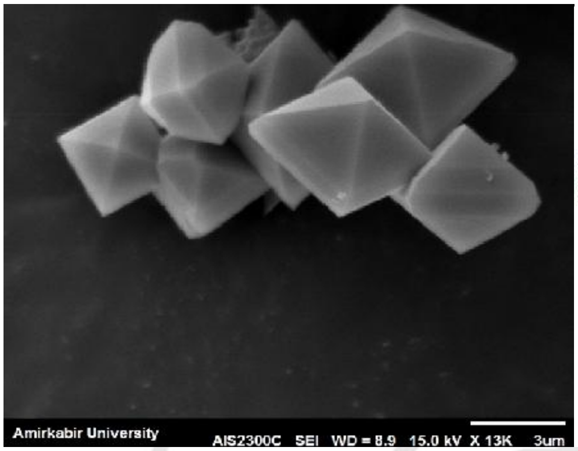

Fig. 1. SEM image of LiFePO$_4$/graphene.

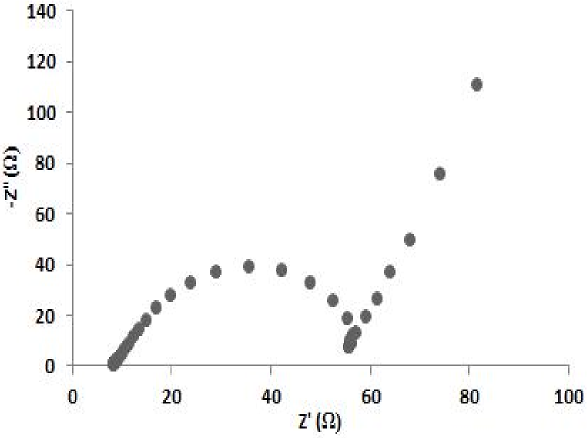

Fig. 2. Nyquist plots of LiFePO$_4$/graphene.

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Synthesis of CeO_2 nano-powders using gel-combustion method in order to make SOFCs

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Abstract

The effect of rare earth oxide on the microstructure of CeO_2 nano-powders using gel-combustion method was investigated. Some nano-powders were studied through XRD and SEM analyses. The XRD patterns confirmed only a ceria structure. The SEM micrograph showed some nano-sized spherical particles with a size range of 50–70nm. The addition of rare earth oxide decreased the crystallite size of ceria.

Keywords: Nanosized materials; SOFCs; Rare Earth Oxides; CeO_2; Fuel Cell; Grain Growth.

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Review of solid oxide fuel cells (SOFCs): Roadmap, advantages, application, and mechanism

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Abstract

Fuel cells are highly energy efficiency technologies and could be effective in achieving energy savings. Fuel cells and hydrogen are fundamental in view of decarbonising world. They will play a significant role in renewable energy storage, in the energy for the transport sector, in the energy for combined heat and power applications in households and districts. The road map of European countries has been studied. The environmental challenges and the fuel cells potential, the advantage, mechanism, and application of solid oxide fuel cell have been discussed.

Key Words: SOFCs; Decarbonising; Fuel Cell; Road map, pollution;SOFC;Mechanism;Environment.

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A comparison of different carbon used as the positive electrode (cathode) in Lithium/Thionyl Chloride (Li/SOCl2) cells

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Abstract

The Li/$SOCl_2$ battery system consists of a Li anode, a carbon cathode, and the $LiAlCl_4$/$SOCl_2$ electrolyte solution. Different varieties of carbon can be used to construct the cathode. According to the literature [1] colloidal Teflon is used as the binding material for fabricating the carbon electrode. The composition of the paste is given as: carbon; 80% by weight; Teflon binder; 20% by weight. The procedure entails rolling the carbon/PTFE mix onto the syringe. The pretreatment of carbon cathodes with acetone has led to an increase in cell voltage and capacity for Li/$SOC1_2$ cells [2]. This treatment is thought to work by removing impurities from the carbon and increasing the total pore volume and average pore diameters. During cell discharge $SOC1_2$ reduction takes place at such a cathode, resulting in the precipitation of reaction products, mainly LiCl, within the pores of the substrate. This leads to eventual passivation of the cathode surface and, hence, cell failure. Most of the Li/$SOC1_2$ cell research under taken is to improve the performance of this positive electrode. For this reason, we studied the reduction reaction of $SOCl_2$ on different carbons in a three-electrode cell by cyclic voltammetry. Carbons that used for this purpose are acetylene black (AB), Vulcan, Multiwalled carbon nanotube (MWCNT), activated carbon and refined carbon from SAFT Li/$SOCl_2$ battery. The cathode substrate in Li/$SOC1_2$ cells provides a conductive surface on which $SOC1_2$ is depolarized. Fig.1 is a comparative cyclic voltammograms (CVs) of the Li/$SOCl_2$ cell with different carbons as cathode in 1 M $LiAlCl_4$/$SOCl_2$. The results of electrochemical techniques show that the reduction rate of $SOCl_2$ on surface of Acetylene black, which consists of submicron sized particles and high surface area is better and like as refined carbons from SAFT Li/$SOCl_2$ battery. The reduction rate of $SOCl_2$ on surface of activated carbon and glassy carbon is the worst of all due to the low conductivity.

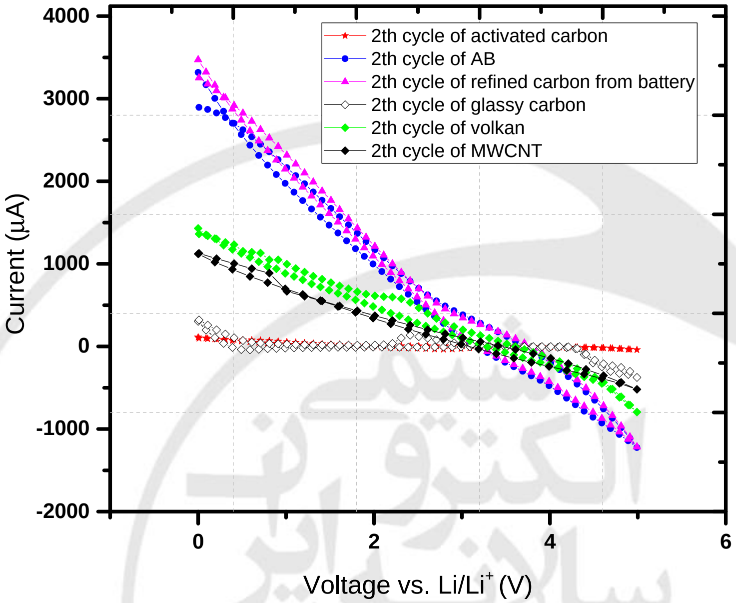

Fig 1.the CVs of 1 M $LiAlCl_4/SOCl_2$ and different carbons as a cathode at 80 mV s^{-1} .

***Keywords**: Lithium thionyl chloride cell, Glassy carbon, Activated carbon, Acetylene black, Multiwalled carbon nanotube, Vulcan*

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Effect of surfactants on electrochemical hydrogen production

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Abstract

Nowadays, the demand for energy is growing and the raw materials for the fossil fuel economy are diminishing (1). Hydrogen is being extensively investigated as an alternative to fossil fuels. Water electrolysis is a simple and large-scale industrial method for production of hydrogen (2). Platinum (Pt) is an ideal catalyst for electrochemical hydrogen evolution reaction (HER) as cathode. However, one thing that could be problematic is that the bubbles caused by hydrogen production remain at the surface of Pt, which reduces the cell current efficiency.

In order to get rid of these bubbles it is necessary to make some changes either in cell design or the materials used in the electrolyte composition. With this in mind, the materials which reduce the surface tension, surfactants have been used in this study for the first time and good results were achieved. In this regard, the capability of three types of surfactants – anionic (SDS), cationic (CTAB), and nonionic (TritonX-100) at the various concentrations as well as in both acidic and basic medium at various temperatures have been investigated. Among the employed surfactants, the best results were obtained by the use of anionic one in the acidic medium.

Keywords: Electrolysis, Surfactant, Hydrogen production, Platinum

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Bio Electerochemistry

Ionic liquid-functionalized carbon nanotube composite in bioanode for enzymatic fuel cell

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Abstract

A biofuel cell is an electrochemical device in which the energy stored in a fuel, such as ethanol, is converted to electrical energy by means of the catalytic activity of either an enzyme or a microorganism. Biofuel cells have traditionally suffered from low power densities and short lifetimes due to the fragility of the bio-catalyst. Utilizing a novel ionic liquid-carboxylated multiwall carbon nanotube nanocomposite for alcohol dehydrogenase enzyme immobilization in a biofuel cell results in increasing the enzyme lifetime to commercially viable levels. Additionally, this method provides sufficient protection to develop a membraneless biofuel cell, an important step for commercialization. Previously, it has not been possible to create a membraneless style biofuel cell due to the denaturing of the enzyme that would occur at the high temperatures experienced during the heat pressing step of fabrication. A nanocomposite consisting of ionic liquid-carboxylated multiwall carbon nanotube provides sufficient protection for the alcohol dehydrogenase to retain the enzyme activity after exposure to temperatures of 40 °C. Thus, a membraneless biofuel cell was prepared. Preliminary results of the biofuel cell revealed the power density ranging from 1.7 to 10 $\mu W/cm^2$ and the open circuit voltage from 0.599 to 0.360 V.

Keywords: *Biofuel cell, Bioanode, Ionic liquid, alcohol dehydrogenase*

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Direct electron transfer of Myriococcum Thermophilum Cellobiose Dehydrogenase on gold nanoparticles

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Abstract

Cellobiose dehydrogenase (CDH, EC 1.1.99.18) is an extracellular fungal redox enzyme, which has recently shown promising properties for applications in both biosensors and biofuel cells [1] capable of oxidizing various sugars including relevant analytes such as lactose or glucose. CDH is an extracellular, monomeric two domain enzyme consisting of a catalytically active, FAD containing domain (DH_{CDH}) connected through a polypeptide linker region with a heme b containing cytochrome domain (CYT_{CDH}). In the catalytic reaction, the substrate is oxidized at the DH_{CDH}, which in turn is deoxidized through a sequential intramolecular electron transfer process (IET) donating the electrons to the CYT_{CDH}. The mechanism of electron transfer from the DH_{CDH} to the CYT_{CDH} is pH dependent but not fully understood. In the final electron transfer step the electrons are transferred from the surface exposed heme b of the CYT_{CDH} directly to the electrode, denoted direct electron transfer (DET). Until now DET has only been shown between the CYT_{CDH} and the electrode surface, never via the DH_{CDH} domain [1]. In this work, a new biosensor, based on deposition of Myriococcum thermophilum Cellobiose Dehydrogenase (*Mt*CDH) onto graphite electrode modified with polyethyleneimine gold nanoparticles (PEI@AuNPs), is presented. The characterization of PEI@AuNPs has been done using transmission electron microscopy (TEM), dynamic light scattering (DLS) and UV-visible spectroscopy. The performance of the biosensor has been studied using cyclic voltammetry and flow injection analysis (FIA). The fabricated lactose biosensor exhibits a linear response between 1 to 100 µM lactose.

Keywords: *Myriococcum thermophilum Cellobiose Dehydrogenase, Biosensor, Gold nanoparticles, Lactose.*

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High performance glucose/O_2 compartment-less biofuel cell using DNA/CNTs as platform for immobilizing BOD as novel biocathode and integrated NH2-CNTs/ DEN/GDH/ NB as anode

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Abstract

Enzyme-modified electrodes are core components of bioelectronic devices, such as biofuel cells, which, generating electricity from natural fuels, like sugars and alcohols [1]. Different methods to electrically communicate enzymes with electrodes were developed [2,3,4]. Herein, bilirubin oxidase enzyme molecules was immobilized with control orientation using deoxy ribonucleic acid (DNA)/multi-walled carbon nanotubes (MWCNTs) modified electrode with enhanced negative charged density as novel platform. The proposed support increased the performance of the direct electron transfer (DET) and oxygen reduction reaction (ORR) three folds in comparison to BOD enzyme which immobilized directly onto MWCNTs and as a result the current density reached to 270 μA cm^{-2} at 0.405 V with an onset potential of 0.57V (vs. Ag/AgCl). The performance of this modified electrode as a biocathode was investigated after assembling with bioanode. The bioanode prepared with covalent attachment of glucose dehydrogenase enzyme (GDH) and nile blue (NB) as an efficient mediator for coenzyme regeneration onto glassy carbon electrode modified with amino-carbon nanotubes(MWCNTs-NH_2) and carboxyl terminated polyamidoamin dendrimer (PAMAM-Den) as a multifunctional linker. Finally, the performance of one-compartment glucose/O_2 biofuel cell without separators was also investigated. Based on the recorded polarization curves, the open circuit voltage of the cell and maximum current density were obtained 660 mV and 172 μAcm^{-2}, respectively, while the maximum power density of 45μWcm^{-2} was achieved at 428 mV of the cell voltage in buffer solution saturated with O2 and containing 50 mM of glucose. The stability of the constructed EBFC was investigated under continuous operation at maximum power. It was observed that the

biofuel cell can retain more than 90% of its performance after 24 h. figure .1 showed the schematic representation of the constructed biofuel cell.

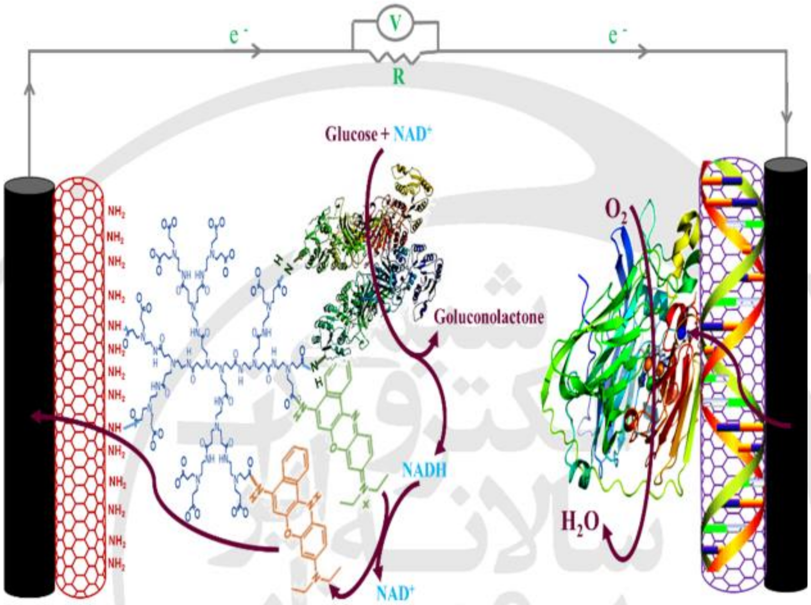

Figure .1 schematic representation of the constructed biofuel cell.

Keywords: *Enzymatic biofuel cell, Membrane less, Glucose dehydrogenase enzyme, Dendrimer, Bilirubin oxidase enzyme, oriented immobilization.*

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Evaluation of kinetic and thermodynamic parameters of Rizatriptan using nano-biosensor

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Abstract

In this research, Nano-graphene (NG), bovine serum albumin (BSA) and agar powder were used as electrocatalyst, selective biological agent and supporting material in construction of novel Rizatriptan benzoate (RB) nanobiosensor, respectively [1,2]. Experimental parameters for RB determination, such as BSA/NG ratio, potential scan rate, pH and supporting electrolyte have been optimized. This optimized nanobiosensor (NBRNBS) was applied for electrochemical assay of RB in phosphate buffer solution (PBS, pH = 7) using cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Under the optimum condition, RB could be linearly detected in the acceptable concentration range of 1.0×10^{-3} M to 1.0×10^{-4} M ($R^2 = 0.9946$). The detection limit was down to around 7.5×10^{-5} M and maximum current response was obtained at pH=7. Kinetic and thermodynamic parameters such as the standard rate constant, diffusion coefficient, activation energy and Gibbs free energy were evaluated [3]. The MBRNBS exhibits a very good performance for detection of RB in the presence of Sumatriptan, Propranolol and Ergotamine in pharmaceutical preparations.

Keywords**:** *Rizatriptan, Bovine Serum Albumin, Nano-graphene, Nano-biosensor, Cyclic voltammetry, Kinetic and Thermodynamic parameters*

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Development of a highly sensitive DNA FFTSW voltammetric genosensor based on CeO_2 NPs-RGO nanocomposite

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Abstract

In recent years, clinical diagnosis methods developed rapidly along with discovery of new genes and their association with disease. Electrochemical DNA biosensors provide sensitivity, selectivity and low cost for detection of specific DNA sequence associated with human disease[1]. In this study, we report the construction of a novel electrochemical DNA genosensor based on reduced graphene oxide decorated with cerium oxide nanoparticles (CeO_2NPs- RGO) [2]. The surface of glassy carbon electrode was modified with CeO_2NPs-RGO/PANI/GCE, and characterized by scanning electron microscopy, cyclic voltammetry and electrochemical impedance spectroscopy methods. Here a novel platform was applied to detect the Apolipoprotein E gene (*ApoE*) point mutation related to the progression of Alzheimer's disease [3]. The ssDNA probe was immobilized into the nanocomposite, via strong interaction between CeO_2 and the phosphate groups in the ssDNA backbone [4]. The fast Fourier transform square wave voltammetry was used for investigation of ssDNA probe immobilization and hybridization with target DNA. Where, the genosensor response was the current decrease of $[Ru(bpy)_3]^{2+/3+}$ after hybridization. The genosensor showed high selectivity and sensitivity toward detection of the ApoE gene, with a good linear relationship between the response signal and logarithmic function of target DNA concentration in a range of 1 fM to 10 nM with a detection limit of 0.1 fM. The represented genosensor in this study can be further used for detection of target DNA in real samples.

Keyword: electrochemical DNA genosensor, reduced graphene oxide, cerium oxide nanoparticles, Apolipoprotein E, Fourier transform square wave voltammetry.

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Using 2-[(thiophene-2-yl-methylene)-amino]-isoindole-1,3-dione as a new selector element to develop the potentiometric iron (III) - selective electrode

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Abstract

A new Fe^{+3} ions selective electrode based on 2-[(thiophene-2-yl-methylene)-amino]-isoindole-1,3-dione was prepared to apply as an indicator electrode in the potentiometric cell. The best electrode response was observed in the slope (20.1±0.9 mV per decade) over a wide neodymium ion concentration range of 1.0×10^{-6} to 1.0×10^{-2} M with a detection limit of 8.5×10^{-7}M.

Keywords: PVC Membrane, Potentiometric Sensor, Ion Selective Electrode, Iron (III)

Introduction

Iron is a metal element in the first transition series with atomic number 26. It is such a mineral element which our body need for numerous functions including forming complexation with oxygen in hemoglobin and myoglobin which are two prevalent proteins to transport oxygen in the body [1]. In present work a new ion selective electrode based on 2-[(thiophene-2-yl-methylene)-amino]-isoindole-1,3-dione (Fig. 1) has been introduced for determination of iron ion by potentiometric method.

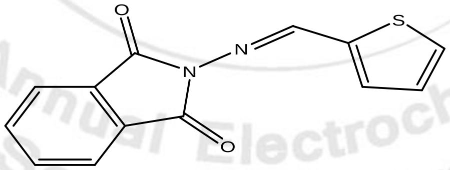

Fig. 1. 2-[(thiophene-2-yl-methylene)-amino]-isoindole-1, 3-dione.

Experimental

The sufficient amount of membrane ingredients were blended and dissolved in 3-4 mL of THF. The resulting mixture was evaporated slowly to obtain an oily concentrated blend. Then, the Pyrex tube (3–5 mm i.d.) was dipped into the membrane solution for about 5 s and kept at room temperature for at least 12 h. Finally, it was filled and conditioned in 1.0×10^{-3} M $FeCl_3$ solution.

Results and discussion

In consideration of the fact that the nature and amount of the membrane ingredients have consequential impress in the electrode responses, the effect of membrane components were investigated on the response of Fe^{+3} ion selective electrode [2]. According to Table1 the membrane composition no. 1 shows the best Nernstian behavior of electrode. The optimized Fe^{+3} electrode displays potentiometric behavior over working range from 1.0×10^{-6} to 1.0×10^{-2} M with the calibration curve slope equal 20.1±0.9 mV/decade of Fe^{3+} ions concentration (fig. 2.a). The detection limit of the electrode was obtained 8.5×10^{-7} M.

According to Fig. 2.b the designed electrode can work independently from pH Changes in the pH range of 1.8 – 4.0. In order to calculate the dynamic response time, the final steady-state potential was measured by applying the various concentrations of Fe^{+3} solutions. Conforming to Fig. 2.c, electrode responds was obtained about 9 s [3].

Table 1. Membrane compositions optimization

Electrode No.	Composition of membrane (wt.%)					Slope (mV/decade)	Dynamic linear range (M)
	PVC	NB	AP	NaTPB	Ionophore		
1	30	66	-	2	2	20.1±0.9	1.0×10^{-6}-1.0×10^{-2}
2	30	-	66	2	2	13.4±0.2	1.0×10^{-4}-1.0×10^{-2}
3	30	67	-	2	1	15.3±0.2	5.0×10^{-6}-1.0×10^{-2}
4	30	65	-	2	3	25.3±0.4	1.0×10^{-6}-1.0×10^{-2}
5	30	67	-	1	2	17.1±0.3	5.0×10^{-6}-1.0×10^{-2}
6	30	65	-	3	2	22.9±0.1	1.0×10^{-6}-1.0×10^{-2}

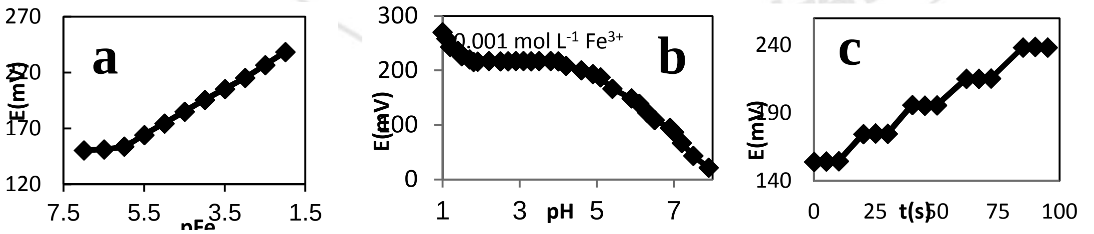

Fig. 2. a) Calibration curves; b) the effect of pH on the potential response; c) Dynamic response time

Conclusion

At present work, a new iron-selective PVC membrane electrode based on 2-[(thiophene-2-yl-methylene)-amino]-isoindole-1,3-dione as a carrier ion with Nernstian behavior was developed.

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Gadolinium (III) PVC-Membrane Sensor based on N'-(2-oxo-1, 2-di (pyridine-2-yl) ethylidene) furan-2-carbohydrazide

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Abstract

N'-(2-oxo-1, 2-di (pyridine-2-yl) ethylidene) furan-2-carbohydrazide was employed as a lipophilic ionophore to preparation of a novel Gd^{+3} ion selective electrode. The electrode demonstrated the Nernstian behavior in concentration range of 1.0×10^{-6} and 1.0×10^{-2} M with the slope of 19.5±0.3 mV/decade and the lower detection limit of 8.0×10^{-7} M.

Keywords: PVC Membrane, Potentiometric Sensor, Ion Selective Electrode, Gadolinium (III)

Introduction

Gadolinium is the eighth element in the lanthanide series with atomic number 64. Because of its wide application in various fields it is sincerely important to choose such a method which including good sensitivity and selectivity [1]. In present work a new ion selective electrode based on N'-(2-oxo-1, 2-di (pyridine-2-yl) ethylidene) furan-2-carbohydrazide (Fig. 1) has been introduced for determination of gadolinium ion by potentiometric method.

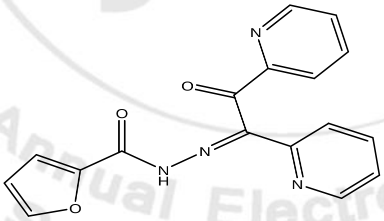

Fig. 1. N'-(2-oxo-1, 2-di (pyridine-2-yl) ethylidene) furan-2-carbohydrazide.

Experimental

The sufficient amount of membrane ingredients were blended and dissolved in 3-4 mL of THF. The resulting mixture was evaporated slowly to obtain an oily concentrated blend. Then, the Pyrex tube (3–5 mm i.d.) was dipped into the membrane solution for about 5 s and kept at room temperature for at least 12 h. Finally, it was filled and conditioned in 1.0×10^{-3} M $GdCl_3$ solution.

Results and discussion

In consideration of the fact that the nature and amount of the membrane ingredients have consequential impress in the electrode responses, the effect of membrane components were investigated on the response of Gd^{+3} ion selective electrode [2]. According to Table1 the membrane composition no. 5 shows the best Nernstian behavior of electrode. The optimized Gd^{+3} electrode displays potentiometric behavior over working range from 1.0×10^{-6} to 1.0×10^{-2} M with the calibration curve slope equal 19.5±0.3 mV/decade of Gd^{3+} ions concentration (fig. 2.a). The detection limit of the electrode was obtained 8.0×10^{-7} M.

According to Fig. 2.b the designed electrode can work independently from pH Changes in the pH range of 2.7 – 10.0. In order to calculate the dynamic response time, the final steady-state potential was measured by applying the various concentrations of Gd^{+3} solutions. Conforming to Fig. 2.c, electrode responds was obtained about 9 s [3].

Table 1. Membrane compositions optimization

Electrode No.	Composition of membrane (wt.%)					Slope (mV/decade)	Dynamic linear range (M)
	PVC	DBP	AP	NaTPB	Ionophore		
1	30	66	-	2	2	12.4±0.3	1.0×10^{-5}-1.0×10^{-2}
2	30	-	66	2	2	17.0±0.5	5.0×10^{-6}-1.0×10^{-2}
3	30	-	65	2	3	18.8±0.7	5.0×10^{-6}-1.0×10^{-2}
4	30		64	2	4	22.3±0.3	5.0×10^{-6}-1.0×10^{-2}
5	30	-	64	3	3	19.5±0.3	1.0×10^{-6}-1.0×10^{-2}
6	30	-	66	1	3	17.2±0.4	1.0×10^{-5}-1.0×10^{-2}

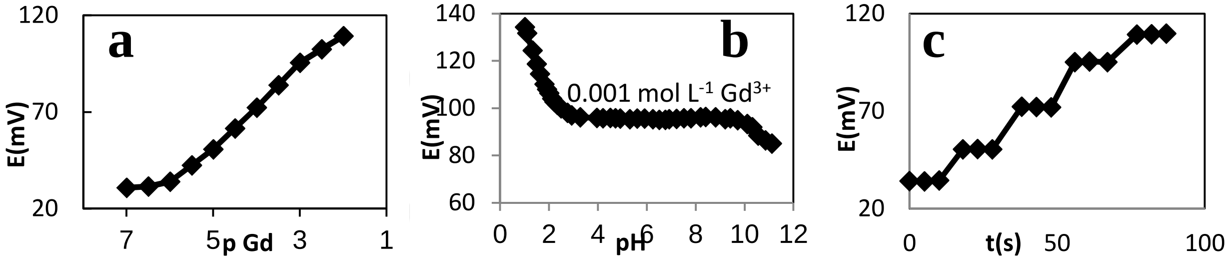

Fig. 2. a) Calibration curves; b) the effect of pH on the potential response; c) Dynamic response time

Conclusion

Due to tendency of N'-(2-oxo-1, 2-di (pyridine-2-yl) ethylidene) furan-2-carbohydrazide to form complexation with Gd^{+3} ions, it was used as a selective ionophore for Gd^{+3} ions to fabricate a new potentiometric ion selective electrode.

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Electrochemical Investigation of Releasing of dopamine from dopamine-loaded liposomes

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Abstract

The formulation of liposomes has remarkable effect on encapsulation property of them. In this study, dopamine-loaded liposomes were prepared through thin layer hydration method. The releasing behavior of loaded dopamine was investigated through immobilizing of biotin tagged liposomes on streptavidin coated micro plates. Two formulations were investigated with different molar ratios of lecithin: cholesterol. For 10:1 molar ratio of lecithin:cholesterola higher loading of dopamine and rapid releasing of dopamine was observed, in contrast for 1:1 molar ratio lower loading and higher stability was obtained.

Keywords: Dopamine-loaded liposomes, electrochemical study, Formulation, Biotin tagged liposomes

Introduction

Liposomes are nano to micro size artificial vesicles composed of lipid bilayers. Because of their capability for encapsulation of hydrophobic and hydrophilic compounds, they are introduced as novel candidates for signal amplification in nano biosensing [1]. The formulation of liposomes has remarkable effect on encapsulation and releasing properties of them that can be useful in their application as signal amplification agents [2]. In this study, the effect of lecithin:cholesterol molar ratio on dopamine loading and releasing was investigated using biotin tagged liposomes and streptavidin coated micro plates.

Experimental

Dopamine-loaded liposomes were prepared through thin layer hydration method [3]. In brief, 10:1:0.1 and 1:1:0.1 molar ratios of L-α-Lecithin, cholesterol and Biotin-X-DHPE (60 mg total) were dissolved in 8 ml methanol-chloroform mixed solvent (1:3 volume ratio), and then it was transferred to a round-bottom flask for thin layer preparation. Liposomes were formed by hydrating the prepared lipid film with 4 ml

PBS (1X) pH 4.5, containing 10 mg dopamine hydrochloride. After proper shaking, sonication by a probe sonicator was used for reducing the size of liposomes. For micro plate studies, 100 µl of liposomal solution was transferred to micro plate. Then, it was incubated for 15 min. After washing four times with 150 µl PBS (1X), 100 µl of methanol was added and it was vortexed. Then the solution was transferred to an electrochemical cell and the oxidation signal of DA was recorded using DPV technique with a GCE/MWCNTs electrode. Electrochemical experiments were performed using AUTOLAB PGSTAT 30 electrochemical analysis system and GPES 4.9 software package (Eco Chemie, The Netherlands). A three-electrode system was used that consists of Glassy Carbon Electrode (with 2 mm diameter) modified by oxidized Multi-Walled Carbon Nanotubes (GCE@MWCNTs), a saturated calomel electrode (SCE) as reference electrode and platinum wire as auxiliary electrode. The DPV studies was carried out by using a positive-going potential scan from 0 to 0.3 v in solution containing phosphate buffer 0.05 M with pH 7.0 and KCl 0.25 M.

Results and discussion

At first stage, the verification of biotinylation of liposomes and complete washing of unloaded DA form micro plates was done. For this means, the procedure was carried out for biotin tagged and biotin free liposomes. The results of DPVs for three cases have been shown in Fig. 1A. Effective washing of micro plates is necessary for obtaining reproducible results on the other hand the unloaded DA can cause false-positive results. As shown in Fig. 1A-a,b, no peaks of DA were observed for waste solution of 4th washing step and for biotin free liposomes. However, for biotin tagged liposomes, a very sharp peak was obtained (Fig. 1A-c). These observations were confirmed effective washing step and tagging of liposomes by biotin using Biotin-X-DHPE phospholipid. The results of releasing of DA from DA loaded liposomes have been shown in Fig.1-B,C. As it was seen for 10:1:0.1 formulation a higher loading of DA was obtained in compared to 1:1:0.1 formulation. However for 1:1:0.1 formulations a very low leakage of DA during time was observed. This observations show that if 10:1:0.1 formulation was used in biosensing, a higher signals can be obtained with freshly prepared liposomes. Although lower signal of DA was obtained for 1:1:0.1 formulations but it shows a very stable signal that can cause reproducible results. The difference of the behavior of these formulations can be related to cholesterol. Duo to hydrophobicity nature of cholesterol, it causes the bilayer of liposomes membrane be hydrophobic and thus lower loading and also lower releasing of hydrophilic DA was observed.

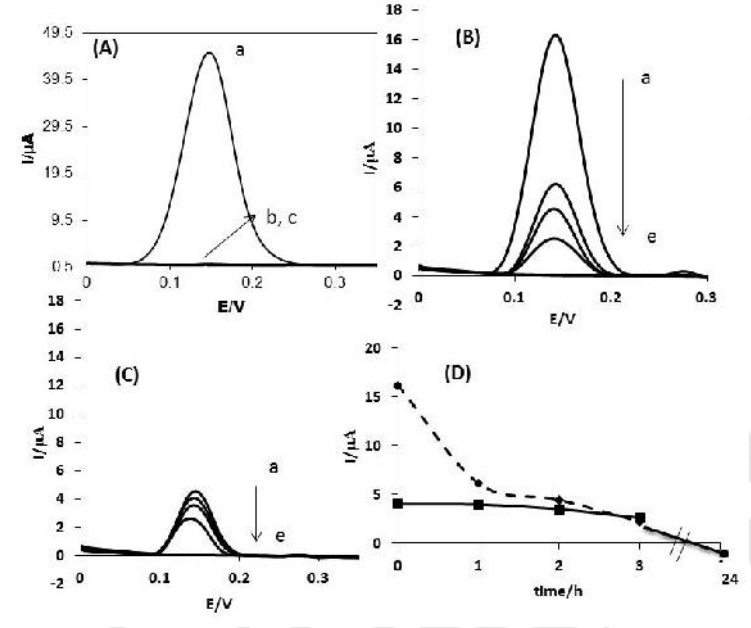

Fig. 1 DPVs of DA for (A) verification of biotinylation(a) and complete washing step and biotin free liposomes (b, c) and DPVs for releasing studies of (B) 10:1:0.1 and (C) 1:1:0.1 formulations, (D) comparison of two formulations.

Conclusions

The releasing behavior of two formulations of 10:1:0.1 and 1:1:0.1 of lecithin: cholesterol: Biotin-X-DHPE was investigated. The results show that the higher amount of cholesterol cause lower amount of loaded DA and a higher stable of liposomes.

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The recent advances in electrochemical biosensors for miRNA quantification

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Abstract

MicroRNAs (miRNAs) are short ribonucleic acid molecules (~19-23 nucleotides), that can play important roles in the regulation of diverse biological processes. Their expression level is tissue or disease-specific and aberrantly, expressed miRNAs have considerable potential to use as biomarkers. Moreover, they are perfectly stable in serum/plasma and also their sampling would be easy and non-invasive. Microarrays, Northern Blotting, Reverse Transcription Polymerase Chain Reaction (RT-PCR), In Situ Hybridization (ISH) are Major conventional methods for quantification of miRNA. In addition to them, the different types of sensors have been developed and commercialized so far, that majority of them are electrochemical. Electrochemical biosensors combining the selective biochemical recognition with the high sensitivity of electrochemical detection. They are inexpensive, capable of being used by semi-skilled operators. Also, their measurement is rapid and need a small volume of sample. This review embraces new approaches used in the electrochemical biosensors platform for miRNA quantification. Different types of electrochemical labels and signal amplification methods have been applied in electrochemical biosensors so far, since the first biosensor have developed in this case at 2007 (5). These innovations are included using biotin-streptavidin system (6-9), application of enzymes (10-12), or using new components as signal transduction such as protein 19 (p19) (13); conjugated copolymer (14), electroactive ferroceneboronic acid (FBA) (15). The

table 1 is representing brief review of some specifications of selected electrochemical miRNA biosensors which have been developed so far.

***Keywords**: miRNA, electrochemical, Nanobiosensor*

Table 1. Specification of some electrochemical biosensors for miRNA detection

Target miRNA	**Electrochemical Method**	**Linear Range**	**Detection Limit**	**Ref**
let-7b	Amp	0.50-400 pM	0.20 pM	(5)
miR-222	DPV	0.01-1 nM	12 pM	(6)
let-7a	CV	20 pM-100 nM	3.4 pM	(7)
miR-16,-15a,-660	DPV	1.3 µM-5.5 µM	2.1 µM	(8)
miR-21	DPV	NA	100 nM	(9)
let-7b	EIS	2.0 fM-2.0 pM	1.0 fM	(10)
miR-720,-1248, let-7b,	Amp	20 fM-10 pM	10 fM	(11)
miR-21,-126	DPV	20 fM-50 pM	5.36 fM	(12)
miR-21	DPV	NA	160 nM	(13)
miR-141,-29b-1,-103	SWV	0.5 pM-0.1 nM	650 fM	(14)
let 7a	DPV	5 nM-5 µM	1 nM	(15)

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Development of anew electrochemical aptasensor for Sensing of epirubicin

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Abstract

Anthracycline antibiotics are the most effective anticancer treatments ever developed, used in cancer chemotherapy (1). Among them, epirubicin (EPI) has been widely used to treat variety of cancers but clinical utilization of EPI is confined, because of dose-related cardiotoxicity and bone marrow suppression (2, 3). Therefore, it is highly desirable, to promote a highly sensitive and selective method for detection of EPI for clinical diagnosis and attaining the best possible therapeutic effect.

Aptamers are artificial single-stranded oligonucleotides that selected through SELEX (4). Upon binding of aptamer with high affinity to targets, tertiary structures were formed. In this manuscript, a novel label free electrochemical aptasensor was fabricated based on the magnetic Nanocomposite for detection of EPI. The immobilization of the magnetic Nanocomposite on the SPE increased the surface area and conductibility of the aptasensor, which amplified the electrochemical signals. Interaction of EPI with the aptamer and the properties of the fabricated aptasensor were examined with cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS).

Keywords: *Aptamer, Epirubicin, Electrodeposited gold nanoparticles, Carbon Screen-printed electrode*

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Development of a new aptasensor based on functionalized SBA-15 modified screen-printed electrode for determination of chloramphenicol

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Abstract

Aptamers are single-stranded oligonucleic acids, which are obtained by an in vitro selection process called systematic evolution of ligands by exponential enrichment (SELEX). Based on their three dimensional structure (3D), aptamers can specifically bind to a variety of targets, such as enzymes, antibodies and drugs (1). In this project, aptamer is used as a molecular recognition element. Hemin also acts as an electrochemical indicator (2, 3). Controlling the immobilization of the aptamer on the electrode surface is an important step in designing this aptasensor. For this purpose, a SPE was modified with the functionalized SBA-15. Then, the electrodeposition of the Au nanoparticles (AuNPs) was performed to transfer these particles on the functionalized SBA-15 surface. This step connects the thiolated aptamer on the electrode by Au-S bonds. In the absence of Cap, hemin bound to the aptamer and produced a weak differential pulse voltammetric (DPV) signal. The presence of Cap, led to stabilization of the folded aptamer, which generated an amplified DPV signal. The experimental parameters such as aptamer concentration, aptamer immobilization time, incubation time and pH were optimized for the analysis of the CAP. Under optimal conditions, two linear ranges were obtained from 0.03 to 0.15 µM and 0.5– 7.0 µM, respectively. The detection limit was 4.0 nM. This constructed biosensor had a good selectivity against the other non-target drugs. Thus the sensor could provide a promising plan for the fabrication of aptasensor.

Keywords: Hemin, Chloramphenicol, Aptasensor, Screen-printed graphite electrode

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Study of Electrochemical Deposition of Platinum Nanoelectrocatalyst for Glucose Oxidation Reaction in Biofuel Cell

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Abstract

Biofuel cells (BFCs) are special kind of fuel cells, employing enzymes as the biocatalyst for the conversion of chemical energy into electrical energy [1]. Although, BFCs have been known for long time [2], they catch enormous attention only in the recent years and are expected to be one of the promising next generation green energy devices. BFCs have numerous applications in the fields such as implantable devices [3], waste water treatment [4], drug delivery [5] and biosensors [6]. Besides, the fuels for BFCs are from renewable energy sources usually sugars or organic acids and most often glucose [7]. Glucose is produced in abundance from both naturally occurring plants and industrial processes. The energy density of glucose on complete oxidation to CO_2 via 24-electron transfer is 2.87×10^6 J mol^{-1} [8]. Glucose is nontoxic, non-flammable, odorless and renewable. These properties make glucose an attractive fuel for various applications, particularly for portable electronic devices [9]. In this research, cyclic voltammetry (CV) method (voltage range: -0.2 to 1.2 V versus Ag/AgCl and 100 mVs^{-1} scan rate) was used for platinum electrodeposition on carbon rod and solution included of H_3PO_4 (0.5 M) and H_2PtCl_6 (0.5mM). Scan numbers in CV method were varied 10 up to 60 at this work.

For evaluating prepared platinum electrocatalyst for glucose oxidation reaction, CV and Linear sweep voltammetry (Lsv) methods were used in glucose solution (0.5 M, KOH (0.5 M)) at 25^{o}C (Fig. 1&2). As it was shown, the scan number of CV method in preparation platinum electrocatalyst processes affects on efficiency of fabricated electrodes for glucose oxidation reaction. According our results the 30 scan number in CV method is optimized condition for preparation platinum electrocatalyst. Fabricated electrode has good activity and power density for glucose oxidation reaction in biofuel Cell.

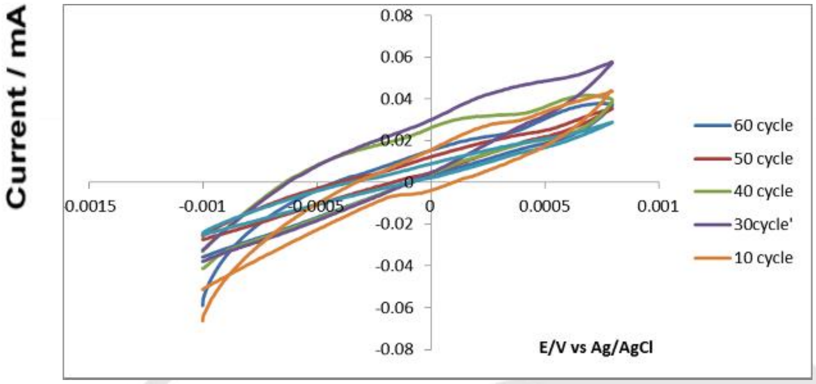

Figure 1 CV diagram of glucose oxidation in alkali solution at 50mVs^{-1} scan rate

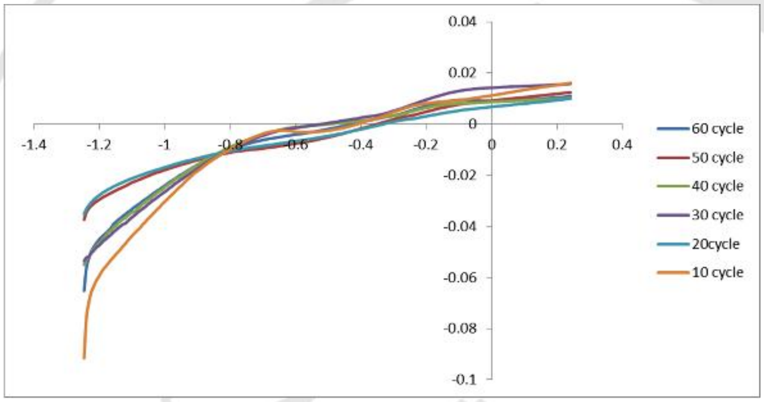

Figure 2 LSV diagram of glucose oxidation in alkali solution

***Keywords*:** Direct glucose fuel cell, Bio fuel cell, Nano electro catalyst, Platinum, Electro oxidation reaction, Electrodeposition, Cyclic voltammetry

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Hydroquinone diphosphate/Ag^+ as an enzymatic substrate for alkaline phosphatase catalyzed silver deposition

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Abstract

Signal amplification by enzyme labels such as alkaline phosphatase (AP) used in affinity assays (immuno or DNA based assays) is ausual strategy to get high sensitive detection methodologies. An advantageous combination of an enzyme substrate Hydroquinone diphosphate (HQDP) with silver ions (Ag^+) in solution is presented in this work as a new enzymatic substrate for AP. This enzyme catalyzes the dephosphorylation of HQDP producing hydroquinone, a reducing agent for silver ions present in solution. Thus by mixing AP, HQDP and Ag^+, metallic silver is deposited where the enzymatic reaction takes place. A qualitative assay is presented in nitrocellulose membranes to demonstrate this mechanism. The affinity reaction between biotin and streptavidinlabelled with AP is also followed by the electrochemical detection of silver deposited on the surface of Screen Printed Carbon Electrodes. Anodic stripping voltammetry of enzymatically deposited silver is showed as a sensitive detection technique for biosensing applications.

A selective and regenerative electhrochemical biosensor based aptamers for determination of homocysteine in biological samples

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Abstract

Homocysteine (HCys) is an amino acid with a free thiol (sulphydryl) group [1]. HCys is not found in the diet but is a mediator formed in the metabolism of methionine to cysteine [2]. In humans, normal levels of HCys in plasma are between 5 and 16 µM [3]. In higher concentrations of HCys are related to different diseases and its cause interesting in determination of HCys [4]. An electrochemical aptasensor was adopted as an analytical platform for the selective and sensitive HCys detection using the aptamer against HCys as the recognition probe in biological samples in presence of interferences such as cysteine and methionine. The HCys aptamer used in this study is a 66-mer truncated variant of DNA aptamer with binding constant of 600 nM for HCys [5]. The conditions for the immobilization of the aptamer and for binding of HCys have been here optimized. The assay protocol of the biosensor is shown in Fig. 1. Under optimized experimental conditions, the assay was linear in the ranges from 0.2 to 10 µM for HCys Determination. The detection limit was 0.01 µM using $3s_b/m$. Repeatability of the aptasensor was estimated at 1.0 µM of HCys resulted in RSD of 5.2%. The results showed this proposal is simple, regenerative and cost effective and also has a good selectivity and sensitivity for electrochemical detection of HCys in biological samples.

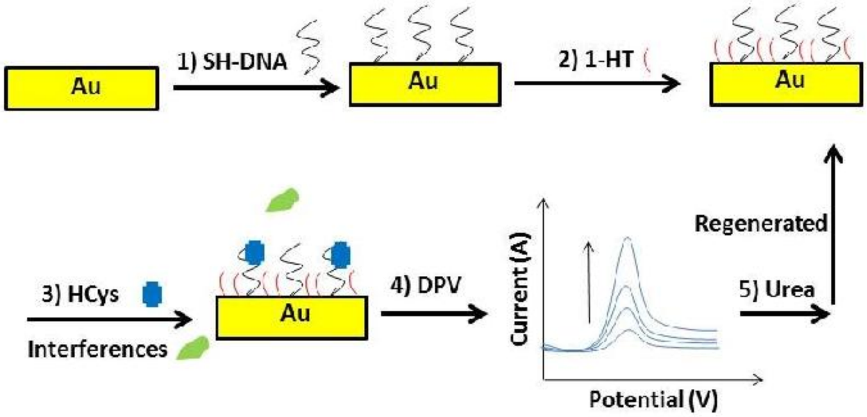

Fig. 1. Schematic routine of the aptamer electrochemical biosensor fabrication and its HCys detection.

Keywords: *Homocysteine*, *Aptamer*, *Aptasensor*, *Electrochemical Biosensor*, *Modify Electrode*,

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Detection of dopamine with a modified-graphene oxide nano sheets paste electrode using voltammetry

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Abstract

Dopamine (DA) is considered as one of the key neurotransmitter and plays vital role in our central nervous system [1]. The high concentrations of DA leads to severe disorders like Parkinson’s disease. Hence, the accurate determination of DA in real samples is of great importance to the readers of analytical electrochemistry [2]. After developing the carbon paste electrode (CPE), it has been used as an appropriate bed for electro-oxidation of organic substances. CPEs are suitable conductive matrixes for preparing chemically modified electrodes (CMEs). The CMEs has good electrocatalytic activity, sensitivity, and selectivity; it has also a low detection limit compared to traditional carbon paste electrodes [3]. Over recent years, with the development of nanoscience and nanotechnology, there have been various attempts to applied novel nanomaterials in creating chemically modified electrodes [4]. In the present work, 2-(4-Oxo-3-phenyl-3,4-dihydroquinazolinyl)-*N'*-phenyl-hydrazinecarbothioamide was synthesized and used to construct a modified-graphene oxide nano sheets paste electrode. The electro-oxidation of dopamine at the surface of the modified electrode was studied using cyclic voltammetry (CV), chronoamperometry (CHA), and square wave voltammetry (SWV). Under the optimized conditions, the square wave voltammetric peak current of dopamine increased linearly with dopamine concentration in the ranges of 5.0×10^{-7} to 4.0×10^{-4} M and detection limit of 9.5×10^{-8} M was obtained for dopamine. Finally this modified electrode was used for determination of dopamine in some real samples.

Keywords*: *Dopamine, Carbon paste electrode, Graphene oxide nano sheets, Cyclic voltammetry.

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Fabrication of a modified carbon paste electrode for enhanced electrocatalytic activity toward the detection of toxic hydrazine in water samples

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Abstract

Hydrazine as an important example of NH_2 containing compounds is a strong reducing agent widely used in various field, including fuel cells, industrial, agricultural, pharmacological, military and aerospace applications [1]. Of note, It is highly toxic and easily absorbed by oral, breathing routes of exposure or even introduced to the skin, which mostly affect the lungs, kidney, liver and central nervous system of living organisms. Moreover, It may cause liver and kidney damages, also irreversible deterioration of nervous system when it absorbs through skin. Accordingly, a sensitive and fast determination in low concentrations in various media is becoming more and more important. Electrochemical methods appear to be very promising since they ensure reasonably good analytical performance characteristics with essentially no need for expensive and complicated instrumentation [2]. Carbon paste is one of the most popular materials to prepare solid-state electrodes, with high applicability in electrochemistry research. The ease and speed of preparation and obtaining a new reproducible surface, low residual current, porous surface and low cost are advantages of carbon paste electrodes (CPEs) over all other solid electrodes [3]. Recently, the application of the carbon paste electrodes modified (MCPEs) with various materials exhibits considerable improvements in electrochemical behavior of many important compounds. As is well-known, nanostructure materials have been used to fabricate a new type of chemically modified electrodes (CMEs) with rapid electron transfer kinetic [4]. In this work, a ferrocene-derivative compound, 2,7-bis (ferrocenyl ethynyl) fluoren-9-one (2,7-BFE), was synthesized and used to construct a modified-graphene oxide nano-sheets paste electrode. The electro-oxidation of hydrazine at the surface of the modified electrode was studied using electrochemical approaches. Under the optimized conditions, the square wave voltammetric

peak current of hydrazine increased linearly with hydrazine concentrations in the range of 2.2×10^{-7} to 3.0×10^{-4} M and a detection limit of 9.8×10^{-8} M was obtained for hydrazine. Finally this modified electrode was used for determination of hydrazine in some water samples.

Keywords: *Hydrazine, Voltammetry, Carbon paste electrodes, Graphene nano-sheets*

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Application of graphene oxide nanosheets to construct a modified carbon paste electrode as a hydroxylamine electrochemical sensor

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Abstract

Hydroxylamine (HA), a derivative of ammonium belongs to an important class of reducing agents, which are commonly used for synthesis of pharmaceutical intermediates and final drug substances. However, it is a well-known mutagen, which induces highly specific mutations with the nucleic acid cytosine. Modest levels of hydroxylamine can be toxic and harmful to human, animals, and even plants [1]. As an electroactive compound, the hydroxylamine has also attracted much interest of electrochemists. But, it is impossible to measure the concentrations of this compound using bare electrodes [2]. One promising method is the use of chemically modified electrodes (CMEs) containing particularly selected redox active materials (homogenous catalysts) immobilized on conventional electrode materials. Among conventional electrodes carbon paste electrode (CPE) is one of the most conductive matrixes for preparing CME. Recently, a wide variety of compounds have been used as the electron transfer mediators for the modification of electrode surfaces with various approaches [3]. In this work a ferrocene-derivative compound, 2,7-bis (ferrocenyl ethynyl) fluoren-9-one (2,7-BFE), was synthesized and used to construct a modified graphene paste electrode. The electrooxidation of hydroxylamine at the surface of the modified electrode was studied using cyclic voltammetry (CV), chronoamperometry (CHA), and square wave voltammetry (SWV). Under the optimized conditions, the square wave voltammetric peak current of hydroxylamine increased linearly with hydroxylamine concentration in the range of 2.0×10^{-7} to 2.5×10^{-4} M and detection limit of 9.0×10^{-8} M was obtained for hydroxylamine. The Tafel slope of 117.0 mV obtained in this case agrees well with the involvement of one electron in the rate determining step of the electrode

process, assuming a charge transfer coefficient of α=0.49. Finally, this modified electrode was used for determination of hydroxylamine in some water samples.

Keywords*: *Graphene oxide nanosheets, Hydroxylamine, Voltammetry, Modified electrode.

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Evaluation of electrocoagulation process for the removal of reactive red 196 dye from textile industry Wastewater

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Abstract

the current study investigated the effect of electrocoagulation treatment on reactive red 196 removals from textile industry wastewater. Since reactive dyes residues in aqueous environments cause skin allergies, poisoning, cancer, mutation, and etc. Therefore, efficient and effective treatment methods against reactive dyes should be applied to overcome these problems [1]. The experiment conducted in a glass reactor with a working volume of 200 mL that equipped with 2 iron electrodes. The effects of operating parameters such as pH solution, initial dye concentration, time of reaction, voltage and inter electrode distance on the color removal efficiency and electrical energy consumption were investigated in the optimum operational condition electrocoagulation, is able to remove color as high as 98. 6% by iron electrodes in pH 8.5 and initial dye concentration 180 mg/l and 10 min at 12.3 V and 1.5 cm inter electrode distance. Under this condition energy consumption was 10.66 KWh/m3of treated wastewater. Increase in the inter electrode distance and initial dye concentration, lead to the decrease in efficiency of dye removal [2]. Figure 1 present the effect of the significant interactions between dye concentration and electrode distance on the dye removal (%) while as the voltage and time of reaction increased, energy consumption, electrode consumption, final pH and color removal, increased too [3]. The results indicate that the electro coagulation is a promising method for the removal Reactive red 196 in textile industry wastewater.

Keywords: *Electrocoagulation, iron electrode, removal, Reactive red 196, dye.*

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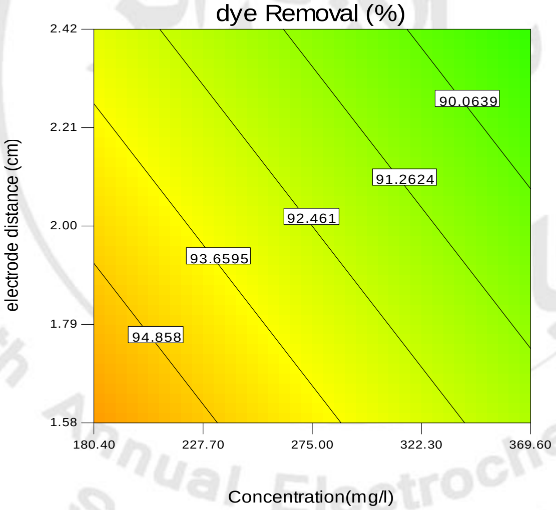

Figure1. Interactions between dye concentration and electrode distance on the dye removal (%)

Optimization of Electro-Fenton Process Efficiency for Removal of Antibiotic Tetracycline from Hospital Wastewater

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Abstract

In recent years, the uncontrolled and continuous entrance of hospital and pharmaceutical wastewaters to aquatic environments has led to pharmaceutical agent's arrival in these environments. Antibiotics are contaminants in the aquatic environment because they have adverse effects on the aquatic life and humans [1]. In this study, removal of tetracycline has been studied by electro-Fenton process using iron electrode. The effect of the important operational variables including pH solution, tetracycline antibiotic concentration, electrical conductivity, current density, H_2O_2 dosage and time of reaction were investigated in order to determine the process efficiency [2]. The results indicated that the optimum conditions for the removal of tetracycline were solution pH 9.5, tetracycline concentration 50 mg /l , Conductivity 3 mS/cm , current density 75 A/m^2, and H_2O_2 dosage of 10 mM/min . In this condition removal tetracycline and energy consumption was found 96.1 and 22.5 kWh m^3 respectively after 17 min reaction, showed in figure 1. According to the obtained results, electro-Fenton process was useful in treatment and removal of antibiotic from hospital wastewater, although economically should be investigated compared to other methods.

Keywords: *electro-Fenton, antibiotic, tetracycline, removal, hospital waste water*

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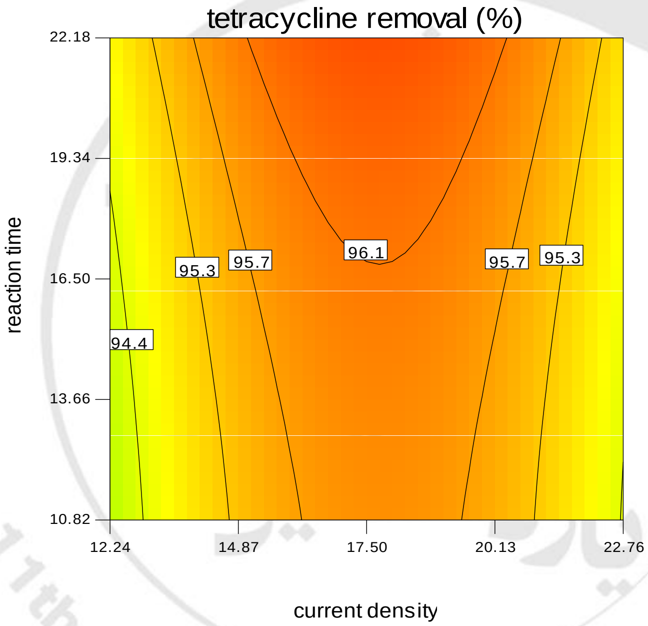

Figure 1: Interactions between current density and reaction time on the tetracycline removal (%).

Hydroquinone analysis in liposome carrier using a voltammetric sensor

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Abstract

Hydroquinone (HQ) has a variety of uses principally associated with its action as a reducing agent that is soluble in water. It is a major component in most black and white photographic developers for film and paper where, with the compound Metol, it reduces silver halides to elemental silver. There are various other uses associated with its reducing power. As a polymerization inhibitor, hydroquinone prevents polymerization of acrylic acid, methyl methacrylate, cyanoacrylate, and other monomers that are susceptible to radical-initiated polymerization. This application exploits the antioxidant properties of hydroquinone [1].

An ionic liquid-modified NiO nanoparticles paste electrode has been fabricated as a voltammetric sensor. . This electrode showed enhanced electrochemical response and strong analytical activity towards the direct electrochemical oxidation of HQ. The electron transfer coefficient, α, and diffusion coefficient of HQ at the modified electrode were calculated. Under optimal conditions at pH 7.0, the anodic peak currents increased linearly with the concentration of HQ in the range of 50.0–400 μM with a detection limit of 30.0 μM (3σ). The interferences of foreign substances were investigated. Cyclic voltammetry was used to check the applicability of the proposed sensor to the determination of HQ in real samples with satisfactory results. Figure 1 shows catalytic effect of recommend procedure at an optimum condition.

Keywords: *Hydroquinone, NiO nanoparticles, Ionic liquids, Voltammetric analysis*

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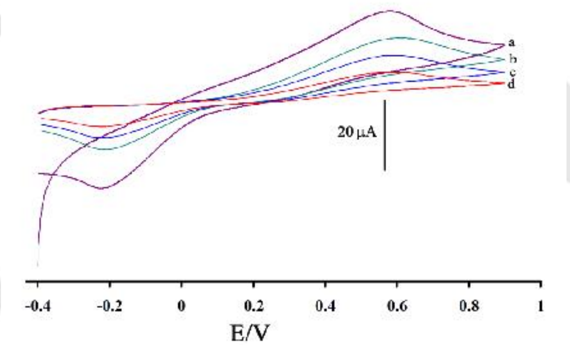

Figure 1: Cycic voltammograms of a) NiO/NPs/ILCPE, b) CP/ILE, c) NiO/NPs/CPE and d) CPE in presence of 500 µm HQ at a pH 7.0, respectively.

Determination of Losartan in Real Samples Using Liquid Membrance Graphite Electrode Based on Molecularly Imprinted Polymer

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Abstract

A Molecularly Imprinted Polymer (MIP) is a polymer that has been processed using the molecular imprinting technique which leaves cavities in polymer matrix with affinity to a chosen "template" molecule. Fast and cost-effective molecularly imprinted polymer technique has applications in many fields of chemistry, biology and engineering, particularly as an affinity material for sensors, detection of chemical and byproduct removal in chemical reaction [1]. Losartan is a powerful and selective antihypertensive administered orally, blocking the interaction between angiotensin and the receptors with the advantage of not affecting bradicinina [2]. Several analytical methods have been applied to the analysis of losartan potassium in biological fluids, such as using high performance liquid chromatography technique (HPLC), thin layer chromatography (HPTLC), capillary electrochromatography (CEC), capillary electrophoresis (CE) and spectrophotometry [3]. Some of these methods are not simple; others are time consuming or involve procedures with rigorous control of the experimental conditions or suffer interference from the tablet matrix and consequently are not suitable for routine analysis. In this work, a potentiometric sensor was fabricated based on molecularly imprinted polymer for the recognition and determination of losartan. The best response was obtained with the membrance having 30 mg PVC, 20 mg MIP and 50 mg dibutyl phethalate. In optimal condition electrode has good behavior Nernst slope in a wide concentration rang 1.0×10^{-8} to 1.0×10^{-2} mol L^{-1} with a lower detection limit. The electrode was successful for measuring losartan potassium in biological samples such as urine and plasma. The sensor show high selectivity and a sensitive response to the template in aqueous system. The electrode has high performance, high sensitivity and good long term stability (more than 5 months). The method was satisfactory and used to the cetirizine assay in tablets and biological fluids.

Keywords: *Molecularly Polymer, Potentiometric sensor, Losartan potassium, Biological samples*

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Electrodeposited Gold Nanoparticles on Glassy carbon Electrode: Correlation between Electrodeposition Time and the Amount of Immobilized Gold Nanoparticle

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Abstract

The glassy carbon electrode, GCE, is widely used as working electrode in different biosensors. Up to now, various methods have been developed to improve the biosensing properties of GCE. Generally, improving of electrical conductivity of this electrode is a major aim of these methods. Recently, immobilization of gold nanoparticls on the surface of glassy carbon electrode using electrodeposition technique is widely utilized for this intention. However, some aspects, particularly optimum condition of this technique are still unclear. So, the effect of eletrodepostion time on the amount of immobilized gold nanoparticle at the surface of glassy carbon electrode, is investigated and reported in this article.

Chloroauric acid ($HAuCl_4$, $3H_2O$) and potassium ferricyanide ($K_4Fe(CN)_6$) purchased from Sigma – Aldrich. $NaNo_3$, potassium phosphate (KH_2PO_4) and dipotassium phosphate (K_2HPO_4) obtained from Merck Ltd. Alumina powder with 1 µM and 0.3 µM diameter obtained from Methrohm AG, Swiss. All aqueous solutions were prepared in double distilled water with a resistance of 18.0 MΩ cm^{-1}. Double distilled, deionized water was prepared using ion exchange system (Millipore, France). Glassy carbon electrode was carefully polished by 1 µM and 0.3 µm alumina powder, respectively. Then, the electrode was rinsed with ethanol %96 using an ultrasonic cleaner (Elma 530H). At the next stage, gold nanoparticles were electrodeposited in deaerated $NaNo_3$ solution containing 0.25 mM chloroauric acid. For electrodeposition, chronoamperometery method using -0.3 V was utilized at different times (0, 10, 120, 240, 420 and 600s) at 10 ºC. In order to evaluation of electrode responses at each electrodeposition time, the voltammograms of modified glassy carbon were recorded in 65 mM ferrocyanide potassium (pH 7) by cyclic voltametry experiments (DropSens 400µ, Spain). Additionally, to evaluate the amount of gold nanoparticls immobilization at the surface of glassy carbon electrode, scanning electron microscopy images were obtained (VEGA3 TESCAN, Czech Republic) at 10s voltage exertion during eletrodepostion process.

Figure 1 show the morphology and distribution of gold nanoparticles on the surface of glassy carbon electrode when 10s was selected for voltage exertion during electrodeposition. The SEM image analysis in which automatically performed by an electron microscope instrument indicated that only 7% of glassy carbon electrode surface was covered by gold nanoparticle with the sizes between 35 to 45 nm. At the next stage, cyclic voltametry experiments carried out. The cathodic (A) and anodic (B) peak currents obtained from cyclic voltammograms considered as the responses of modified glassy carbon electrode and presented in figure 2 (curves A and B). As shown in this figure both peak currents increased with increasing the time of voltage insertion during electrodeposition. Also, according to this figure the response of the modified electrode reached to its maximal amount when 240s was chosen for voltage exertion during electrodeposition process. As a result, 240s can be chosen as an optimum time for electrodeposition of gold nanoparticles on the surface of glassy carbon electrode. This study showed that the further time of voltage exertion has no positive effect and it seems that the surface of the electrode is completely covered by gold nanoparticles during 240s of voltage exertion.

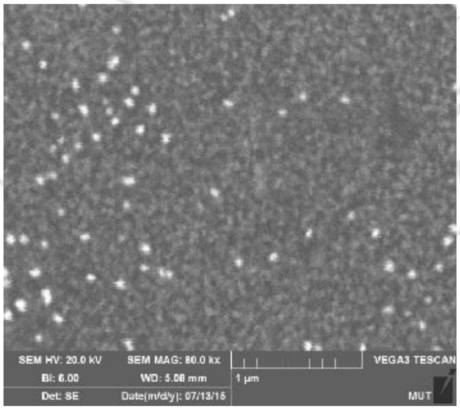

Figure 1. Gold nanoparticls distribution on the surface of glassy carbon electrode 10s after electrodepositon. The image is taken by electron scanning microscopy.

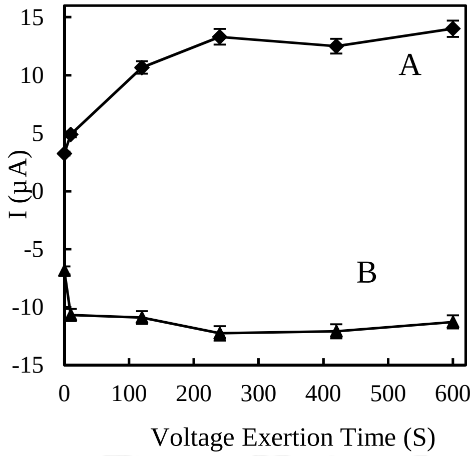

Figure 9. The cathodic (A) and anodic (B) peak currents as responses of modified glassy carbon electrode at different times of electrodeposition.

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Voltammetric determination of bisphenol using a nanostructure based electrochemical sensor

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Abstract

Bisphenol A, is a chemical intermediate widely used in the synthesis of polycarbonate and epoxy resins, unsaturated polyester-styrene resins and flame-retardants (Lee et al. 2015). Bisphenol A is mainly released into the environment in wastewater from plastics-producing industrial plants and landfill sites [1]. Graphene, a new class of promising carbon material, is of great interest. Because of these properties, a wide spread range of novel materials and applications have already been generated in various fields, including biomedical sensors, nanoelectronic devices, transparent electrodes, photodetectors, hydrogen storage, solarcells, fuel cells, electrical batteries and supercapacitors [2]. In the present work, a novel carbon paste electrode modified with graphene oxide nanosheets and an ionic liquid was fabricated. The electrochemical study of the modified electrode, as well as its efficiency for voltammetric oxidation of bisphenol A, is described. Square wave voltammetry exhibits a linear dynamic range from 9.0×10^{-8} to 2.5×10^{-4}M and a detection limit of 55.0 nM for bisphenol A. Finally, this new sensor was used for determination of bisphenol A in water samples using standard addition method.

Keywords: Bisphenol A, Graphene oxide nano sheets,Carbon paste electrode, Ionic liquids

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Electrocatalytic determination of hydrazine and phenol using a carbon paste electrode modified with ionic liquids and nano composites

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Abstract

Hydrazine is highly toxic and easily absorbed by oral, breathing routes of exposure or even introduced to the skin, which mostly affect the lungs, kidney, liver and central nervous system of living organisms. Another important kind of pollutant is phenol, also known as carbolic acid, and widely exists in water, canned food, atmosphere and chemical productions [1].

As is well-known, nanostructure materials can decrease the overpotential of the redox process of electroactive species due to their large surface to volume ratio. Nanocomposite materials as a subclass of nanostructure materials have been used to fabricate a new type of chemically modified electrodes (CMEs) with rapid electron transfer kinetic [2].

In this work, a carbon paste electrode was modified with 2-(4-Oxo-3-phenyl-3,4-dihydroquinazolinyl)-*N′*-phenyl-hydrazinecarbothioamide, magnetic core–shell $Fe_3O_4@SiO_2$/MWCNT nanocomposite and ionic liquid (n-hexyl-3-methylimidazolium hexafluoro phosphate). Square wave voltammetry (SWV) exhibits a linear dynamic range from 7.0×10^{-8} to 5.0×10^{-4} M and a detection limit of 40.0 nM for hydrazine. The prepared modified electrode exhibits a very good resolution between the voltammetric peaks of hydrazine and phenol that makes it suitable for the detection of hydrazine in the presence of phenol in real samples.

Keywords: Hydrazine, Phenol, $Fe_3O_4@SiO_2$/MWCNT nanocomposite, Ionic liquids, Modified electrodes

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Enhanced performance of a duel chambered microbial fuel cell with ssDNA/CPE as bio-cathode

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Abstract

With the rapid development of economy and the fast growing of the world's population, demands for energy are increasing markedly. On the other hand, industrial contaminants and domestic wastewater are also constantly increasing. The simultaneous production of energy and wastewater treatment can provide economic and environmental benefits by using microbial fuel cells (MFCs) [1]. Wastewaters are renewable energy resources in the form of biodegradable organic matters. It means that renewable energy, which reduces greenhouse gas emissions can be extracted from wastewater [2]. MFCs are bio-electrochemical systems that convert the chemical energy of organic waste material to electrical energy by using bacteria as biocatalysts [3]. A typical MFC is composed of two compartments, anodic and cathodic chambers separated by proton/cation exchange membrane. Generally, the bacteria at the anode chamber decompose organic material to proton and electron anaerobically. The electrons are transferred from the anode electrode to the cathode electrode through an external circuit. The protons migrate to cathode through proton exchange membrane separator. Electrons in the cathodic chamber combine with protons and oxygen to produce water (Fig. 1) [4]. Many factors influence on the electrochemical performance of a MFC system. Among all factors, the cathode as a significant performance-limiting component and the reduction kinetics in MFCs has a great effect on the electricity generation characteristics [5]. At the present study, low-cost and high performance MFC was developed by using DNA as a final electron acceptor in the cathodic chamber. Single-stranded DNA was employed for the modification of carbon paste electrode (ssDNA/CPE) as bio-cathode in the MFC to enhance its performance. When the bare CPE was used as cathode,

the MFC got the power density of 3.01 mW m^{-2} at a current density of 28.70 mA m^{-2}, whereas if the ssDNA/CPE was used as bio-cathode, the maximum power density was increased to 501.87 mW m^{-2} at a current density of 1190.77 mA m^{-2}, indicating ssDNA/CPE provided high catalytic activity for reduction reaction in cathodic chamber. While the internal resistance in water without aeration was accounted 352.04 Ω and 42.51 Ω for the bare CPE and ssDNA/CPE as cathode electrodes, respectively. Therefore, use of ssDNA/CPE as a bio-cathode markedly improved the performance of a MFC system compared with a MFC using CPE. Finally, the effect of DNA sequence composed of pure bases involved only adenine, cytosine, thymine and guanine sequences was examined in MFC output.

Keywords: Microbial fuel cell, Wastewater treatment, DNA/CPE, Bio-cathode.

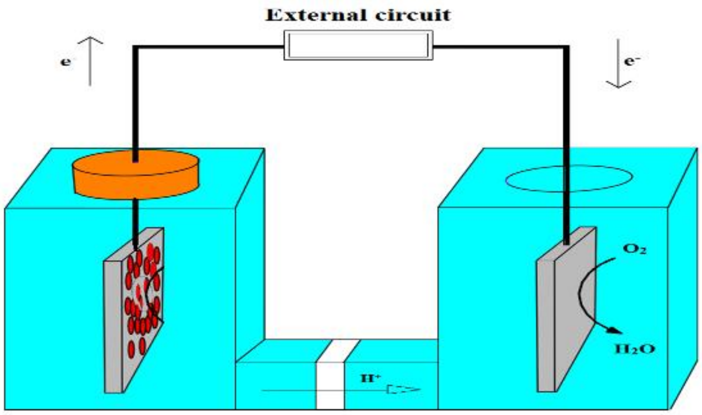

Fig. 1. Schematic of a duel chambered MFC.

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Simultaneous determination of hydrochlorothiazide and propranolol in pharmaceuticals using a carbon nanotube modified glassy carbon electrode

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Abstract

Hydrochlorothiazide (HCTZ) and propranolol hydrochloride (PRO) combination is used to treat hypertension. HCTZ/PRO is a non-selective β-adrenergic receptor (β-blocker) and thiazide diuretic combination. Hence, the determinations of these drugs in the pharmaceutical and clinical samples have drawn tremendous attention and a reliable and sensitive detection method is highly expected [1]. Among various analytical methods, modern electrochemical techniques have attracted considerable interest due to the good simplicity, sensitivity, selectivity, stability and often do not require any pre-treatments or pre-separation [2]. Glassy carbon electrodes (GCEs) are very versatile as electrode material for trace level determination of organic molecules because they provide high sensitivity, negligible porosity, and good mechanical rigidity. Modifier such as polymers, nanoparticles, carbon-ceramic, carbon ionic liquid and carbon nanotubes could enhance the transfer rate of the electron and reduce the over-potential for the oxidation of substrates [3]. Multi-wall carbon nanotube (MWCNT) is one kind of the most extensively used materials to modify electrodes due to a huge, cylindrical surface area and graphene sheet MWCNT have extraordinary properties, such as high electrical and thermal conductivity, chemical stability, high elasticity, high tensile strength and in some instances, metallic conductivity and catalyst support [4]. In the present work, a glassy carbon electrode modified with a novel 1-benzyl-4-ferrocenyl-1H-[1,2,3]-triazole (BFT) and carbon nanotubes have been applied to the electrocatalytic oxidation of hydrochlorothiazide (HCT) which reduced the overpotential by about 870 mV with obviously increase the current response. Due to its strong electrocatalytic activity towards hydrochlorothiazide, the modified electrode can resolve the overlapped voltammetric waves of hydrochlorothiazide and propranolol into two well-defined voltammetric peaks with peak-to-peak separation in potentials of about 270 mV. This property allows to selective determination of hydrochlorothiazide in the presence of propranolol. The transfer coefficient (α) for the electrocatalytic oxidation of hydrochlorothiazide and diffusion coefficient of this substance under the experimental conditions were also investigated. In phosphate buffer solution (PBS) of pH 8.0, the oxidation current increased linearly from 0.1 to 500.0 µM. The detection limit (3σ) obtained by square wave voltammetry (SWV) was 0.08 µM. The proposed method was successfully applied to the determination of hydrochlorothiazide, and propranolol in real samples.

Keywords**:** *Hydrochlorothiazide, Propranolol, Glassy carbon electrodes, Multi-wall carbon nanotube*

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The Application of Ion Selective Electrode Modified with Molecularly Imprinted Polymer based on Liquid Membrane for the Determination of Methylmercury in Real Samples

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Abstract

Recent years have seen increased interest in molecular imprinting technology. Molecular imprinted polymers (MIPs) have become an important tool in the preparation of artificial and robust recognition materials capable of mimicking natural systems [1].Molecular imprinted polymers (MIPs), described as artificial "locks" for "molecular keys", have the ability to recognize the used template from a mixture of closely related compounds. Due to the molecular recognition ability, MIPs have been proposed for promising applications in a wide variety of fields, such as chemical/biological sensors, chiral separation, catalyst, and solid-phase extraction [2].Mercury is considered to be a major environmental pollutant on a global scale. Environmental and health risks for mercury are caused by methyl mercury that is formed by bio methylation of mercury (II) which is carried out by microorganisms in sediment and soil. Methyl mercury concentrations, however, usually does not exceed 1.5% of the total mercury content in sediments. Methyl mercury binds strongly with biological ligands containing sulfhydryl groups affecting the function of enzymes and interfering with protein synthesis. It is a neurotoxin that readily crosses bio- logical membranes and accumulates to harmful concentrations in organisms and biomagnifies in aquatic food webs to concentrations of toxicological concern [3]. Until now methods such as using cold vapor atomic absorption, thermal analysis, and absorption of X-rays have been used to measure methyl mercury.

In this study a membrane electrode based on molecularly imprinted polymer were designed and prepared. The best response characteristics were obtained using the composition: 20% molecularly imprinted polymer as ionophore, 50% dibutyl phthalate as plasticizer and 30% polyvinyl chloride.The electrode exhibited a near Nernstian response of 60 mV/decade over the activity range 1×10^{-2} to 1×10^{-5} M.The operational pH range of the sensor is 4.0–8.0. The

electrode shows a response time of 20 s and can be used for at least five weeks without any considerable divergence in potentials. It exhibits very good selectivity relative to a wide variety of alkali, alkaline earth, transition and heavy metal ions. The proposed electrode used as determining methylmercury in real examples like canned tuna, cow milk and wastewater based on calibration graph.

*Keywords***:** *Mercury, Molecular imprinted polymers, Molecular keys, Biological sensors*

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Designing of Liquid Membranc Electrode Based on Molecularly Imprinted Polymer and its Applicability to Determination of P-nitrophenol in the Pharmaceutical Samples.

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Abstract

Molecular imprinting is an emerging technology which enables us to synthensize the materials with highly specific receptor sites towards the target molecules. Molecularly imprinted polymers (MIPs) are a class of highly cross-linked polymer that can bind certain target compound with high specificity. The MIPs possess several advantages over the conventional immunosorbent (IS). The MIPs can be used repeatly without loss of activity with high mechanical strength and durable to harsh chemical media, heat and pressure compared to biological receptors (Lavignac et al., 2004) [1]. P -Nitrophenol (also called *p*-nitrophenol or 4-hydroxynitrobenzene) is a phenolic compound that has a nitro_group at the opposite position of hydroxyl group on the benzene ring4-Nitrophenol is a colorless to light yellow solid with no odor. 4-Nitrophenol is an intermediate in the synthesis of paracetamol. P -nitrophenol is used as the precursor for the preparation of phenetidine and aceto phenetidine, indicators, and raw materials for fungicides. Acute inhalation or ingestion of 4-nitrophenol in humans causes headaches, drowsiness, nausea, and cyanosis. Contact with the eyes causes irritation. Also, by the now, p-nitrophenol has been determination by CV, DPV, SEM, GC and spectroscopy methods [2].

In this work, an electrode using synthensised MIP as unufor was desined for determination of trace amount of p-nitrophenol in real samples such as acetophenetidine, aceto phenetidine. The effects of different parameters including pH, scan rate, electrolyte kind and concentration, and time of response were investigated. The electrode exhibited a best Nernestian slope in the concentration range from 1.0×10^{-8} to 1.0×10^{-2} mol L^{-1} and showed a good selectivity for p-nitrophenol. It also successfully applied in the determination of target analyte in real samples.

Proposed electrode can be used in determination of p-nitrophenol in different biological and pharmacology samples.

Key words: Potentiometric Sensor, Ion Selective Electrode , P-nitrophenol , Molecularly Imprinted Polymers , Real Samples

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Electrochemical Characterization of Au/ZnO/PPy/graphene nanocomposite and its application for simultaneous determination of ascorbic acid (AA), epinephrine (EP) and uric acid (UA)

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Abstract

Metal nanoparticles due to the unique electrical, magnetic and optic properties have been taken highly into consideration [1]. Polymer materials were used extremely for making sensors, within recent decade. One of advantages of polymers is that they may be synthetized on various beds such as graphene, carbonnanotube, gold [2]. Using quick, easy, sensitive and precise methods for simultaneous measurement of some chemical compounds is highly important [3].

Here, we report sensor based on graphene oxide/ polypyrrole/zinc oxide (ZnO)/Au nanoparticles nanocomposite modified glassy carbon electrode (GO/Ppy/ZnO/Au GCE) for simultaneous determination of ascorbic acid (AA), epinephrine(EP) and uric acid (UA). The morphology and structure of GO/Ppy/ZnO nanocomposites were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), and Fourier transform infrared (FT-IR). The GO/Ppy/ZnO/Au, GCE-based sensor exhibited excellent electrocatalytic activity and high stability for determination of AA, EP and UA. The prepared electrode separates the oxidation peak potential of AA-EP by 90 mV, and EP-UA by 210 mV, while the bare GCE cannot resolve them. The electrochemical sensor shows a wide linear response and detection limit was found to be 100, 50 and 70 nM for AA, EP and UA respectively. In addition, the proposed sensor shows good selectivity and stability along with good precision and consistency.

Keywords: ascorbic acid, Epinephrine, uric acid, nanoparticles,Simultaneous determination

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A novel biosensor for simultaneous determination of two neurotransmitter Dopamine and serotonin in the presence of ascorbic acid using GCE/RGO/PPy/Pt NPs

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Abstract

Simultaneous determination of dopamine (DA) and serotonin (5-HT) is of greater value because of their coexistence in biological systems. These facts have encouraged chemists to develop faster, simpler, and more sensitive techniques and many works have been published describing the determination of DA and 5-HT concentrations using chemically modified electrodes [1]. Graphene has been used for the sensitive determination of various drugs molecules, due to their excellent conductivity because of π-π stacking and synergetic effects with other materials [2]. Polypyrrole has been considered as one of the most promising electrode materials to enhance the sensing sensitivity because of its low cost, easy synthesis, relatively high conductivity and good electrochemical/mechanical properties [3]. Platinium nanoparticles (PtNPs), due to their large aspect ratio (surface area to volume), biocompatibility, and high electerical conductivity have also been widely employed as a modifier in voltammetry analysis [4]. The morphology and structure of the nanocomposite were characterized by the scaning electron microscopy (SEM), X-ray diffraction (XRD) and Fourier transform infrared (FT-IR). Among the bare (GCE) and GCE/RGO, GCE/RGO/PPy and GCE/RGO/PPy/Pt modified electrode namely GCE/RGO/PPy/Pt exhibited much higher electrocatalytic activities toward oxidation of DA and 5-HT.The measurement were carried out in pH 7.0 PBS, by Cyclic voltammetry (CV) and Differential pulse voltammetry (DPV). The peak potential differences were 215 mV .The detection limits for DA, 5-HT both were 50 nM. The sensor showed excellent sensitivity, selectivity, and stability.

Keywords: *Dopamine, Serotonin, Platinum nanoparticles, Polypyrrole, Graphene*

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Determination of Silver Ion in Water Wamples Using Potentiometric Sensor Based on Molecularly Imprinted Polymer

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Abstract

For over three decades now, molecularly imprinted polymers have successfully been used for selective chemical sensing because the shape and size of their imprinted molecular cavities perfectly matched those of the target analyte molecules [1]. Due to the molecular recognition ability, MIPs have been proposed for promising applications in a wide variety of fields, such as chemical/biological sensors, chiral separation, catalyst, and solid-phase extraction [2].

Silver is an important element that is widely used for human life. It is obvious that in order to monitor silver concentration in natural waters and to study silver toxicity effects on bio organisms in oceanographic research and survey work, highly sensitive and selective methods for silver determination are required. Conventional techniques which have been applied to the extraction of soluble silver metal from its solutions include solvent extraction, precipitation, ion exchange and electrodeposition. The majority of these techniques have shortcomings such as high cost, poor selectivity, extensive labor, and time consumption. In the last decade significant research effort have been directed towards techniques improving the selective extraction of silver ions; and ion imprinted polymeric materials with different functional groups have been frequently used[3].

A silver ion selective electrode (ISE) based on an ion-imprinted polymer (IIP) as a novel ionophore has been prepared and studied. The ion-selective electrode (ISE) was prepared by dispersing silver (IIP) particles in dibutyl phthalate as a plasticizer and then embedding them in a polyvinylchloride polymeric matrix. The silver (ISE) showed a nernstian response for silver over the dynamic concentration range of 1.0×10^{-5} mol L^{-1} – 1.0×10^{-2} mol L^{-1}, with a slope of 67.2 mV per decade. The limit of detection was 1.0×10^{-7} M. The proposed electrode revealed good selectivity over a wide variety of other cations including alkali, alkaline earth, heavy and

transition metals. The accuracy of the proposed electrode was checked through the analysis of spiked water samples.

Keyword: *Silver, Molecularly imprinted polymers, Cation*

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Combination of electro membrane assisted solid phase micro extraction with electrochemical detection a new strategy for selective and sensitive electroanalysis

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Abstract

This paper aims to introduce a new analytical strategy based on electromembrane-assisted solid phase micro-extraction (EMSPME) coupled with electrochemical detection for the electroanalysis of tramadol as a model analyte from urine samples. For this purpose, reduced graphene oxide (r-GO) spin-coated pencil lead was used not only as a solid sorbent for SPME and reinforced cathode of electromembrane extraction (EME) but also, as the working electrode (pencil modified electrode) in electrochemical analysis. A Box–Behnken design and the response surface methodology were used for the optimization of different variables affecting the extraction efficiency. In optimized condition, the detection limit of tramadol was obtained to be 0.0030 µg mL-1. Dynamic ranges of the method were obtained within the range of 0.010 to 0.50 and 0.50 to 50 µ g mL-1. The process of coupling SPME with EME decreases the detection limit of the method in urine samples. In addition, EM-SPME can remove the interfering effect of acids, carbohydrates, anions and also other polar compounds that suppress low log P during the measurement.

Keywords: *Electro membrane extraction, Solid phase micro extraction, Spin-coating, Reduced graphene oxide, Tramadol electrochemical sensor*.

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Determination of methyldopa by a novel enzymatic biosensor; detection of methyldopa in medical and pharmaceutical samples

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Abstract

A novel biosensor composed of horseradish peroxidase trapped in silica sol-gel/multi walled carbon nanotube matrix on carbon paste electrode, developed and applied for determination of methyldopa by electrocatalytic oxidation of methyldopa with horseradish peroxidase in presence of H_2O_2. Modified electrode showed wide linear response in two ranges of 1 μM to 3.5 mM and 3.5 mM to 0.012 M. detection limit was obtained about 25.3 nM, also response time and biosensor stability were suitably acceptable. This developed biosensor was successfully used for accurate determination of methyldopa in urines and pharmaceutical samples. Current biosensor provided an accurate, sensitive and repeatable method for measurement of methyldopa in pharmaceutical and urine samples.

Keywords: *Biosensor, Voltammetry, Horseradish peroxidase, Methyldopa, Enzyme immobilization.*

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Fabrication of CoHCF-PAni and MWCNTs hybrid modified CPE for electrochemical determination of thioridazine by voltametric method

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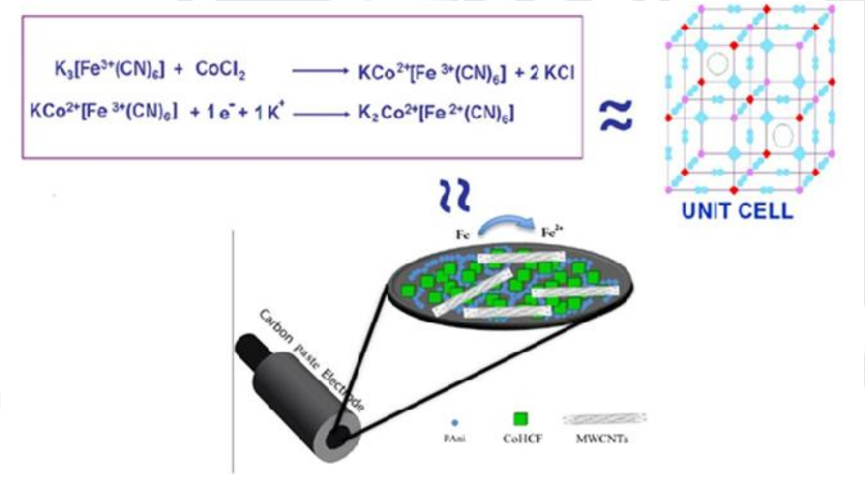
Abstract

Conducting polymers are known to be compatible with biological molecules when in a neutral aqueous solution, and hence, they are extensively used in the fabrication of accurate, fast, and inexpensive devices, such as biosensors and chemical sensors in medical diagnostic laboratories (1). Transition metal hexacyanoferrates (MHCFs), represent an important class of mixed-valence compounds that have been studied extensively for many years. MHCFs are widely employed in many fields, such as sensors, electroanalysis, and electronic devices (2). Wide application have been found of these compounds due to interesting properties such as ion-exchange properties, electrochromism, mixed-valence electrical conductivity, and high catalytic activity (3). Among the various conducting polymers, polyaniline (PANI) has been considered most attractive because of its high conductivity, good redox reversibility, environmental stability and facile method of preparation (4). Among the MHCFs, cobalt hexacyanoferrate (CoHCF) catches scientists' eyes. In this compound, both the cobalt and iron elements have two oxidation states of (II) and (III) leading to a multitude of compound stoichiometries and redox states. CoHCF has wide applications in molecular magnets,optomagnets, humidity sensors, electrochromic devices as well as electrocatalysis (5).

Electrochemical response of cobalt hexacyanoferrate-polyaniline hybrid and multi-walled carbon nanotubes-modified carbon paste electrode (MWCNTs/CoHCF/PAni/MCPE) toward thioridazine (Tz) was studied by means of cyclic voltammetry (CV) and differential pulse voltammetric (DPV). The modified electrode displayed an obvious increase in the peak current compared to the bare carbon paste electrode (CPE). The results indicated that MWCNTs/CoHCF/PAni/MCPE remarkably enhanced electrocatalytic activity towards the

oxidation of Tz. The effects of pH, modifier amount, scan rate, and time of accumulation has been examined. Under the optimum conditions, the anodic peak current increases linearly with increasing Tz concentration in the ranges of 1.0×10^{-7}–$1.0\ \times10^{-4}$M of Tz with a linear correlation coefficient (R^2) of 0.995 with a low detection limit of 0.03 µM by calibration curve with DPV as a sensitive method for Tz. The measurement repeatability of the MWCNTs/CoHCF-PAni/MCPE was examined and the relative standard deviation (RSD) was obtained 2.7% for ten successive assays. Seven modified electrodes showed an acceptable reproducibility with RSD of 3.5%. The interferences of some ions and organic compounds have been investigated. In addition, successful applicability of the electrode in the real sample (blood serum) was studied and good accuracies were obtained.

Graphical abstract



Keywords: Cobalt hexacyanoferrate, Poly aniline, Carbon paste, Electrochemical determination, Nanocomposite, Hybrid, Thioridazine

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Determination of Pb+2 ions in environmental samples using graphite electrode modified with liquid membrane based on molecularly imprinted polymer

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Abstract

Molecular imprinting is a useful technique for the preparation of functional materials with molecular recognition properties. The molecular imprinting technique is a powerful method for preparing artificial recognition sites with predetermined selectivity for a wide range of target molecules. Molecular imprinted polymers (MIPs) are being extensively used as synthetic polymer-based receptors or as artificial antibodies, because of their ability to mimic natural systems. However, when compared to natural recognition products, they offer several advantages such as robustness, specificity, reusability and cost-effectiveness. They also exhibit resistance to extreme conditions, like high temperature, acidic and basic environments, and therefore lend themselves to engineering possibilities compared with biological counterparts.

Lead is one of the most toxic chemicals that pose a wide range of dangers to human's health. In addition to renal disease, cardiovascular effects and reproductive toxicity may cause irreversible neurologic damage. As described elsewhere, continuous exposure with lead may cause adverse and poisonous effects to the brain, blood, kidneys, nervous and reproductive system along with other diseases. Therefore, it is desired to develop the simple, selective, sensitive, efficient and eco-friendly methods for the determination of trace levels of Pb2+ ions in environmental and biological samples. In recent years, various instrumental techniques including; spectrophotometric methods, atomic absorption and emission spectroscopy and mass spectrometry have been applied to the determination of Pb2+. However, most of these techniques are either time consuming, involving multiple sample manipulations, or too expensive for most analytical laboratories.

A membrane electrode based on molecularly imprinted polymer were designed and prepared. The best response characteristics were obtained using the composition: 5% molecularly imprinted polymer as ionophore, 63% dibutyl phthalate as plasticizer and 30% polyvinyl chloride. The sensor exhibits a Nernstian response for lead ions over a wide concentration range of 1.0×10−2 to 1.0×10−6M with a slope of 29.3 ±0.1 mV/decade of activity. It has a fast response time of about 20 s and can be used for at least five weeks without any divergence in potential. The electrode can be used in the pH range4.0–8.0The proposed sensor shows fairly good discriminating ability towards lead ions in comparison with some alkali, alkaline earth, transition and heavy metal ions. At the end of the electrode performance by using analytical measurement of Pb2 + ion in real samples of well water, municipal and industrial waste water by using a calibration graph was demonstrated.

Keywords: *Ion-selective electrode, Membrane PVC, Lead (II), Moleculary imprinted polymer, Polyvinyl chloride*

Designing of Potentiometric Sensor Modified with Liquid Membrane Base on Surface Molecularly Imprinted Polymer for the Determination Methyldopa in Real Samples

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Abstract

MIPs (Molecularly Imprinted Polymers) are engineered cross-linked polymers that can exhibit high affinity and selectivity towards a single compound or they can be designed to exhibit 'Class Selectivity' for a family of related compounds. MIPs are able to bind analytes even when these are present in complex matrices (e.g. plasma, urine, muscle tissue, food matrices, environmental samples, process solutions etc). An important strength of MIPs is that they are able to bind to trace levels of the target analyte, in the presence of large excess of other compounds that have similar physico-chemical properties [1]. Methyldopa is a catechol derivative (catecholamine) widely used as antihypertensive agent. It is a centrally acting α-2-adrenoceptor agonist, which reduces sympathetic tone and produces a fall in blood pressure. The spectrum of activity of methyldopa lies between those of the more potent agents, such as guanethidine, and the milder antihypertensive, such as reserpine. Methyldopa is a structural analogue of dihydroxyphenyl alanine [2].Several types of analytical procedures have been reported for the analysis of methyldopa in bulk form, pharmaceutical form or biological fluids [3]. These include spectrophotometry and chromatography Furthermore, cyclic voltametry electrochemical oxidation, high-performance liquid chromatography (HPLC) and kinetic methods. Some of these methods are not simple; others are time consuming or involve procedures with rigorous control of the experimental conditions or suffer interference from the tablet matrix and consequently are not suitable for routine analysis.

In this study a novel PVC membrance for determination of methyldopa designed and was used. The best concentration range is 1.0×10^{-7} to 1.0×10^{-3} mol L^{-1}.The sensor response is independent of pH in the range of (5-7).the proposed electrode shows a good selectivity for methyldopa. It's also successfully applied in the determination of methyldopa in real samples.

Keywords: *Molecularly Polymer, Potentiometric sensor, Methyldopa, real samples*

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Determination of dopamine in the presence of uric acid and folic acid based on dopamine electrocatalytic oxidation by CuO nanoparticle/hemoglobin

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Abstract

This work describes the development of a novel biosensor for determination of dopamine in presence of H_2O_2 and folic acid and uric acid as interferences. The Biosensor was fabricated from a carbon paste electrode modified with electrostatically immobilized hemoglobin on cooper oxide nanoparticles and multi walled carbon nanotube. Because some phenolic compound biosensors were developed using the peroxidase properties of hemoglobin, this can cause the reduction of phenolics in the presence of H_2O_2. However, the presence of hemoglobin in this electrode led to catalytic oxidation of dopamine at the electrode surface in the presence of H_2O_2. The biosensor's performance for phenolic compound detection depends on hemoglobin acting as an electron mediator. This biosensor presents a sensitive response for dopamine. The parameters of the electrode fabrication with experimental conditions for hemoglobin immobilization on CuO nanoparticles were optimized. Linearity for the detection of the dopamine was observed from 5 μM to 1 mM. Its detection limit was calculated at ~20 nM. Electrode response reached 80% of its primary response after 30 days. The response time of the developed electrode was about 10 seconds.

Keywords: *Biosensor, cooper oxide nanoparticles, Hemoglobin, Dopamine, Uric acid, Folic acid.*

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Evolution of reduced graphene oxide modified carbon screen printed electrode for determination of buprenorphine

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Abstract

In this research, we have developed an electrochemical buprenorphine (BN) sensor based on reduced graphene oxide (r-GO) as an electrode modifier on the screen printed carbon electrode (SPCE) surface. BN oxidation pathway was proposed using voltammetric studies and with the aid of Density Functional Theory (DFT). The effects of various parameters including pH, modifier amount, accumulation time, and accumulation potential on the oxidation peak current of BN were optimized. Under the optimized conditions, the linear response range and the limit of detection were obtained as 0.50–100 µM and 0.16 µM (S/N=3) using differential pulse voltammetry (DPV), respectively. The selectivity of the modified electrode in the presence of potential interferences was also studied, and finally the electrode was. successfully employed for the determination of BN in spiked urine samples.

Keywords: *Buprenorphine (BN) · Screen printed carbon electrode (SPCE) · Reduced graphene oxide (r-GO) · Density Functional Theory (DFT) · Electrochemical sensor · Modified electrodes.*

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Simultaneously electrochemical determination of dihydroxybenzen isomers using nano carbon paste electrode modified with Cu (II) complex

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Abstract

Benzenediols or dihydroxybenzenes are organic chemical compounds in which two hydroxyl groups are substituted onto a benzene ring. These aromatic compounds are classed as phenols. There are three isomers of benzenediol: 1,2-benzenediol (the ortho isomer) is commonly known as catechol (CC), 1,3-benzenediol (the meta isomer) is commonly known as resorcinol (RC), and 1,4-benzenediol (the para isomer) is commonly known as hydroquinone (HQ) [1]. There are extremely toxic and some of the harmful effects of these are difficulty with breathing, fever, headache, nausea, swelling, vomiting, worsening of pain, redness and swelling. Therefore, the rapid in situ determination of dihydroxybenzenes pollutants is an important environmental challenge because of the easy penetration of such species through membranes or skins of plants, animals and humans. Thus, the simultaneous determination of three isomers for quality control analysis and for medical control is very important [2]. Carbon paste electrodes (CPEs), is inexpensive kind of electrode and possess many advantages such as low background current, wide range of potential application, easy fabrication, rapid surface renewal and compatibility with various types of modifiers, have been widely used as suitable matrixes for preparation of modified electrodes [3]. Recently, the modified electrode with Multi-walled carbon nanotube has good electrocatalytic activity, sensitivity, and selectivity; it has also a low detection limit compared to traditional carbon paste electrodes. Also over recent years, transition metal complexes have been employed for the modification of the electrode surfaces. In this work, a highly sensitive electrochemical sensor for the simultaneous determination of o-, m-, p-dihydroxybenzene isomers was fabricated on modified carbon paste electrode. Under the optimum conditions, the calibration curves for CC, RC and HQ were obtained in the range of 1–500 µM with the sensitivity of 5.0 $\mu A\,\mu M^{-1}\,cm^{-2}$, 5.62 $\mu A\,\mu M^{-1}\,cm^{-2}$ and 7.45 $\mu A\,\mu M^{-1}\,cm^{-2}$,

respectively. The detection limits were found to be 0.3 μmol L^{-1} for CC, 0.1 μmol L^{-1} for RC and 0.4 μmol L^{-1} for HQ based on S/N of 3. The developed method was successfully applied to the simultaneous determination of dihydroxybenzene isomers in synthetic and real samples, and the results are satisfactory.

Keywords**:** *Catechol, Resorcinol, Hydroquinone, Modified electrode, Voltammetry*

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Simultaneous determination of epinephrine and uric acid using glass carbon electrode modified with nanoparticles

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Abstract

Epinephrine (EN), is an important compound for the message transfer in the mammalian central nervous system [1], which exists as an organic cation in the nervous tissue and biological body fluids. The determination of epinephrine levels in biological fluids yields important information on its physiological functions. Quantitative determinations of them are significant method for developing nerve physiology, making diagnosis and controlling medicine [2]. Uric acid (UA) is the primary product of purine metabolism in the human body and it has been shown that extreme abnormalities of UA levels are symptoms of several diseases (e.g. gout, hyperuricemia and Lesch–Nyhan syndrome). Therefore, it is essential to develop simple and rapid methods for the determination of these biological molecules in routine analysis. Electrochemical procedures have been developed to determine them based on their electrochemical activities. Noble metal nano-structures like Au, Pt and perovskite have attracted tremendous attention in recent decades, due to their excellent optical, electrochemical and electronic properties, which are different from those of bulk metal materials. Particularly, due to the unique properties of perovskite nanoparticles, such as good conductivity, useful electrocatalytic and biocompatibility, several researchers utilized perovskite nanoparticles to fabricate electrochemical sensors and biosensors [3]. The modified glass carbon electrode with $LaMnO_3$ nanoparticle showed an excellent electrocatalytic activity for EP, and UA oxidations and for accelerated electron transfer between the electrode and the substances. Calibration curves in the ranges 7.5×10^{-7} to 4.0×10^{-4} M and 5.0×10^{-7} to 4.0×10^{-4} M were obtained for EP and UA, respectively. The lowest detection limits (S/N = 3) were 5.5×10^{-8} M and 7.5×10^{-8} M for EP and UA, respectively. The proposed procedure was also successfully applied for the simultaneous detection of EP, and UA in injectable medicine, blood plasma, and urine samples.

Keywords*: *Epinephrine, Uric acid, Modified electrode, Voltammetry

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Preparation of a cation selective Nano-Composite carbon paste electrode based on N, N'-dipyridoxyl (1,3--propanediamine)

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Abstract

Potentiometric sensors have shown to be very effective tools for analysis of a wide variety of metal ions. Among them, carbon paste electrods (CPEs) have attracted interest as a result of their improved renewability, stable response, and low ohmic resistance compared to membrane electrodes.N,N′-dipyridoxyl (1,3-propanediamine) (PYPA) seemed to be a suitable ion carrier for metal ions due to the presence of hard donating O and intermediate donating N atoms and even the existence of electron rich double bound in its structure. Preliminary solution study shows the selectivity of (PYPA) toward Cr (III) ions in comparison of other common cations, including alkali, alkaline earth, transition and heavy metal ions. To have a long-term stable electrode for potentiometric uses, (PYPA) was applied as ionophore in preparation of anano-composite carbon paste electrode.

Keywords: *Potentiometry, Sensor, CPE Membrane, Ion Selective Electrode*

Introduction

Multi-walled carbon nanotubes (MWCNTs) have been recently used in composition of Carbon paste electrodes [1-4]. CNTs have very interesting physicochemical properties, such as ordered structure with high aspect ratio, ultra-light weight, high mechanical strength, high electrical conductivity, high termal conductivity, metallic or semi- metallic behavior and high surface area[5]. The combination of these characteristics makes CNTs unique material with the potential for diverse applications. Using MWCNTs in the carbon paste improves the conductivity and, therefore, conversion of the chemical signal to an electrical signal.

Experimental

2.1. Reagents

The N,N'-dipyridoxyl(1,3- propanediamine) (PYPA), nanosilica, graphite powder with a 1-2 µm particle size (Merck) and high-purity paraffin oil (Aldrich) were used for the construction of the carbon pastes. The multi-wall carbon nanotubes (MWCNTs) with 10-40 nm diameters, 1-25 µm length, SBET: 40-600 m2/g and with 95% purity were purchased from Research Institue of Petroleum Industry (Iran). The chloride and nitrate salts of cations were all purchased from Merck Co. Triply distilled de-ionized water was used throughout.

2.2. Preparation of the carbon paste electrode

Different amount of the ionophore PYPA along with appropriate amount of graphit powder, nanosilica and MWCNTs were thoroughly mixed. The resulting mixture was transferred into a glass tube. The electrode body was fabricated from a glass tube of i.d. 5 mm and a height of 3 cm. After the mixture homogenization, the paste was packed carefully into the tube tip to avoid possible air gaps, often enhancing the electrode resistance. A copper wire was inserted into the opposite end to establish electrical contact. The external electrode surface was smoothed with soft paper. A new surface wa produced by scraping out the old surface and replacing the carbon paste. The electrode was finally conditioned for 24 h by soaking in a 1.0×10^{-3} mol L^{-1} Crl(NO$_3$)$_3$ solution.

2.3. Results and discussion

Electrode No.	Composition of Carbon Paste (wt.%)					Slope (mV/decade)	Dynamic linear range (M)
	Binder (Paraffin oil)	ligand	Graphite Powder	MWCNTs	Nano-Silicon		
1	25	2	73	0	0	15.9 ± 0.8	1.0×10^{-5}-1.0×10^{-2}
2	30	2	68	0	0	13.5 ± 0.21	5.0×10-5-1.0×10^{-2}
3	35	2	63	0	0	11.2 ± 0.3	5.0×10^{-5}-1.0×10^{-2}
4	25	2	72.9	0	0.1	15.1 ± 0.3	1.0×10^{-5}-1.0×10^{-2}

5	25	2	72.7	0	0.3	14.5 ± 0.2	1.0×10^{-5}-1.0×10^{-2}
6	25	2	70.9	2	0.1	16.8 ± 0.3	1.0×10^{-5}- 1.0×10^{-2}
7	25	2	69.9	3	0.1	18.0 ± 0.5	1.0×10^{-6}-1.0×10^{-2}
8	25	1	70.9	3	0.1	17.2 ± 0.6	5.0×10^{-6}-1.0×10^{-2}
9	25	3	68.9	3	0.1	20.2 ± 0.7	1.0×10^{-6}-1.0×10^{-2}

Conclusion

The carbon paste electrode composed of 3% MWCNT, 0.3% NS, 4%PYPA, 30% paraffin oil, and 62.7% graphite powder showed the best response. The proposed sensor exhibits a Nerstian slope of 19.9 ± 0.5 mV decade-1 toward Cr3+ ions in the range of 1.0×10-9 –1.0×10-2 M and detection limit of 8.0×10-10mol L-1. The response of the sensor was found to be pH independent in the range of 1.6 – 4.3 and has a fast response time of <5.۹ s.This electrode was used as an indicator electrode in the potentiometric titration of Cr (III) ions with EDTA.

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Nonenzymatic glucose detection based on copper oxide-Palladium/CNT nanocomposite

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Abstract

For diagnosis and management of diabetes, precise and accurate detection of glucose is very important. Therefore, producing high-performance analytical tools for diagnosis of diabetes and management of blood glucose is very crucial. Glucose oxidase based biosensors have been proved to be powerful devices for glucose determination thanks to their high selectivity, sensitivity and low detection limit. However, these biosensors due to the intrinsic feature of enzymes have some defects in stability and reproducibility. Therefore, the non-enzymatic glucose biosensors based on metal nanoparticles and metal oxides have received more and more attentions. non-enzymatic biosensors have many advantages such as simple preparation, low cost, high stability and sensitivity. In current study, we combined CuO nanoparticles with Palladium and carbon nanotubes to produce a nanocomposite (CuO-Palladium/CNT) for non-enzymatic detection of blood glucose. Based on cyclic voltammetric results CuO-Palladium/CNT nanocomposite has a high sensitivity (2000 μA mM^{-1} cm^{-2}), good linear range (0.002-7 mM), low detection limit (0.2 μM) and short response time, good anti-interference and anti-toxicity, long-term stability (over 8 weeks). Non-enzymatic glucose biosensors like CuO-Palladium/CNT nanocomposite alleviated the problems of enzyme-based biosensors such as insufficient stability, sensitivity to temperature, pH and humidity, lower reproducibility, thermal and chemical instability. Because of these properties and easy preparation method, CuO-Palladium/CNT nanocomposite is a promising material for marketing of glucose biosensors. Also complementary experiments to examine the sensor for detection of glucose in real human serum are considered.

Keywords*: *Biosensor; Blood glucose; Non enzymatic nanoparticles; Copper oxide; Diabetes

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Determination of ascorbic acid using Cu (II) complex-modified glass carbon electrode

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Abstract

Ascorbic acid, hereafter referred to as AA, a water soluble vitamin, is an extremely important substance which plays a unique redox and electrochemical role. AA is a compound that takes part in many important life processes [1]. Therefore, AA has been determined by numerous techniques. The oxidation of AA at a glassy carbon electrode gives a very poor electrochemical response. Therefore, developing simple and reliable methods for fabrication of new modified electrodes for AA determination have been always a goal for research groups. Although a few modified electrodes have been used successfully for AA determination, but most of them have certain disadvantages such as considerable leaching of modifier, poor long-term stability, and contamination. Hence, it is necessary to explore and develop a simple and reliable method to fabricate modified electrodes with other modifiers for electrocatalytic determination of AA [2]. In recent years, the transition metal complexes have been used as modified material on electrode surface to form chemically modified electrodes. Due to their ability to construct specific stacking and generalized electrostatic interactions, transition metal complexes have been exploited as impactful host matrices for guest molecules with appropriate size and structure [3]. Currently, there are many studies on the mechanism of action of transition metal complexes and drug molecules. In the present work, a glassy carbon electrode modified with a novel $[Cu(L)_3]^{2+}$ (L = N-(4,5-Diazafluoren-9-ylidene)aniline) complex have been applied to the electrocatalytic oxidation of AA. Under the optimized conditions, the square wave voltammetric peak current of AA increased linearly with concentrations in the range of 1×10^{-7} to 200×10^{-4} M and a detection limit of 8.8×10^{-8} M was obtained. Finally this modified electrode was used for determination of AA in some real samples.

Keywords: *Ascorbic acid, Glassy carbon electrode, Cu (II) complex, N-(4,5-Diazafluoren-9-ylidene)aniline*

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The fabrication of a Cu (II) complex and its application for the determination of dopamine with modified glass carbon electrode

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Abstract

Dopamine (DA), an important catecholamine neurotransmitter, which is widely distributed in the mammalian central nervous system, plays a significant role in human metabolism as well as in the renal systems by participating in many biochemical reactions, such as reward-related behavior, movement and exciting signals transmission. Various neurodegenerative diseases are due to the abnormality of DA, including Schizophrenia and Parkinsonism Senile dementia [1]. Therefore, it is of critical importance in applying in diagnostic and medical investigations. Various methods have been developed for the determination of DA. Electrochemical method has drawn much attention by offering advantages including simplicity, good stability and low costs [2]. Transition metal complexes are also usually employed as electrochemical mediators because of their catalysis in low potential, reversible property of electrode reaction and peculiar biological function [3]. Considering these precedents, it emerges that it is advantageous to enhance the electrochemical performance of the electrode by modifying the transition metal complexes on the electrode surface. Because of easy preparation, convenient modification and the versatility of electrochemical sensors based on transition metal complexes $[cu(phen)_2(L)]^{2+}$ (phen=1,10-phenanthroline, L=4,5-diazafluoren-9-one) coupled was used as a modifier to fabricate a chemically modified electrode in this paper. The electrode modified with $[cu(phen)_2(L)]^{2+}$ showed good electrocatalytic activities toward the oxidation of DA and possible applicability for DA determination in real samples. Under the optimum experimental conditions, the linear calibration curve was obtained in the range from 2.5 to 500 $\mu mol\cdot L^{-1}$ with a low detection limit of 1.50 $\mu mol\cdot L^{-1}$ (at a signal-to-noise ratio of 3).

Keywords*: *Dopamine, Transition metal complex, 1,10-phenanthroline, 4,5-diazafluoren-9-one

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Adrenaline biosensor based on carbon nanotube modified electrode

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Abstract

The present work describes the performance of an enzyme biosensor based on immobilized polyphenol oxidase of single walled carbon nanotubes (SWCNTs). This electrode was prepared by first modification of electrode surface by 10 μL acetone solution of 1 mg/mL SWCNTs and then enzyme immobilization was applied on the surface of modified electrode.

***Keywords**: Enzyme, Biosensor, Carbon nanotube, Electrochemistry*

An electrochemical biosensor is an analytical device which converts a biological response that produce by electro-active species into electrical signals. The term biosensor is often used to cover biological sensor. The analytes can be various molecules such as DNAs, bacteria, viruses or simple molecules like glucose, drugs and pollutants. Enzymes are biorecognition molecules and have high selectivity and catalytic activity (1-3). Enzyme based electrochemical biosensors are presently the focus of extensive research for the development of various applications in clinical diagnosis, biomedical and environmental monitoring (4). Polyphenol oxidase is copper containing metalloprotein and essential enzyme in melanin biosynthesis. This enzyme is known as type 3 copper proteins having a diamagnetic spincoupled copper in the active center. Polyphenol oxidase can catalyze the oxidation of phenol derivative in the presence of O_2.

Voltammetry belongs to a category of electroanalytical techniques and there are various forms of voltammetry. Cyclic voltammetry is one of the most applied forms and it is useful to obtain information about the redox potential and electrochemical and bioelectrochemical reaction rates.

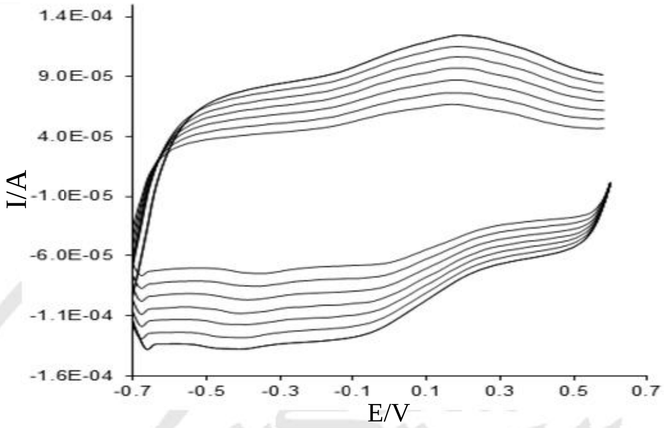

Fig. 1. Cyclic voltammograms of the Enzyme/SWCNTs/GC electrode at various scan rates, from inner to outer: 350, 400, 450, 500, 550, 600 and 650 mV/s.

Fig. 1 shows a pair of redox peaks, observed at the Enzyme/Single walled carbon nanotubes/glassy carbon (Enzyme/SWCNTs/GC) electrode as prepared biosensor at a range of scan rates. The biosensor presented a reductive peak potential at 168 mV, matching the oxidative peak potential at -354 mV (at 350 mV/s), demonstrating adsorbed polyphenol oxidase enzyme molecules on SWCNTs. The difference of anodic and cathodic peak potential values was 522 mV. It was attributed to the redox reaction of enzyme electroactive centers (copper centers). The formal potential was -93 mV with respect to the reference electrode. Also, differential pulse voltammograms of the prepared biosensor for various concentrations of adrenaline are demonstrated. The oxidation peak current of the biosensor increased and gives a catalytic current.

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Electrocatalytic oxidation of L-Dopa by novel biosensor based on immobilization of HRP on nucleophilic-functionalized MWCNT composite

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Abstract

A novel and selective enzymatic biosensor was designed and constructed for voltammetric determination of levodopa (L-Dopa) in aqueous media (phosphate buffer solution, pH=7). Biosensor development was on the basis of to physically immobilizing of horse radish peroxidase (HRP) as electro chemical catalyst by sol-gel on glassy carbon electrode modified with organic nucleophilic carbon nanotube composite which in this composite p-Phenylenediamine (pPDA) as organic nucleophile chemically bonded with functionalized MWCNT (MWCNT-COOH). The differential pulse voltammetry (DPV) was used for determination of L-Dopa from 0.1 µM to 1.9 µM with a low detection limit of 40 nM (for S/N=3) and sensitivity was about 35.5µA/µM. Developed biosensor was suitably stable for about 60 days. The developed biosensor was characterized by SEM, energy dispersive X-ray analysis (EDX), FT-IR spectroscopy and CVs.

Keywords: *HRP biosensor, Nucleophilic functionalized carbon nanotube, Levodopa, Sol-gel.*

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Fabrication of adehyde oxidase and xanthine oxidase electrochemical biosensors based on Fe_3O_4/Go/CHIT and inhibition studies of purines, perymidines and flavonoides

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Abstract

Molybdenum-containing enzymes, aldehyde oxidase and xanthine oxidase, are important in the oxidation of N-heterocyclic xenobiotics. These are present in the liver, as well as some other tissues of humans and other mammalian species such as the rat, guinea pig, monkey, and rabbit.

In this work a bienzymatic biosensor based on the coimmobilization crude rat liver xanthine oxidase and aldehyde oxidase have been designed for inhibition study of a few purien, pyrimidine and flavoneied compounds. For this purpose, Firstly, carbon past electrode modified with Fe_3O_4/Go/CHIT by electrodeposition. At the next stage, the biosensor of two enzyme was prepared by dropping 20µL of crude extracted enzyme–BSA on the CPE/ Fe_3O_4/Go/CHIT. The surface of modified electrodes characterized by FE-SEM (Fig1). Results indicated the homogeneous immobilization of the crude enzymes on the modified electrode. Optimum condition for biosensor of two enzyme are BSA=1mgmL^{-1} pH=7.5, T=35ºC and E=-0.5V (vs.Ag/AgCl). The linear response of biosensor, limit of detection, sensitivity, for xanthine and phenanthridine are 0.1 to 18 µM and 0.1-12 µM, 0.1 µM, .05 µM ,0 .446 µA µM^{-1} 0.65 µA µM^{-1} and Lineweaver–Burk plot gave the apparent K_m value of 2.2 µM and 4.6 µM for immobilized enzymes respectively. All of the inhibitors tested for two enzymes, results indicated that purines compound for xanthine oxidase and pyrimidines compounds for aldehyde oxidase have original inhibition.

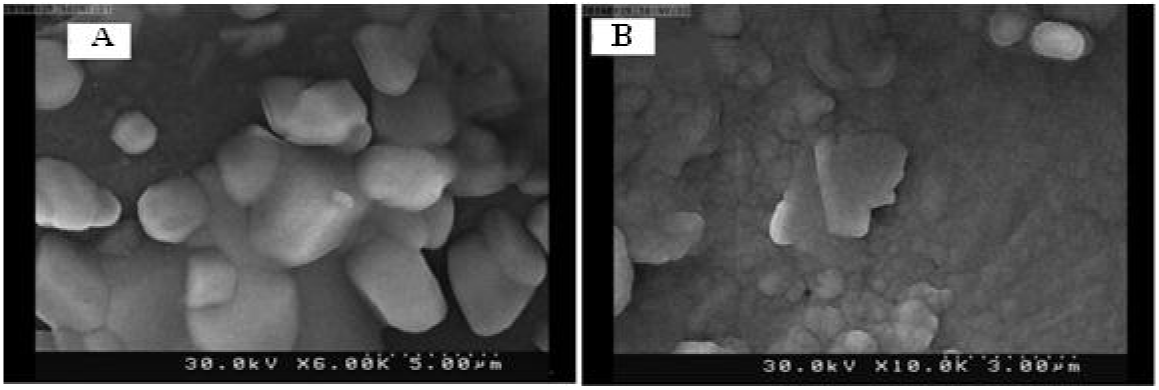

Fig1. FE-SEM images of (A) Fe_3O_4/GO/CHIT and (B) Fe_3O_4/GO/CHIT/BSA-Enzyme

Keywords*: Aldehyde oxidase, Xanthine oxidase, Electrochemical biosensor, Inhibition, nanocomposite*

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Electrochemical behavior study and determination of isoniazidon the sol-gel electrode modified with carbon nanotubes

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Abstract

Isoniazid is considered as the first choice for treatment and recovery of phthisis diseases. The phthisis diseases are contagious and known as the main reason of human death in all over the world. Therefore, determination of isoniazid, the Anti-T B drug, as first-line TB drugs and the main treatment regimen for tuberculosis in all over the world can be very valuable [1-2]. Therefore, design and development of a sensor with the aim of isoniazid determination can be valuable in order to determination of this important material. However, electro oxidation of isoniazid on bare electrodes needs high over potentials and is kinetically slow. Therefore, various modified electrodes with the aim of improvement of the rate of electron transfer and over-potential reducing were introduced. In modified electrodes, the surface of conventional electrodes were covered with thin layer of a chemical compounds, which cause in change in properties of electrode surface and electrochemical behavior of electro-active compounds [3]. Recently carbon nanotubes have attracted more attention in chemistry specially in electro-analytical chemistry. Carbon nanotubes are unique tubular structures with diameter on nanometer and high ratio of length to width [4]. Because of high chemical stability, high surface area, unique electronic and mechanical properties, carbon nanotubes have attracted much attention. Carbon nanotubes could be act as electron transfer mediator between electro-active species and electrode surface and therefore created a new approach for construction of sensors and biosensors [5].

In this study, the electrochemical behavior of isoniazid at a carbon nano tube modified sol-gel electrode has been studied using cyclic voltammetry and differential pulse voltammetric techniques. High sensivity and diminution of the overpotential for isoniazid oxidation at nano tube modified sol-gel electrode a carbon is the main advantage of designed sensor.

The numerous factors affecting the oxidation peak currents of isoniazid electrode were optimized to maximize the sensitivity. The modified electrode presented a linear response range for isoniazid from 0.05 to 1.8 mM, from 1 to 70 µM with detection limits8.58 µM and 0.13µM for Cyclic voltammetry and differential pulse voltammetry respectively. The results showed that the modified electrode has very high catalytic ability for electro oxidation of isoniazid. In addition, thise proposed modified electrode exhibited excellent sensitivity, reproducibility and stability. Moreover, the modified electrode wase used for determination of isoniazid in tablets and spiked serum as real sample.

Keywords*: *Isoniazid, Sol – gel, Modified electrode, Carbon nanotubes

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Nanoelecterochemistry

Comparative Study of Carbon Nanotube Dispersion Using Surfactants

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Abstract

The discovery of carbon nanotubes offers exciting opportunities for the development of novel high property materials. Disaggregation and uniform dispersion are critical challenges that must be met to successfully produce such high property materials, since carbon nanotubes tend to self-associate into micro-scale aggregates. This results in products with inferior mechanical and electric performance. Recognizing this problem, extensive research has been reported in the literature on development of dispersion technologies based on both mechanical and chemical approaches. A surfactant's property of accumulation at surfaces or interfaces has been widely utilized to promote stable dispersions of solids in different media [1–5]. Here, we review recent progress and advances that have been made on dispersion of carbon nanotubes in aqueous and organic media by non-covalent adsorption of surfactants and polymers. Carbon nanotube structure, properties and mainly self-assembly are discussed in detail.

Keywords*: *Carbn nanotube, surfactant, sodium dodecyl sulfate, Triton X-100, cetyl trimethyl ammonium Bromide,

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Application of an Electrochemical Sensor Based on Multi-Walled Carbon Nanotubes Modified Platinum Electrode for Determination of Doxorubicin in Biological Fluids and Preliminary Study on Drug-DNA Interactions

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Abstract

In this work, an electrochemical sensor was fabricated based on multi-walled carbon nanotubes modified platinum electrode (Pt/MWCNTs) for determination of doxorubicin as a chemotherapy drug. Doxorubicin effectively accumulated on the surface of Pt/MWCNTs and caused a pair of redox peaks at around 0.522 and 0.647 V (vs. Ag/AgCl) in Britton Robinson buffer (pH 4.0, 0.1 M). The electrochemical parameters including pH, kind of buffer, accumulation time, amount of modifier and scan rate have been optimized. Under the optimum conditions, there was a linear correlation between cathodic peak current and concentration of doxorubicin in the range of 0.2 to 4.0 □g L^{-1} with the detection limit of 0.02 □g L^{-1}. The number of electron transfers (n) and electron transfer-coefficient (α) were estimated as 2.0 and 0.5 respectively. The constructed sensor displayed excellent precision, sensitivity, repeatability and selectivity in the determination of doxorubicin in plasma. Moreover, cyclic voltammetry studies of doxorubicin in the present of DNA showed an intercalation mechanism with binding constant (K) of 1.12×10^5 L mol^{-1}.

Keywords: *Doxorubicin, MWCNTs, Electrochemical Sensor, Plasma, DNA study.*

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Electrochemical determination of anti-HIV drug Nevirapine with a nanocomposite modified graphite electrode by gold nanoparticles and poly (methylene blue) on multi wall carbon nanotube substrate

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Abstract

In this work the graphite electrode was modified by electrodepositing of Au nanoparticles on electropolymerized methylene blue (p-MB) and multi-walled carbon nanotubes (MWCNTs) for determination of nevirapine (NEV), an anti-HIV drug. The electrochemical oxidation of NEV was studied by voltammetric techniques. NEV is a non-nucleoside reverse transcriptase inhibitor (NNRTI) of HIV, that causes acquired immunodeficiency syndrome (AIDS). The HIV reverse transcriptase is an important antiviraltarget for the chemotherapy of AIDS because of its key rolein virus replication[1].

Electrochemical method is an alternative approach with the advantages of simple, quick and low cost. The electropolymerization of MB from aqueous solution and its electrocatalytic activity towards biomolecules and different inorganic compounds have already been reported [2-5].

The effects of pH and scan rates on the oxidation of NEVwere studied. Differential pulse voltammetry (DPV) technique was employed for the determination of NEV and the obtained results confirmed that the oxidation peak currents increased linearly with NEV concentrations in the ranges of 0.2-46 μM with detection limit of 50 nM. Finally, the Au NPs/p-MB/MWCNTs/GE was successfully used for the determination of NEV in serum and pharmaceutical samples.

Keywords: *Nevirapine, anti-HIV drug, poly (methylene blue), MWCNTs, modified graphite electrode*

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Electrochemical polymerization of Methylene blue on a electrode and Its utilization for improved Sensor Performances

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Abstract

In this review the use of methylene blue for modified electrode and its properties is studied. Methylene blue (MB) is a well-known redox indicator in analytical chemistry, because of its electron mediating characteristic between enzymes and substrates. Methylene blue (MB) exhibits a fast and reversible redox couple according to reaction. Some of the uses of methylene blue are proposed as a sulfur sensor, as a photosensitizer for the production of singlet oxygen that damage in biological systems (eg DNA), and when polymerized on noble metals, as a conductive polymer with bioelectrochemical activity [1-2].

The presence of PMB in the composite film enhances the functional properties and overall increase in the sensitivity of the composite film modified electrodes. Methylene blue is an electroactive conjugated cationic dye, which can be polymerized on the electrode surface by electrochemical method. Electrochemical polymerization can make the modified material uniformly and stably fixed on the electrode surface, and three-dimensional conductive interface can be easily formed. It is an ideal method for modified electrodes.

Keywords: polymer, poly (methylene blue), bioelectrochemica , modified electrode biosensor

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Determination of Phenylephrine by Nano Structure Electrochemical Sensor in Pharmaceutical Sample

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Abstract

In the present study, the glassy carbon electrode modified with sodium–dodecyl sulfate and multi wall carbon nanotubes and used for electrochemical oxidation study and determination of phenylephrine by anodic stripping voltammetry.

Phenylephrine is a drug used for nasal congestion, sinusitis, swelling of the mucous membrane of the nose, as well as medical eye examinations for dilation of the pupil. Phenylehrine can narrow coronary heart also used to treat hypotension associated with anesthesia(1,2). This electrode constructed in room temperature. After the optimization of chemical and instrumental parameters, determination of phenylephrine was performed in phosphate buffer solution pH 5 in pharmaceutical sample and blood serum. The aim of this work is present of a simple and new sensor with wide linear range and low detection limit for determination of phenylephrine. This purposed sensor has a high sensitivity respect to other sensors.

The obtained linear range and detection limit was 100nM to 25µM and 50nM respectively.

Keywords: phenylephrine, sodium–dodecyl sulfate, carbon nanotubes

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Application of bimetallic Pt-Pd /graphene nanosheets for determination of environmental pollution such as hydrazine

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Keywords: *Hydrazine, Graphene, Nanoparticles, Bimetallic*

Introduction

Hydrazine is a powerful reducing agent and widely used in various fields, such as racket fuel and synthesis of insecticides. Despite these advantages, hydrazine is a toxic material. Therefore, an easy and sensitive analytical method for detection of hydrazine is necessary [1]. Graphene is a new class of carbon material with large surface area (2675m^2g^{-1}) and high electrical conductivity used in sensors [2]. In this work, bimetallic Pt-Pd nanoparticles due to electrocatalytic activity [3] were deposited on the surface of graphene, then the modified electrode was applied for electrochemical oxidation and detection of hydrazine. Electrocatalytic activity of a bimetallic Pt-Pd nanoparticle/ electrochemically reduced graphene (ERGO)/glassy carbon electrode (GCE) has been studied by cyclic voltammetry and amperometry for determination of hydrazine.

Experimental

Platinum wire, Ag|AgCl (3M KCl solution) and GCE were used as counter, reference and working electrodes, respectively. At first, graphite oxide (GO) was deposited on GCE and then GO film was electrochemically reduced to (ERGO) in 0.5 M $NaNO_3$ solution. After that, bimetallic Pt-Pd nanoparticles were deposited on the surface of ERGO. Finally, this electrode was used as working electrode for detection of hydrazine.

Result and discussion

Fig.1 shows the electrochemical response of 2mM hydrazine in 0.1 M NaOH solution at different electrode investigated by cyclic voltammogram (CV). At bare GCE, a relatively small oxidation peak with the potential of 0.82 V is appeared for oxidation of hydrazine (Fig. 1a). At ERGO/GCE, an enhancement in oxidation peak current of hydrazine is observed, which could be attributed to the large specific surface area and high conductivity of ERGO. Also, at bimetallic

Pt-Pd /ERGO/GCE (Fig. 1b), the oxidation current of hydrazine increases greatly and oxidation potential shifts negatively to -0.71 V. This indicates the synergistic effect of ERGO and Pt –Pd and faster electron transfer rate of hydrazine oxidation on modified electrode. Fig.2 indicates amperometric response of modified electrode with addition of hydrazine with concentration in the range of 7µM-6500. The detection limit is calculated 5.3 µM.

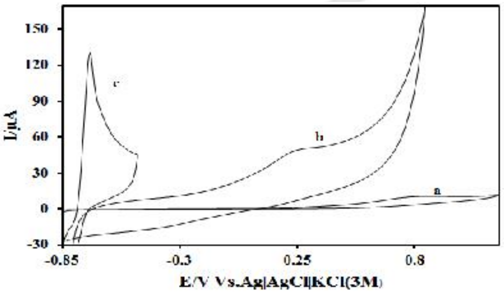

Fig.1.show the cyclic voltammetry (CV) of (a) GCE, (b) ERGO/GCE and (c) Pt-Pd/ERGO/ERGO in 0.1M NaOH Solution in the presence of 2mM Hydrazine at Scan rate of 0.05 V s^{-1}.

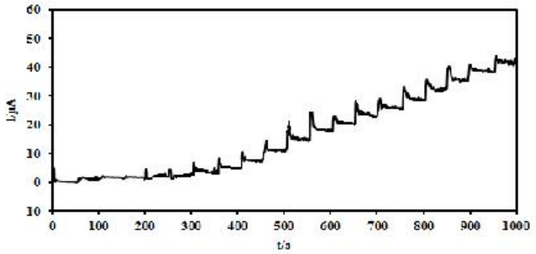

Fig. 2. Amperometric response of bimetallic Pt-Pd/ERGO/GCE by stepwise addition of hydrazine in to 0.1 M NaOH solution.

Conclusions

In this work, bimetallic Pt-Pd was successfully deposited on ERGO film. The modified electrode shows good electrocatalytic activity for hydrazine oxidation by increasing the oxidation peak and decreasing oxidation overpotential. The sensor indicates remarkable analytical performance, including rapid response and high sensitivity.

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Design and Development of a Nanostructure Sensor for Determination of TBQ with MIP using Central Composite Design

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Introduction

(TBHQ), a phenolic antioxidant used as a food additive, and its metabolite 2-tert-butyl-1,4-benzoquinone (TBQ) was cytotoxic in human monocytic leukemia U937 cells, TBQ being the more strongly cytotoxic. Both compounds induced caspase activity towards DEVD-MCA as a substrate and the cleavage of poly (ADP-ribose) polymerase in cells. The inhibition of monooxygenation activity was accompanied by redox cycling due to the tert-butylquinone produced during BHA metabolism, as measured by increased NADPH and oxygen consumption or hydrogen peroxide and superoxide anion production [1]. Accordingly, there is a need for a method to assess and determination of particular drug. Electrochemical sensor may serve the purpose due to its relative simplicity, selectivity, low-cost and fast response time [2]. Molecularly imprinted polymer (MIP) were synthesized of TBQ (template), methacrylic acid as functional monomer, ethylene glycol dimethacrylate as cross-linking agent and 2,20-azobisisobutyronitrile as initiator . Then, the MIPs were used to modify the carbon paste electrode (CPE) [3].

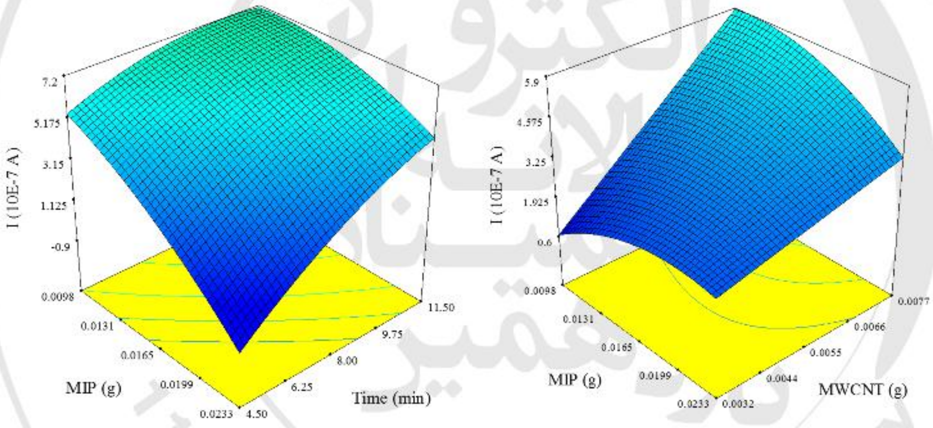
Method

Characterization of MIP was done with FTIR and the modified electrode demonstrated with cyclic voltammetry (CV) and differential pulse voltammetry (DPV), and impedance analysis that the modified electrode is responsive towards the target molecule [4].

Conclusion

This MIP would provide a new platform for high-throughput, sensitive, specific, and multiplex assay in public health, environmental monitoring, and the developing world [6]. Fig.1a shows the response surface and 3D plots were shown as a function of time (4.5 to 11.5 min) and MIP (0.0098 to 0.0233 g) at constant condition of pH= 5.4 and MWCNT=3.2×10^{-3} g and Fig. 1b shows the response surface and 3D plots were shown as a function of MWCNT (0.0032 to 0.0077 g) and MIP (0.0098 to 0.0233 g) at constant condition of pH=8/0 and time= 6.1 min. A linear range of peak current in (DPV) was obtained over 14.0 to 450.0 nM with the limit of detection of 3.2 nM.

Keywords: TBQ, Molecularly imprinted polymer, carbon paste electrode, cyclic voltammetry, differential pulse voltammetry



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Electrochemical sensor for Hematoxylin based on carbon paste electrode modified with molecularly imprinted polymer and multiwall carbon nanotube

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Introduction

One of the bioactive flavonoid compounds, which is present in enormous amounts in plants, is hematoxylin [1]. Hematoxylin is widely used as a biological stain in biomedical research laboratories and diagnostic procedures [2]. In the present work we will report the electrochemistry and electrocatalytic activity of the hematoxylin modified carbon paste electrode [3].

Purpose of research

Among all the carbon electrodes, the carbon paste electrode (CPE) is an appealing and widely used electrode material in the fields of electrochemistry, electro analysis, etc. due to its attractive advantages, such as simple preparation, low-cost implementation, renewability, low background current, and wide potential window [4]. In the current study, the preparation of hematoxylin multi-wall carbon nanotubes (HMWCNT) modified carbon paste electrode (CPE) and its application for the electrocatalytic oxidation of hematoxylin have been reported [5]. In order to construction of electrode, amount of MWCNT and MIP, also solution pH and time of hematoxylin accumulation on MIP–MWCNT–CPE was optimized. Fig.1 shows the voltammograms of different CPE electrode with different composition.

Method

Finally, a suitable method for determination of hematoxylin was presented. Molecularly imprinted polymer (MIP) were synthesized of hematoxylin (template), methacrylic acid as functional monomer, ethylene glycol dimethacrylate as cross-linking agent and 2,20-

azobisisobutyronitrile as initiator. Then the MIP were used to modify the carbon paste electrode (CPE) [6].

Conclusion

Characterization of MIP was done with FTIR and the modified electrode demonstrated with cyclic voltammetry (CV) and differential pulse voltammetry (DPV), and impedance analysis that the modified electrode is responsive towards the target molecule. A linear range of peak current in (DPV) was obtained over 7.0- 500 nM with the limit of detection of 2.8 nM.

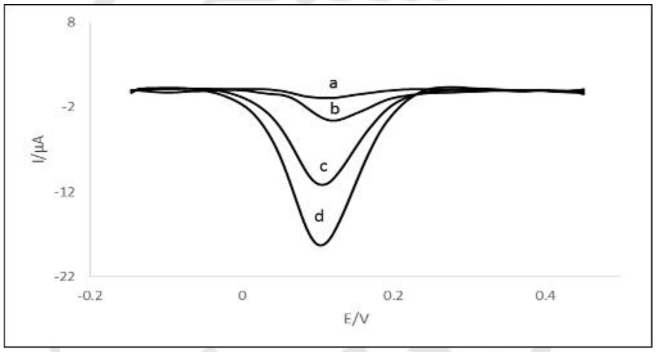

Fig. 1 Differential pulse voltammograms of the different carbon paste electrode in 0.1 M phosphate buffer (pH 7.0) related to (a) CPE, (b) MIP- CPE, (c) MIP and MWCNT-CPE and (d) MWCNT-CPE.

Keywords: Hematoxylin, Carbon paste electrode, molecularly imprinted polymer, Multiwall carbon nanotube

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Demulsification of Crude Oil-in-Water Emulsions Driven by Graphene Oxide Nanosheets

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Abstract

During its production most crude oil occurs as a water-in-oil emulsion whose continuous phase depends on the water to oil ratio, the natural emulsifier systems contained in the oil, and the origin of the emulsion [1]. The emulsifiers are complex chemically and as new oil fields are developed, and as production conditions change in older fields, there is a constant need for new, effective demulsifiers. Demulsification of crude/heavy oil-water emulsion is a major issue that received sustained attention for decades in the petroleum industry [2]. Many strategies including the gravity separation, coalescence technology filtration/membrane separation, absorption, air flotation, coagulation sedimentation, electrolysis process, ultrasonic treatment, and biological treatment etc. have been widely adopted to separate the oil from the O/W emulsions [3,4]. However, most of the separation technologies are high costly, energy intensive, complex, and time-consuming. Therefore the addition of chemical demulsifiers is the most widely used method. The process is evaluated using some conventional techniques such as interfacial tensiometry, Dynamic Light Scattering (DLS), and bottle test. Graphene oxide sheets, normally referred as graphene oxide (GO), are the liquid phase oxidation-exfoliation product of graphite. In form of graphene sponge and mesh, graphene is often used to absorb or filter oil based on its low surface energy, low density and high surface area. In this work an amphiphilic material, graphene oxide nanosheets (GO), was introduced as a versatile demulsifier to break up the oil-in-water emulsion at room temperature. It was encouraging to find that the small oil droplets in the emulsion quickly coalesced to form the oil phase and separated with the water within a few minutes. Operating condition was investigated and optimized by studying effect of the GO dosage and

interfacial tension on the demulsification As an environmental friendly and high efficient demulsifier, GO might find its application in separating oil from the O/W emulsion in the petroleum industry.

Keywords: *demulsifier, graphene oxide nanosheets (GO), interfacial tension (IFT), Crude oil.*

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Effect of Demulsifier on Water Destabilization in Oil/water Emulsions

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Abstract

Crude oil emulsions commonly exist in the form of water-in oil emulsion. There are natural surface-active fractions such as asphaltenes, resin, naphthenic acid, and porphyrin materials which can be adsorbed onto the interface and form a firm film at the oil–water interface resulting in high stability of crude oil emulsions [1]. The demulsification of produced crude oil emulsions is a significant problem in the oil field industry. There are various methods for crude oil demulsification such as electrosedimentation, supersonic demulsification, centrifugation and chemical demulsification [2]. Among the mentioned methods, the Chemical demulsification process has been widely used in oil industry regarding its appropriate lipophilic hydrophilic balance and ability to break the water/oil interface. The efficiency of demulsifier is strictly dependent upon the structure especially head groups and chain length properties. Additionally, the medium parameters mainly affect the demulsification process such as temperature, pH, viscosity, and also the salinity [2]. The process is evaluated using some conventional techniques such as interfacial tensiometry, tensiometry, Dynamic Light Scattering (DLS), and bottle test. The case study of this work is the oil of Omidyie and Ydavaran regions, south in Iran. Enhanced oil recovery (EOR) is often pursued through using promising demulsifiers in industrial projects. Ionic Liquids (IL's) and some polymers are the promising candidates to improve the demulsification of water in oil recovery. The findings indicate that IL's significantly improve the oil recovery.

Keywords: demulsifier, Ionic liquid, interfacial tension, Dynamic Light Scattering, Enhanced oil recovery

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Determination of Sudan I in food samples using a modified nanostructure paste electrode

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Abstract

Sudan dyes belong to a family of industrial dyes normally used for colouring plastics and other synthetic materials. Up to now four Sudan dyes have been detected in certain food products, in particular Sudan I and Sudan IV (or Scarlet Red) [1]. Sudan I has also been adopted for colouring various foodstuffs, especially curry powder and chili powder, although the use of Sudan I in foods is now banned in many countries, because Sudan I, Sudan III, and Sudan IV have been classified as category 3 carcinogens (not classifiable as to its carcinogenicity to humans) [2] by the International Agency for Research on Cancer.[2] Sudan I is still used in some orange-coloured smoke formulations and as a colouring for cotton refuse used in chemistry experiments [2]. Therefore, determination of sudan I is very important in food samples.

In this work, a simple and high sensitivity electrochemical sensor was developed to determine Sudan I based on NiO/NPs ionic liquid modified carbon paste electrode using cyclic voltammetry, electrochemical impedance spectroscopy (EIS) and square wave voltammetry (SWV) methods. The novel sensor exhibited an obviously catalytic activity towards the oxidation of Sudan I, which can be confirmed by the increased oxidation peak current and the decreased oxidation peak potential when compared with the bare carbon paste electrode (CPE). The linear response range and detection limit were found to be 0.1–550 µM and 0.07 µM, respectively. Other species did not interfere with the determination of Sudan I at a surface of propose sensor in the optimum condition. The proposed sensor was successfully applied for the determination of Sudan I in food samples with satisfactory results.

Keywords: *Sudan I, Food analysis, Voltammetric sensor, Ionic liquid*

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Electrocatalytic determination of captopril using a ferrocene-derivative modified nanostructure carbon paste electrode

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Abstract

Hypertension (high blood pressure) is a risk factor and increases human chance of developing heart disease. For treatment of hypertension we can lose weight if it is overweight, cutting back if we drink a lot of alcohol, regular physical activity, stopping smoking, and using medication treatment with usual drugs such as captopril [1]. CAP is used to treat hypertension, congestive heart failure, diabetes kidney problems, and to improve survival after a heart attack. However, CAP is not recommended for pregnant women [2]. According to the above points, suggestion of a high sensitive and selective volammetric sensor is very important for CAP determination in drug and urine samples.

The study of electrochemical behavior and determination of captopril, as an angiotensin-converting enzyme inhibitor using a 1, l′-bis(2-phenylethan-1-ol)ferrocene modified ZnO nanoparticles carbon nanotubes paste electrode is reported. The cyclic voltammetric results indicate that the modified electrode system can remarkably enhance electrocatalytic activity toward the oxidation of captopril in aqueous buffer solution pH 8.0. Under the best experimental conditions selected, the calibration curve for captopril was linear in the concentration range from 0.09 to 450 µM and a detection limit of 0.05 µM was obtained. The influence of pH and potential interfering substances on the determination of captopril were studied. Electrochemical impedance spectroscopy was used to study the charge transfer properties at the electrode–solution interface. Finally, the sensor was examined as a selective, simple, and precise new electrochemical sensor for the determination of captopril in real samples, such as drugs and urine. Satisfactory results were obtained.

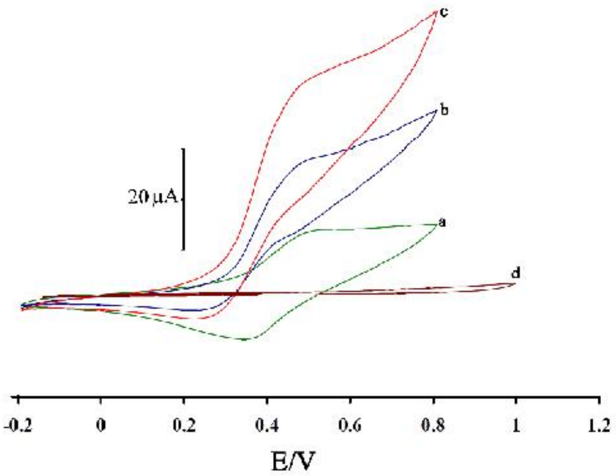

Figure 1: Cyclic voltammograms of (a) 0.1 mol L^{-1} PBS at 1,1/-BEOF/ZnO/NPs/CPE; (b) 0.1 mol L^{-1} PBS plus 1.0 mmol L^{-1} CAP at 1,1/-BEOF/CPE; (c) 0.1 mol L^{-1} PBS plus 1.0 mmol L^{-1} CAP at 1,1/-BEOF/ZnO/NPs/CPE and (d) 0.1 mol L^{-1} PBS plus 1.0 mmol L^{-1} CAP at ZnO/NPs/CPE. Conditions: Scan rate of 20 mV $s^{-1}$and pH 8.0.

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Keywords**:** *Captopril analysis, ZnO nanoparticles, Ferrocene derivative, Voltammetric analysis*

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Electrochemical Determination of Tetracycline using Glassy Carbon Electrode Modified with β-Cyclodextrin Functionalised Graphene Nano Sheet as a Host Gust Molecule

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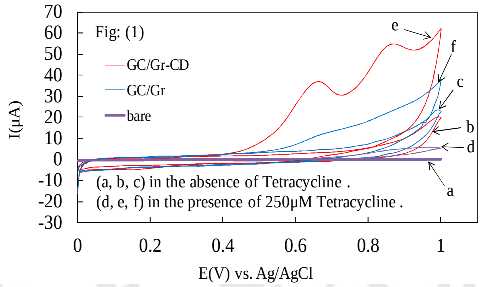
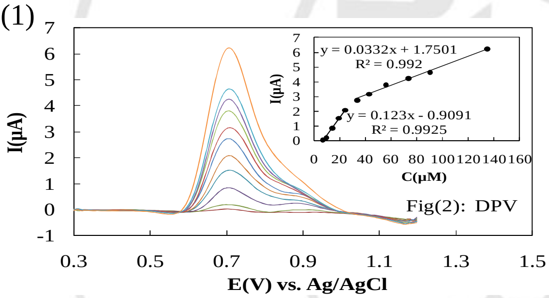
Abstract

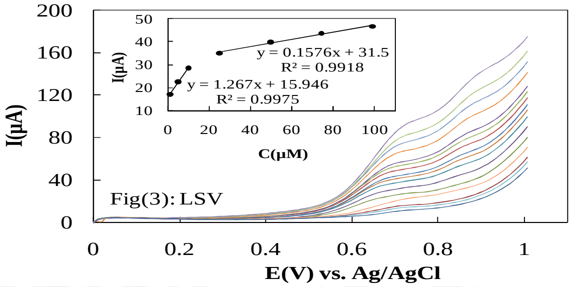
Antibiotics are one of the most important bioactive and chemotherapeutic groups of compounds made by microbiological synthesis. Tetracycline (TC) or its derivatives such as chlorte-tracycline (Chlor-TC), oxytetracycline (Oxy-TC) and doxycycline (Doxy-TC) are employed extensively as bacteriostatic and antibiotic drugs. Several analytical methods have been reported for TCs antibiotic residues determination. Chromatographic methods are the most currently applied despite they demand long and tedious extraction procedures, skilled personnel and are quite expensive. The Cyclodextrins (CD) have a truncated cone-resembled shape with a hollow cavity. The sizes of the primary and secondary sides of the CDs are dependent on the unit number of glucose. The depth of the hollow cavity is 0.78 nm for all three types of CDs. Thus, a variety of guests can be encapsulated into the cavity via the host-guest interaction in aqueous conditions and even in the solid state. On the other hand Graphene (Gr) has proved to be an excellent nanomaterial for applications in electrochemistry. because of its very large 2-D electrical conductivity, large surface area and low cost. In comparison with CNTs, two advantages of graphene are apparent, as follows. Therefore β-Cyclodextrin functionalised graphene is able simultaneously possessing unique properties of graphene and β-Cyclodextrin. In this study fabricated modified glassy carbon electrode with β-yclodextrin functionalised graphene (GC/Gr/β-CD) and applied for electrochemical measurement of TC. Cyclic voltammetry was employed to evaluate the electrochemical performance of modified electrode and compare its electrochemical performance with modified glassy carbon with graphene (GC/Gr) and bare electrode. As can be seen of fig (1) GC/Gr/β-CD is capable in TC oxidation than other two electrodes. After optimization all effective parameter in measurment such as pH, instrumental parameter we obtain calibration curve for TC determination By methods of differential pulse

voltammetry (DPV) and linear sweep voltammetry (LSV) that shown in Fig (2) to (3). In Table (1) show the results obtain from calibration curves and Compared with other works. To examine the predominant type of mass transport a study was carried out using cyclic voltammetry on scan rate effect and the result shows electrooxidation reaction is an adsorption controlled process.

Keywords: graphene, cyclodextrin, Host Gust Molecule, modified electrode, Tetracycline.







Table(1)

Analyt	Linear range	LOD	Modified electrode	Reference
TC	0.045 - 22.5 μM	0.009 μM	Pt foil	1
TC	90 - 900 μM	4.5 μM	Pt disk	2
TC	2.25 - 22.5 μM 22.5 - 225	0.23 μM	gold microelectrode	3
TC	2.5 - 100 μM	0.12 μM	multi-walled carbon nanotubes-glassy carbon electrode	4
TC	5.6 - 180 μM	0.06 μM	nickel-glassy carbon chemically modified electrode	5
TC	1 - 100 μM	0.23 μM	$Ru(bpy)^{2+}_3$ -doped silica nanoparticles/Nafion-glassy carbon electrode	6
TC	4 - 40 μM	2.8 μM	Graphite–polyurethane composite electrode	7
TC	1 - 500 μM	0.96 μM	Screen-printed gold electrode	8
TC	2.08 - 20.8 μM	0.187 μM	Gold modified microelectrode	9

	20.8 - 208				
TC	0.11 - 22 μM	0.030 μM		Multi-wall carbon nanotube-ionic liquid modified glassy carbon electrode	10
TC	0.12 - 60 μM	0.012 μM		Acetylene black modified carbon paste electrode Fe/Zn–	11
TC	0.104 - 52 μM	0.0107 μM		iron/zinc cations–exchanged montmorillonite catalyst modified glassy carbon electrode	12
TC	1 - 10 μM 25 - 100	0.23 μM	LSV	β-Cyclodextrine Functionalised Graphene Nano Sheet modified glassy carbon electrode	This work
TC	7 - 25 μM 35 - 150	0.590 μM	DPV		

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Pencil lead electrode modified with graphene oxide and gold nanoparticles as a novel sensor for the determination of tramadol in biological samples

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Abstract

Tramadol hydrochloride is a synthetic, centrally acting, analgesic agent, used for the relief of moderate to chronic pain and has no clinically relevant cardiovascular or respiratory depressant activity. Furthermore, it does not have a prostaglandin inhibitory effect [1]. The dosage of tramadol should be adjusted to the intensity of pain and to the response of an individual patient (its therapeutic plasma concentration is in the range of 100–300 ng L^{-1}) [2]. Several analytical methods described for the determination of tramadol in biological and pharmaceutical samples involve a number of high-performance liquid chromatographic (HPLC), electrochemical, spectrophotometric and potentiometric methods [3].

In the present study, electrochemical behavior of tramadol a pencil lead electrode modified with graphene oxide and gold nanoparticles is studied. Some thermodynamic and kinetic parameters using voltammetric and chronoamperometric methods were determined. The ability of this modified electrode for the determination of tramadol at trace amounts using differential puls voltammetry as a sensitive electrochemical technique was investigated. Finally developed sensor successfully used for the determination of tramadol in biological samples.

Keywords: *Tramadol, Graphene oxide, Gold nanoparticles, Pencil lead electrode*

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Voltammetric determination of naloxone at pencil lead electrode modified with graphene oxide and gold nanoparticles: Application to the analysis of biological samples

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Abstract

Naloxone is a mu-receptor antagonist used mainly for the treatment of opioid overdose and to reverse opioid-induced depression following surgery [1]. In addition, it has been shown to elevate blood pressure in patients with shock and to have a mild diuretic effect in patients with liver cirrhosis [2]. The literature survey reveals that several methods have been reported for determination of naloxone mainly including high performance liquid chromatography, high performance liquid chromatography coupled with mass spectrometry, gas–liquid chromatography, and chemiluminescence [3]. However, these methods are time consuming, expensive and often need the pretreatment step. Electrochemical methods have shown remarkable advantages in the analysis of drugs in pharmaceutical preparations and human body fluids. Therefor development of an electrochemical sensor for the determination and mechanistic investigation of naloxone is very favorable.

In this study, electrochemical behavior of naloxone at pencil lead electrode modified with graphene oxide and gold nanoparticles is investigated. Some thermodynamic and kinetic parameters using voltammetric and chronoamperometric methods were determined. Diffusion coefficient of naloxone (D), charge transfer coefficient (α), n_a and n were calculated and the possible mechanism for oxidation of naloxone was proposed. Finally the ability of the developed modified electrode for the determination of naloxone at trace amounts was investigated. Also developed sensor successfully used for the determination of naloxone in biological samples.

Keywords: *Naloxone, Graphene oxide, Gold nanoparticles, Pencil lead electrode*

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Simultaneous determination of ascorbic acid and NADH in pharmaceutical and biological samples using voltammetric sensor

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Abstract

Vitamins play significant roles in human bodily functions such as immunity, metabolism and digestion. According to experts, vitamin C is one of the safest and most effective nutrients in food science. Most of the studies shows used 500 daily milligrams of vitamin C is necessary to achieve health results. Therefore, it is very important for determination of vitamin C in food samples. Nicotin amide adenine dinucleotide (NADH) is an important coenzyme and plays a key and virtual role in energy metabolism by accepting and donating electrons. On the other hand, NADH oxidation in ocular tissues can be effective on the presence of ascorbic acid [1]. So, determination of the above compounds is very important in biological, food and pharmaceutical samples. A high sensitive sensor based on carbon paste electrode modified with CdO nanoparticle and 1-methyl-3-butylimidazolium bromide was used for the voltammetric analysis of vitamin C in the presence of nicotin amide adenine dinucleotide. The high sensitive sensor shows excellent enhancement and electrocatalytic activity towards vitamin C. The variation of pH shows the number of proton is equal to number of electron for vitamin C electrooxidation. The electro-oxidation peaks current of vitamin C and nicotin amide adenine dinucleotide increased linearly with their concentration in the ranges of 0.07–480 µmol L^{-1} vitamin C and 0.5–700 µmol L^{-1} nicotin amide adenine dinucleotide. The limit of detection for vitamin C and nicotin amide adenine dinucleotide were 0.03 µmol L^{-1} and 0.1 µmol L^{-1}, respectively. Simultaneous determination of vitamin C and nicotin amide adenine dinucleotide was investigated by using square wave voltametry technique. The proposed sensor showed good stability, sensitivity, selectivity, reproducibility and can be used for some important food samples analysis.

Keywords: *Ascorbic acid; NADH, Ionic liquids, Voltammetric analysis*

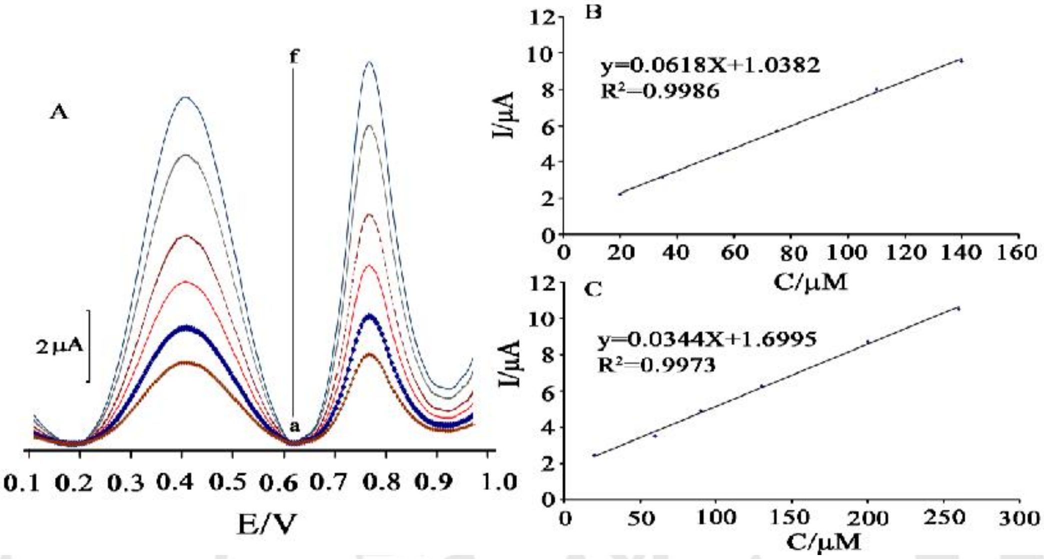

Fig. 1. The plots of the electrocatalytic peak current as a function of vitamin C concentration. Inset; SWVs of CdO/NPs/ILs/CPE in 0.1 M PBS (pH 7.0) containing different concentrations of vitamin C–NADH in µmol L^{-1}. a–f; 20.0+20.0, 35.0+60.0, 55.0+90.0, 75.0+130.0, 110.0+200, and 140.0+260.0, respectively.

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Determination of Streptomycin Based on Grapheneoxide Oracet blue Silver Nanoparticles modified Screen Printed Electrode

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Introduction

Streptomycin, the earliest of the aminoglycosides, that is an antimicrobial organic base produced by Streptomyces griseous and has found widespread use in both human and veterinary medicine [1,2]. In agriculture it is used to control bacterial and fungal diseases of selected fruits, vegetables, seeds, specialized field crops, ornamental crops and in ornamental ponds and aquaria to control algae [3]. Although antibiotic residues in food have no direct toxic effect on human health, numerous adverse effects can range from fever and nausea to major allergic reactions including photodermatitis and anaphylaxis [4]. Therefore introducing a selective and sensitive method for accurate determination of antibiotics is crucial. . Recently, electrochemical techniques have been applied to determine antibiotics because they offer an opportunity for portable, rapid and cheap methodologies.

Purpose of research

In this work, the electrocatalytic oxidation of Streptomycin on a screen printed electrode modified with graphenoxide, oracet blue and silver nanoparticles (GOBAgNPs-SPE) has been studied. The (OBAgNPs-SPE) shows highly catalytic activity toward Streptomycin electrooxidation. The results indicated that Streptomycin peak potential at GOBAgNPs−SPE shifted for 340 mV to negative values as compared with bare electrode surface. Fig.1 shows the electrocatalytic effect of GOBAgNPs-SPE toward oxidation of STR. The kinetic parameters, such as the electron transfer coefficient, α, and the standard heterogeneous rate constant, k’, for oxidation of Streptomycin at the GOBAgNPs-SPE were determined. The amperometric detection of Streptomycin was carried out at 400 mV in a 0.1 mol L^{-1} phosphate buffer solution (pH 7.0) resulting in two linear response ranges of 0.4 to 240.0 nM and 240.0 to 720.0 nM and the detection limit of 0.17 nM.

Conclusion

The GOBAgNPs−SPE can decrease the oxidation peak potentials of Streptomycin. Therefore, determination of the analyte (Streptomycin) is possible without any interference. Moreover, the GOBAgNPs−SPE was used to determine Streptomycin in real samples with satisfactory results.

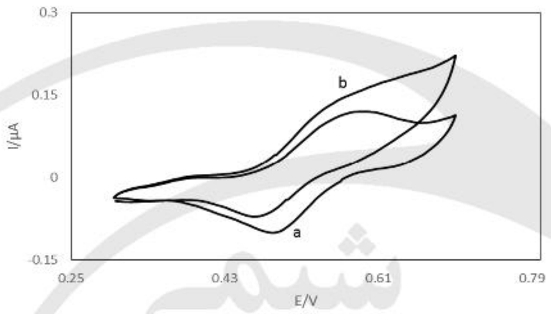

Fig. 1 Cyclic voltammograms of the GOBSNPs-SPE, in the 0.1 M phosphate buffer (pH 7.0) at scan rate 20 mV s^{-1} in (b) absence and (a) presence of 0.1 mM STR.

Keywords: *Graphenoxide; Oracet blue; Streptomycin; Silver Nanoparticle; Screen printed electrode*

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Electrodeposition of PbS nanostructure on stainless steel 304 substrate in nitric acid solution and cyclic voltammetry and chemical impedance spectroscopy studies

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Abstract

Lead chalcogenides (PbS, PbSe and PbTe) and their alloys have been the subject of considerable research due to the technological importance of these materials, in crystalline and polycrystalline forms [1]. In this work, preparation of nanostructure film of lead sulfide used of electrochemical deposition method. Electrochemical cell containing sulfur prepare and lead salt precursors at optimised temperature and pH in present of three electrodes involve refrence Ag/AgCl (3 M Cl^-) electrode, pt electrode as the counter electrode and stainless steel 304 as the working electrode provided and deposition process was performed using cyclic voltametry. After that, SEM results and EDX of prepared sampele, and proved formation of lead sulfide film with nanostructure and a stoichiometric ratio of 1:1. Also the XRD test results approved formation of nanocrystals of lead sulfide. In a similar experiment to evaluate the effect of complexing agent on the morphology of the prepared film, added certain amount of complexing agent EDTA into the electrolyte solution and result of deposition compared with the sample that provide in absence EDTA by AFM analysis and conclusion significant that the surface in present of EDTA is mostly uniform. Amount of band gap in prepared film obtained with deposition of lead sulfide film on transparent glass tunicated with tin doped and then performed reflection uv test and it was equal to 3.5 eV. Then inorder to calculat the flat band potential and concentration of majority carriers, we used of chemical impedance spectroscopy and nyquist curve of prepared film obtained. Then according to results of this curves, mott-schottky plot for obtaining of flat band potential and concentration of majority carriers drawed and accord data produced.

Keywords: *Impedance spectroscopy, Equivalent circuit, Semiconductor, Lead sulfide, Mott-Schottky plot, cyclic voltammetry*

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Fabrication of Sensitive Electrochemical Arsenic (III) Aptasensor

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Abstract

Arsenic (III) contamination in water is a serious worldwide threat for human health. According to the world health organization’s (WHO) report, the maximum permissible contamination of arsenic in the drinking water is 10 ppb [1]. So early detection of arsenic in low concentration is important. Therefore in this work, a sensitive electrochemical aptasensor was developed for detection of As (III). Various chitosan-nanocomposites were investigated for immobilization of As (III) aptamer molecules on the surface of glassy carbon electrode (GCE) [2]. Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), Fourier transform infrared spectroscopy (FT-IR) and ultraviolet-visible spectroscopy (UV-Vis) were used for characterization of fabricated aptasensor. In the present work the effect of various variables such as concentration of glutaraldehyde linker, glutaraldehyde incubation time, capture probe concentration, capture probe incubation time, aptamer probe concentration, aptamer probe incubation time and nanocomposite composition were investigated. Ander optimum conditions very sensitive As (III) aptasensor was fabricated. Electrochemical impedance spectroscopy was used to detection of As (III) concentration [3]. The fabricated impidimetric As (III) aptasensor showed very good analytical parameter such as high sensitivity, low detection limit, wide linear range and high selectivity.

Keywords: *Aptasensor, Arsenic (III), Electrochemical Impedance Spectroscopy, Electrode*

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Preparation of Poly (vinyl alcohol)/cupric acetate Nanofibers by Electrospinning Method: Application for Hydrazine Hydrate Electrooxidation

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Abstract

In this work, polyvinyl alcohol/cupric acetate nanofibers were prepared by electrospinning method and copper oxide nanoparticles (CuO-NPs) were produced after thermal treatment. The results demonstrated that the renewable CuO-NPs modified carbon paste electrode exhibited high electrocatalytic activity and good performance towards hydrazine hydrate oxidation.

Keywords: *Electrospinning; Nanofiber; Copper oxide nanoparticle; Hydrazine hydrate; Electrocatalysis*

Introduction

Electrospinning is a well-known and versatile method to fabricate continuous fibers with diameter ranging from tens of nanometers to several micrometers with surface-to-volume ratio [1]. Hydrazine with high hydrogen content is an ideal candidate fuel for direct hydrazine fuel cell [2]. Besides the precious metals, some non-noble metals and their alloys were used due to relatively low cost and high activities [3]. In this work, a method of generating a rapidly renewable and reproducible CuO-NPs bulk modified carbon paste electrode (CPE) was proposed.

Electrospinning process

In a typical synthesis, PVA aqueous solution (7.3 wt %) was prepared by dissolving PVA powder in preheated distilled water under magnetic stirring. Triton X-100 was added to 23.72 g PVA aqueous solution under continuation of stirring. Then, copper acetate was added slowly into the above solution until a viscous gel was obtained. The electrospun fibers were collected on the aluminum foil covering the drum. Finally, the obtained fibers were calcined at air in a furnace to form the electrospun CuO-NPs.

Results

Fig. 1A shows the SEM image of the precursor, indicating that a large quantity of nanofibers with diameter ranging from 200-300 nm with tens of micrometers in length can be obtained. Fig. 1B shows the morphology of the CuO nanoparticles with sizes at about 60-80 nm.

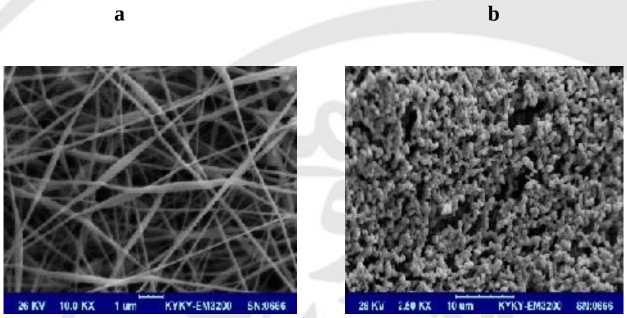

Fig. 1. SEM images of the PVA/Cu(OAc)$_2$ nanofibers **(a)** and electrospun CuO-NPs **(b).**

Electrocatalytic oxidation of hydrazine

The catalytic activity of the electrocatalyst at the hydrazine oxidation was investigated by cyclic voltammetry (Fig. 2). The oxidation peak potential was 0.75 and 0.45 V at the bare CPE and non-electrospun CuO/CPE, respectively, whereas it was shifted to 0.35 V at the CuO-NPs/CPE.

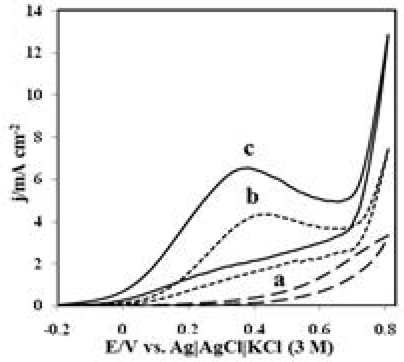

Fig. 2. CVs of the CPE (a), CuO/CPE (b) and electrospun CuO-NPs/CPE (c) in the presence of hydrazine in 0.2 M NaOH solution at $\upsilon = 20$ mV s^{-1}.

Conclusion

The SEM showed that ultrafine CuO-NPs were formed after calcination for 5 h in air. The proposed electrode exhibited high electrocatalytic activity towards hydrazine oxidation in alkaline solution, showing a satisfactory stability and durability when stored in ambient conditions.

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Fabrication of sensitive electrochemical aptasensor for detection of mercury ion using graphene based nanomaterials

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Abstract

Mercury (Hg) is an extremely toxic heavy metal, both to human health and to the environment. Mercury ion has been implicated in a number of fatal diseases such as Minamata disease, pulmonary edema, cyanosis and nephrotic syndrome [1]. According to the US Environmental Protection Agency (EPA) and World Health Organization (WHO) reports, the maximum allowable level of Hg^{2+} ions in drinking water is about 10 nM which is much lower than the detection limits of most available assays [2]. In this work, an electrochemical mercury (II) aptasensor was fabricated. Various ratio of chitosan/reduced graphene oxide (rGO) nanocomposite investigated for immobilization of aptamer molecules on the surface of glassy carbon electrode [3]. Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), Fourier transform infrared spectroscopy FT-IR, transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were used for characterization of fabricated aptasensor. In the present work, the effect of various variables such as glutaraldehyde linker concentration, glutaraldehyde incubation time, aptamer probe concentration and incubation time, and nanocomposite composition were investigated. Under optimum conditions, very sensitive mercury aptasensor was fabricated. Electrochemical impedance spectroscopy was used for detection of Hg (II) concentration. The fabricated impidimetric Hg (II) aptasensor showed very good analytical parameter such as high sensitivity, low detection limit, wide linear range and high selectivity.

Keywords: Mercury Ion, Aptasensor, Electrochemical Sensor, Graphene

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Electrocatalytic oxidation of warfarin using poly ionic liquid/Ni complex nanocomposite and nafion

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Abstract

Warfarin sodium, 4-hydroxy-3-(3-oxo-1-phenyl-butyl) coumarin sodium, is a widely used anti-coagulant drug prescribed to treat the blood clots (thrombosis) which can form in both the arteries and veins. The formation of thrombosis can be attributed to an induction of platelet adhesiveness, or an increase in the activation of clotting factors, such as prothrombin. Thrombosis can severely reduce or stop blood flow in the circulation, resulting in permanent damage or death [1]. Warfarin sodium is an antagonist of Vitamin K, and inhibits the synthesis of prothrombin leading to a decrease in the ability of the blood to form clots [2]. The drug is almost completely bound to the surface of plasma proteins, principally albumin. It is bio-transformed in the liver into inactive metabolites, which are excreted via the kidney with urine. Warfarin sodium usually detectable in the plasma within 1 h of oral administration and peak blood concentrations are reached within 2–4 h of administration [3]. Ionic liquids, which have been widely promoted as green and ‘designable’ solvents, are attracting considerable attention due to their chemical stability, low flammability, negligible vapor pressure, high ionic conductivity, and wide electrochemical window. Depending on their unique properties, ILs can be used in a wide variety of research fields, such as solvents for organic synthesis and polymerization reactions, catalysts, electrochemistry, and media for extraction processes [4]. Polymeric nanoparticles have received increasing attention in both theoretical and applied research fields due to their potential applications as nanocarriers for catalysts, molecules with electronic and photonic functions, biological and medical species, drug carriers [5].In this paper, an electrochemical method for the determination of warfarin at nanaocomposite of [Ni(CN)2(NH3] and poly[MImEO2BS] and nafion (NCPMNINGCE) film modified glassy carbon electrode (GCE) was presented by using cyclic differential pulse voltammetry. The

electrochemical behavior of warfarin was investigated with cyclic voltammetry. It has been found that the oxidation of warfarin at the surface of modified electrode occurs at a potential of about 230 mV less positive than that of an unmodified carbon paste electrode,. (SWV) exhibits linear dynamic range from 1.0×10^{-6} to1.0×10^{-4} M and detection limits of 1.5×10^{-7} M for warfarin. The present method was applied to the determination of warfarin in commercial pharmaceutical samples.

Keywords: *warfarin, poly ionic liquids, nanocomposite, glassy carbon electrode*

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Electrocatalytic Glucose Oxidation Based on Nickel Nanoparticles/PEDOT: PSS Nanocomposite

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Abstract

Glucose is a simple monosaccharide found in plants. It is one of the three dietary monosaccharides, along with fructose and galactose that are absorbed directly into the bloodstream during digestion. The determination of glucose concentration is very important in clinical, biological samples and chemicals as well as in food processing and fermentation. Many efforts have been tried for the direct electro-oxidation of glucose on different substrates, for example metal-complex[1-2]. A sensitive non-enzymatic electrochemical glucose sensor with excellent sensitivity, very low detection limit and low glucose oxidation potential was prepared by electrodeposed of nickel nanoparticles on the surface of PEDOT:PSS suspending media. Electrochemical activity of the electrode toward the oxidation of glucose was studied using cyclic voltammetry, chronoamperometry, linear sweep voltammetry and amperometry. Electrochemical measurements indicated that the high sensitivity of 162.91 $\mu A \mu M^{-1} cm^{-2}$ and a detection limit of 0.028 µM was obtain. In addition, the interference from the oxidation of uric acid, dopamine, acetamidophenol and ascorbic acid could be effectively avoided. Meanwhile, the non-enzymatic glucose sensors exhibited excellent selectivity, stability and repeatability. Thus, this novel non-enzyme sensor has potential application in glucose detection [3-4].

Keywords*: *Glucose, Nanoparticle, Sensor, PEDOT: PSS

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A New potentiometric Sensor for Determination of Vitamin B6 Based on Nano silver Modified Carbon Paste Electrode

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Abstract

This research introduces design and construction of a nano composite carbon paste electrode for fast and simple determination of Vitamin B6 in pharmaceutical formulation. A potentiometric sensor for Vitamin B6 (VB6) based on carbon paste electrode modified by silver nanoparticles were prepared and fully characterized in terms of composition, usable pH range. This electrode illustrated fast, stable and Nernstian response over a relatively wide concentration range of 1×10^{-6} -1×10^{-2} M with a detection limit of 4.84×10^{-7} M was obtained for vitamin B6. Validation of the method shows suitability of the sensors for application in quality control analysis of drug in pharmaceutical formulation.

Keywords: *potentiometric, Carbon Paste Electrode, Vitamin B6, Nano silver*

Introduction

Vitamin B6 (VB6) plays a vital role in the activities of many enzymes. It is essential for the breakdown and use of proteins, carbohydrates and fats from food and for the release of stored carbohydrates for energy. It is involved in the production of red blood cells and antibodies and in the maintenance of a healthy skin and healthy digestion. It is also important for normal function of the nervous system and several hormones. Therefore, developing a sensitive and simple analysis method for VB6 is very important in food and pharmaceutical industries[1-2]. The advantages of carbon paste electrodes, such as chemical inertness, robustness, low cost, renewability, very low background current, stable response, low ohmic resistance and no need for internal solution over conventional polymeric membrane electrodes has attracted the attention of researchers in recent years [3-6].

The aim of this study was to measure the vitamin B_6 using silver nanoparticles modified carbon paste electrodes (CPE). The sensor could be used successfully in the estimation of vitamin B6 in injection samples.

Materials and equipment

Vitamin B_6 drug, Silver nitrate ($AgNO_3$), Sodium boron hydrate ($NaBH_4$), Dry methanol, Graphite powder, Silicon oil, Phosphoric acid, Purchased from Merck. All potentials were measured with potentiometer (model PTR 79), which is made of a calomel electrode as a reference and a carbon paste electrode as an identifier, to measure the amount of Vitamin B6. On the other hand, a pH meter Metrohom (Model EIL 744) to measure pH solutions. All solutions prepared by double distillated water.

Conclusion

In the present work, a potentiometric sensor was constructed for determination of Vitamin B6 in pharmaceutical formulation. The sensors demonstrated a potential responses across the range of 1×10^{-6} -1×10^{-2} M with detection limit of 4.84×10^{-7} M for Vitamin B6. The best electrode performance in case of CPE was obtained with the paste composition of 45.5% graphite, 45.5% psilicon oil and 9% nanosilver. This electrode illustrated fast, stable and Nernstian response over a relatively wide concentration range.

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Electrocatalytic Oxidation of Glucose on the Ni-Al LDH/GQD/RGO Nanocomposite: Electrochemical determination

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Abstract

Development of the fast, sensitive and selective sensors for glucose determination is important in food industry, clinical analysis, biotechnology and many other areas [1]. In the recent years, remarkable attention has been paid to develop non-enzymatic modified electrodes to solve the disadvantages of the enzyme-modified electrodes in the determination of glucose, such as instability, high cost, complicated immobilization procedure and critical operating situation [1-3]. In this work a non-enzymatic glucose sensor based on a new Ni-Al LDH/GQD/RGO nanocompositewas developed. Firstly, Ni-Al LDH/GQD/RGO nanocomposite was synthetized via co-precipitation method and characterized by X-ray diffraction and cyclic voltammetry. Secondly, the electrocatalytic activity of the Ni-Al LDH/GQD/RGO nanocomposite modified electrode was studied toward the oxidation of the glucose in 0.1 M of NaOH solution. Glucose was oxidized at potential about -0.037 V vs SCE on the Ni-Al LDH/GQD/RGO nanocomposite modified electrode and corresponding anodic signal greatly increases by increasing the glucose concentration.The calibration plot is linear over the wide concentration range with a unique correlation coefficient and low detection limit.

Keywords: Electrochemical sensor, Glucose determination, Non-enzymatic, Electrocatalysis, Nanocomposite

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Sensitive electrochemical detection of risperidone with a poly ionic liquid/Ni complex nanocomposite and nafion modified glassy carbon electrode

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Abstract

Risperidone (RIS) (3-[2-[4-(6-fluoro-1,2-benzisoxazol-3-yl)-1-piperidinyl] ethyl]-6,7,8,9-tetrahydro- 2-methyl 4H-pyrido[1,2-a] pyrimidin-4-one) is a benzisoxazole antipsychotagent, used to treat schizophrenia and other psychoses. It exerts its effect by blocking serotonin and dopamine receptors and causes a lower incidence of extrapyramidal side effects than standard neuroleptic drugs. It is effective in the treatment of schizophrenia and other psychiatric illnesses in adults and children including pervasive developmental disorders, autism and attention deficit disorder. For adequate support of clinical studies with RIS, an analytical method is required for the determination of plasma levels of RIS. It is necessary to establish a simple, accurate and specific analytical technique, which permits measurements of RIS in biological specimens at different therapeutic levels [1]. Ionic liquids, given their favorable properties such as high conductivity, good chemical and electrochemical stability, and negligible volatility, are now under investigation for use in many electrochemical energy conversion devices [2]. Polymeric ionic liquids (PILs) are polymeric analogues of ionic liquids obtained via polymerization of ionic liquid monomers, mainly imidazolium based ionic liquid monomers. Being a novel polymeric material, PILs exhibit the advantages of both ionic liquids and polymers, such as enhanced ionic conductivity, thermal stability and excellent mechanical properties. Owing to their unique properties, PILs have attracted great interest in various fields. For example, PILs have been proved to be effective stabilizer or modifier for the synthesis and functionalization of various nanomaterials, such as noble metal nanoparticles. With the modification of PILs, the as-synthesized nanomaterials not only maintained their own properties, but also are endowed with

improved conductivity, excellent hydrophilicity and positive charged [3]. In this study, a glassy carbon electrode (GCE) modified with nanaocomposite of [Ni(CN)2(NH3] and poly[MImEO2BS] and nafion (NCPMNINGCE), was used to prepare a novel electrochemical sensor for the detection of RIS. Under the optimum pH, It has been found that the oxidation of risperidone at the surface of modified electrode occurs at a potential of about 130 mV less positive than that of an unmodified carbon paste electrode. (SWV) exhibits linear dynamic range from 5.0×10^{-7} to 8.0×10^{-5} M and detection limits of 7.3×10^{-8} M for risperidone. The present method was applied to the determination of RIS in some real samples.

Keywords: *risperidone, poly ionic liquids, nanocomposite, glassy carbon electrode*

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Voltammetric determination of butylated hydroxytoluene using modified nanostructure carbon paste electrode

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Abstract

Butylated hydroxytoluene (BHT), also known as dibutylhydroxytoluene, is a lipophilic organic compound, chemically a derivative of phenol, that is useful for its antioxidant properties [1]. European and U.S. regulations allow small amounts to be used as a food additive. In addition to this use, BHT is widely used to prevent oxidation in fluids (e.g. fuel, oil) and other materials where free radicalsmust be controlled.

In this research the electrochemistry of BHT was studied by electrochemical methods at a carbon paste electrode modified by CdO/CNTs and ionic liquids as a binder. For this goal we describe synthesis of CdO/CNTs using chemical precipitation method and then characterize with different methods such as scanning electron microscopy (SEM) and X-ray diffraction (XRD) in the first step. The oxidation peak potential of the BHT at a surface of modified electrode appeared at 570 mV that was about 100 mV lower than the oxidation peak potential at the surface of the unmodified carbon paste electrode (CPE) under similar condition. Under the optimized conditions, the oxidation peak current of BHT showed linear dynamic range (in 0.1–600 µM) with a detection limit of 0.06 µM, using square wave voltammetry (SWV) method. The proposed sensor was successfully applied for the determination of BHT MDOP in food samples.

Keywords: *Butylated hydroxytoluene, CdO/CNTs, Modified electrode, Food analysis*

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Functionalization of Graphene Nanosheets with 4-Amino Benzoic Acid and its Application in Pb^{2+} Sensing

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Abstract

Herein, reduced graphene oxide (RGO) was functionalized with benzoic acid via using the diazonium grafting route to produced benzoic acid functionalized graphene (BFG). The prepared RGO and BFG were characterized by XRD, FT-IR, TEM, AFM and electrochemical methods. Then a carbon paste electrode was modified with BFG (CPE/BFG). The prepared modified electrode, electrochemically characterized in the presence of $Fe(CN)_6]^{3-/4-}$ as a redox probe. Sensing ability of the modified electrode toward two valet cations was evaluated by following striping voltammetry responses of pre-concentrated ions on top of the CPE/BFG. The CPE/BFG electrode showed selective response to Pb^{2+} ion. Consequently, the electrode response was evaluated as a function of solution pH, pre-concentration time, and ion concentrations. Finally, in optimized conditions, a linear ranges from1.0×10^{-9} to 1.0×10^{-3} M Pb^{2+} was observed. The obtained results will be presented and described here.

Keywords: *Graphene, Surface functionalization, Modified electrode, Pb^{2+} detection.*

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Determination of epinephrine using a carbone paste electrode modified with core shell nanocomposite and modifier

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Abstract

Epinephrine (EP), commonly called adrenaline, is one of the important catecholamine neurotransmitters in the mammalian central nervous system and plays a very important role in the function of the central nervous, hormonal, and cardiovascular systems. Many diseases are related to a change of catecholamine concentration, therefore it is necessary to develop quantitative methods for the determination of catecholamine concentration in order to study its physiological function and to be able to diagnose some diseases in the clinical medicine field [1]. The electrochemical methods using chemically modified electrodes (CMEs) have been widely used as sensitive and selective analytical methods for the detection of the trace amount of biologically important compounds [2].One of the most important properties of CMEs has been their ability to catalyze the electrode process via significant decreasing of overpotential respect to relatively selective interaction of the electron mediator with the target analyte in a coordination fashion. These electrodes are capable to considerably enhance the selectivity in the electroanalytical methods [3]. Some advantages of using themodified electrode are ease of preparation, low cost, potential window, ease modification, excellent electrical conductivity and increasing the surface of the electrode [4]. In this work, a sensitive and selective electrochemical method for the determination of EP was developed using a modified carbon paste electrode (MCPE) with modifier andcore–shell magnetic nanoparticles. The electrochemical response characteristics of the modified electrode toward EP were investigated by cyclic and square wave voltammetry. It has been found that under optimum condition (pH 7.0) in cyclic voltammetry, the oxidation of epinephrine occurs at a potential about 100 mV less positive than that of an unmodified carbon paste electrode.

Keywords: *Epinephrine, Core–shell magnetic nanoparticle, Electrocatalytic, Carbon paste electrode, Modifier*

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Modification of carbon paste electrode with synthesized aluminum oxide nanoparticles for determination of gallic acid by cyclic voltammetry

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Abstract

In this work, aluminum oxide nanoparticles were prepared by using microwave irradiation of aluminum nitrate solution in basic medium. The sample characterization has been achieved by powder X-ray diffraction (XRD) and scanning electron microscopy (SEM). The effect of microwave radiation power and irradiation time on the final morphology of nano-Al_2O_3 has been investigated. The results showed that the best morphology was obtained at 360W and 4 min. Then the electrochemical behavior of gallic acid is investigated on the surface of a carbon-paste electrode modified with Al_2O_3 nanoparticles. Cyclic voltammetry study of the modified electrode demonstrated that the anodic peak current was enhanced by 2.5 fold compared with the non modified electrode and the current was due to diffusion process. The electrochemical behavior was further described by characterization studies of pH, scan rate, supporting electrolyte and concentration of gallic acid. The Al_2O_3-carbon paste electrode has a limit of detection of 4μM with linear range between 0.01 to 1 mM. Also good recovery and reproducibility was obtained when this modified electrod used for determination of gallic acid in real sample.

Keywords: *aluminum oxide nanoparticles, Microwave, Cyclic voltammetry, Gallic acid.*

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Simultaneous measurement of uric acid and dopamine using electrode modified with the carbon Nano tube and copper- Quinizarine nanoparticles.

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Abstract

One of the best methods for simultaneous determination of dopamine (DA) and uric acid (UA) in biological samples, without interferences of other species, is electrochemical methods using modified electrodes. In this research cupper - Quinizarine nanoparticles (Cu – AQ-NPS) were synthesized via co-precipitation method and then were mixed with Singel wall carbon nano tube(SWCNT). This mixture was utilized for the modification of the surface of a glassy carbon electrode. The modified electrode was used for simultaneous determination of DA and UA (Fig.1).

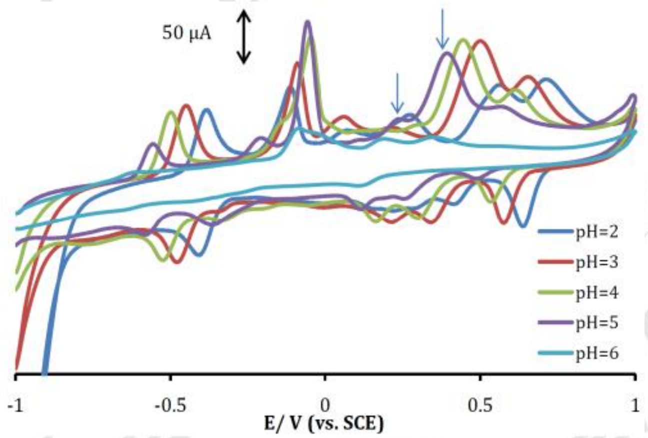

Fig. 1. The voltagram of GC/CNT/Cu-AQ-NPs in pH=2-6 in presence of 39.70 μM of both analytes.

Study the electrochemical behavior of the modified electrode in acetate buffer solution with pH=5 using cyclic voltammetry technique revealed that this electrode could exhibit an oxidation peak for DA and also an good oxidation peak for UA (Fig. 2, 3). Under optimized conditions the detection limit were obtained as 0.88 μM and 1.42 μM for DA and UA, respectively. Precision and accuracy of the proposed method for simultaneous analysis of DA and UA are in acceptable

range and eventually the modified electrode was successfully used for determination of DA and UA in human blood serum samples.

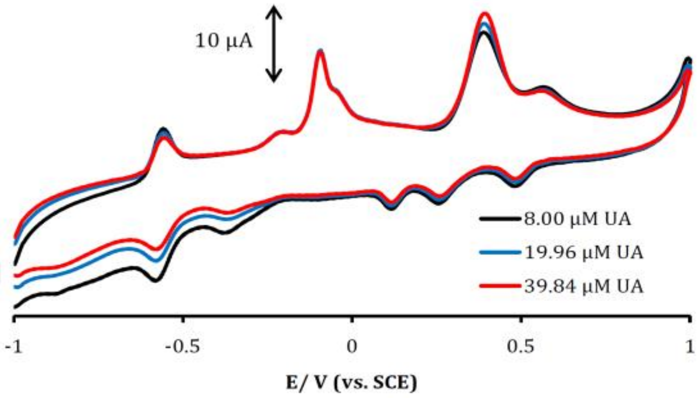

Fig. 2. Cyclic voltagram of GC/CNT/Cu-AQ-NPs in pH=5 in presence of different concentrations of UA

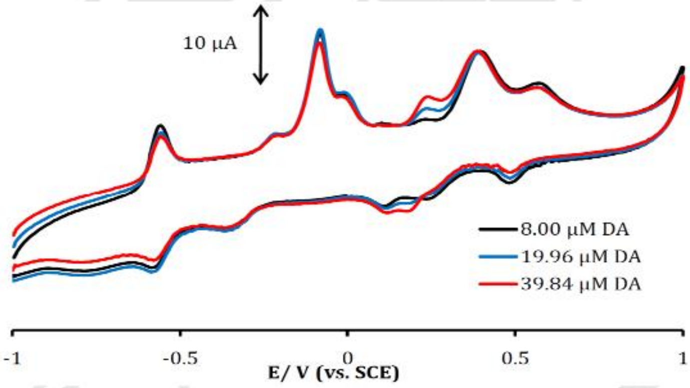

Fig. 3. Cyclic voltagram of GC/CNT/Cu-AQ-NPs in pH=5 in presence of different concentrations of DA

Keywords: *Dopamine, Uric acid, Cupper - Quinizarine Nanoparticles, Modified Electrode*

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Iron oxide nanoparticles modified carbon paste electrode as an effective electrochemical sensor for sensitive voltammetric determination of ascorbic acid

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Abstract

This research describes the development and electrochemical utilization of iron oxide nanoparticles on a multi walled modified carbon paste electrode. The electrochemical behavior of ascorbic acid on this modified electrode was studied using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) techniques. The electrochemical profile of the prepared modified electrode by cyclic voltammetry showed a considerable shift of the oxidation peak potential of ascorbic acid to less positive value and the anodic peak current was enhanced several times in comparison to the unmodified carbon paste electrode. The effect of some experimental parameters such as pH, scan rate, concentration of ascorbic acid and supporting electrolyte were investigated. The results exhibited that the oxidation of ascorbic acid was irreversible and demonstrated diffusion controlled process depending on pH. At the optimum conditions, the concentration of ascorbic acid in 0.1 M phosphate buffer solution at pH 6.0 was performed by using cyclic voltammetry in a linear range of 0.05 to 7.5 mM with a correlation coefficient of 0.997 and detection limit of 0.001 mM and using differential pulse voltammetry in a linear range of 0.05 to 7.5 mM with a correlati0n coefficient of 0.999. These results show that the modified carbon paste electrode has high sensitivity, reproducibility and repeatability. This electrode also used for determination of ascorbic acid in real samples.

Keywords**:** *Ascorbic acid, cyclic voltammetry, differential pulse voltammetry, iron oxide nanoparticles, Carbon paste electrode.*

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Application of bimetallic Pt-Pd /graphene nanosheets for determination of environmental pollution such as hydrazine

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Introduction

Hydrazine is a powerful reducing agent and widely used in various fields, such as racket fuel and synthesis of insecticides. Despite this advantage, hydrazine is a toxic material. Therefore, an easy and sensitive analytical method for detection of hydrazine is necessary. [1]. graphene is a new class of carbon material with large surface area (2675m^{2}g^{-1}) and high electrical conductivity used in sensors. [2]. In this work, bimetallic Pt-Pd nanoparticles due to electrocatalytic activity [3] were deposited on the surface of graphene, then the modified electrode was applied for electrochemical oxidation and detection of hydrazine. Electrocatalytic activity of a bimetallic Pt-Pd nanoparticle/ electrochemically reduced graphene (ERGO)/ glassy carbon electrode (GCE) has been studied by cyclic voltammetry and amperometry for determination of hydrazine.

Keywords: *Hydrazine, Graphene, Nanoparticles, Bimetallic*

Experimental

Platinum wire, Ag|AgCl (3M KCl solution) and GCE were used as counter, reference and working electrodes, respectively. At first, graphite oxide (GO) was deposited on GCE and then GO film was electrochemically reduced to (ERGO) in 0.5 M $NaNO_3$ solution. After that, bimetallic Pt-Pd nanoparticles were deposited on the surface of ERGO. Finally, this electrode was used as working electrode for detection of hydrazine.

Result and discussion

Fig.1 shows the electrochemical response of 2mM hydrazine in 0.1 M NaOH solution at different electrode investigated by cyclic voltammogram (CV). At bare GCE, a relatively small oxidation peak with the potential of 0.82 V is appeared for oxidation of hydrazine (Fig. 1a). At ERGO/GCE, an enhancement in oxidation peak current of hydrazine is observed, which could be attributed to the large specific surface area and high conductivity of ERGO. Also, at bimetallic

Pt-Pd /ERGO/GCE (Fig. 1b), the oxidation current of hydrazine increases greatly and oxidation potential shifts negatively to -0.71 V. This indicates the synergistic effect of ERGO and Pt –Pd and faster electron transfer rate of hydrazine oxidation on modified electrode. Fig.2 indicates amperometric response of modified electrode with addition of hydrazine with concentration in the range of 7µM-6500. The detection limit is calculated 5.3 µM.

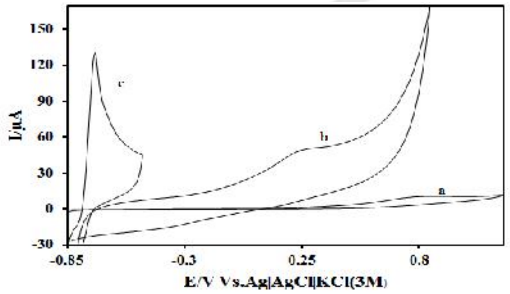

Fig.1.show the cyclic voltammetry (CV) of (a) GCE, (b) ERGO/GCE and (c) Pt-Pd/ERGO/ERGO in 0.1M NaOH Solution in the presence of 2mM Hydrazine at Scan rate of 0.05 V s^{-1}.

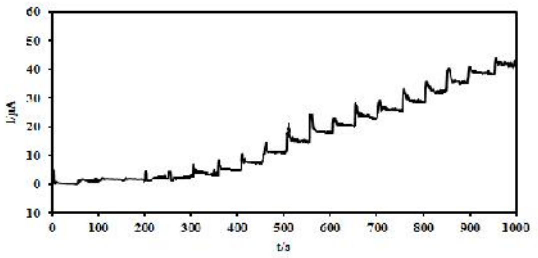

Fig.2 Amperometric response of bimetallic Pt-Pd/ERGO/GCE by stepwise addition of hydrazine in to 0.1 M NaOH solution.

Conclusions

In this work, bimetallic Pt-Pd was successfully deposited on ERGO film. The modified electrode shows good electrocatalytic activity for hydrazine oxidation by increasing the oxidation peak and decreasing oxidation overpotential. The sensor indicates remarkable analytical performance, including rapid response and high sensitivity.

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Synthesis and characterization of copper oxide nanoparticles by microwave and modified carbon paste electrode with synthesized nanoparticles as a sensor for determination of ascorbic acid

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Abstract

Microwave irradiation as a heating method has found a number of applications in chemistry. The microwave synthesis, which is generally quite fast, simple, and energy efficient, has been developed, and widely used for nanoparticles and ceramic materials, etc. Compared with conventional method, microwave synthesis has the advantages of very short time, small particle size, narrow particle size distribution, and high purity. In this study, copper oxide nanoparticles were prepared by microwave irradiation of copper nitrate solution in basic medium. The effect of irradiation time and microwave radiation power on the final morphology of nano-CuO obtained through the microwave assisted technique has been investigated. The characterization of the samples has been carried out by scanning electron microscopy (SEM) and powder X-ray diffraction (XRD). The results showed the best morphology was obtained at 540W and 2 min. Then The electrochemical behavior of oxalic acid is investigated on the surface of a carbon-paste electrode modified with CuO nanoparticles. Cyclic voltammetry study of the modified electrode indicated that the anodic peak current was enhanced by 2.5 fold in comparison to the non modified electrode and the current was due to diffusion process. The electrochemical behavior was further described by characterization studies of pH, scan rate and concentration of ascorbic acid. The CuO-carbon paste electrode has a limit of detection of 22 μM with linear range between 0.075 to 10 mM. Also good reproducibility and recovery was obtained when determining the presence of ascorbic acid in real sample.

Keywords**:** *Microwave, Nanoparticles of CuO, Cyclic voltammetry, ascorbic acid.*

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Positively Charged Sulfonamide Carbon Nanoparticles /SDS Modified Carbon Paste Electrode: A Voltametric Sensor for Ciprofloxacin

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Introduction

Nano-carbon based electrodes e.g. based on carbon nanotubes, carbon nanofibers, graphene, or carbon nanoparticles are of interest in electrochemical processes due to their often highly active surface characteristics and their ease of functionalisation. The modification of functional groups at carbon surfaces provides an important tool for achieving chemical selectivity [1].

Ciprofloxacin is a second-generation fluoroquinolone employed for treatment of different kinds of bacterial infections in the body. An overdose of ciprofloxacin results in severe hepatotoxicity. Thus, there is a need to develop reliable, sensitive, simple and rapid method for the determination of CFX in pharmaceutical preparations and body fluids [2].

In this study, the surface functionalities of commercial sulfonate-modified carbon nanoparticles have been converted from negatively charged to positively charge. To evaluate the electrochemical sensing ability of the positively charged carbon nanoparticles, modification of carbon paste electrode has been performed by casting method. The modified electrode has been used for voltammetric measurements of Ciprofloxacin. Differential pulse voltammetry has been applied for sensitive determination of Ciprofloxacin in real samples.

Methods

Voltammetric experiments were performed using a Metrohm Computrace Voltammetric Analyzer model 797 VA. A conventional three-electrode.

To evaluate the electrochemical sensing ability of the CNP-NH_3^+ -SDS through Ciprofloxacin, modification of carbon paste electrode has been performed by casting method. 10 µL of CNP-NH_3^+ suspension was casted on the CPE surface and dried in the air to evaporate solvent. SDS modified electrodes (denoted as CNP-NH_3^+-SDS electrodes) were prepared by soaking the CNP-NH_3^+ modified electrode in SDS solution (8.0 mM) for 10 s immersion time. The modified electrode has been used for voltammetric measurements.

Result and Discussion

Morphology and structure of the resultant product were characterized by SEM, FT-IR spectroscopy and electrochemical techniques (estimation of capacitive current, absorbed redox systems, Electrochemical Impedance Spectroscopy and cyclic voltametry). The affinity of CFX to adsorb CNP-NH$_3^+$-SDS film at the carbon paste electrode is been studied in pure electrolyte after pre-immersion of the electrode into CFX. Fig. 1 shows a considerable enhancement in the peak current using the CNP-NH$_3^+$-SDS modified electrode obtained. Differential pulse voltammetry has been applied for sensitive determination of Ciprofloxacin in real samples.

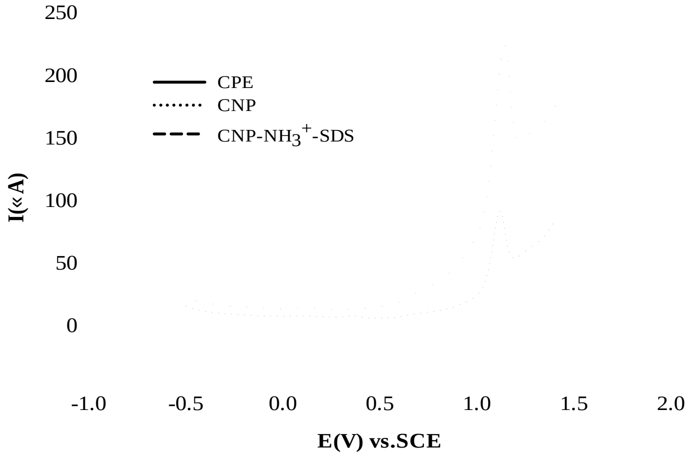

Fig. 1. DPV of 1.0 × 10^{-5}M solution of CFX in buffer solution pH 3.0 (dash line) at CNP-NH$_3^+$-SDS/CPE electrode. For pre-adsorption measurements the modified electrode is immersed for 5 min in CFX solution (phosphate buffer, pH 3) and then rinsed and transfer into clean phosphate buffer solution pH 3.0 for cyclic voltammetry analysis at CNP/CPE electrode (dotted line) and at CPE electrode (solid line). Scan rate was 100 mV s^{-1}.

Conclusion

The covalently modification of carbon nanoparticles with ethylene diamine functional groups is demonstrated. The new carbon nanoparticle substrate is versatile and can be employed for sensitive and selective extraction of CFX. Enhanced voltammetric responses are observed for pre-adsorbed CFX at the surface of CPE/CNP-NH$_3^+$-SDS electrode, high sensitivity with low levels of CFX are achieved.

Keywords**:** *Carbon nanoparticle, SDS, Covalently modification, voltammetric sensor, Ciprofloxacin*

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Evaluation of different fuel cell catalyst nano particle loading on carbon nanotube as catalyst layer support using homemade half cell

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Abstract

Fuel cells are considered as a source of green energy of the past two decades. Polymer electrolyte membrane fuel cells are devices in which, hydrogen and oxygen electrochemically react and produced water, electricity and heat. Basic cell is formed of two cathode and anode electrodes, which separated by an electrolyte. Electrode is made of three-phase of catalyst, ionomer and substrate. During the electrochemical reaction, the electrons pass through substrate and protons pass through the ionomer. Therefore, catalyst particles should have a good electrical connection with the carbon substrate and are in close contact with the membrane. Also, fuel cell electrode in addition to the electrical conductivity should be porous enough to enter reactant gases and leave the produced water of oxygen reduction. Multi wall carbon nanotubes (MWCNTs) are used to increase the available surface area of platinum, as oxygen reduction reaction catalyst. Also, due to the nanotube pores, the access of reactant gases to the three-phase interface could be easier. In this work, a commercial gas diffusion layer and multi wall carbon nanotube is used as substrate to improve the efficiency of the catalyst (1).

Catalyst layer ink preparation

Deposition of Pt nanoparticles on MWCNTs was achieved by reducing the Pt salt, $H_2PtCl_6.6H_2O$, precursor in an ethanol-water solution. In a typical experiment, the commercially CNTs were put in a 50 mL flask. An appropriate amount of the precursor was added to the flask. The reduction reactions were performed under reflux conditions. Then, the CNTs with Pt nanoparticles on them were separated from the ethanol solution in the centrifuge and washed with distilled water (2).

Preparation of the electrode

To prepare the two layer electrode, a homogeneous suspension was produced from the proper amounts catalyst layer ink (10 wt% Pt), ethanol (Merck), water, and Nafion solution (5% from

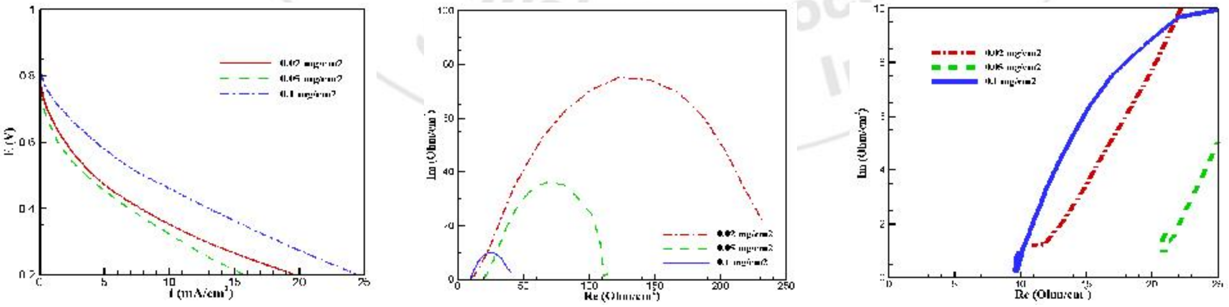
Merk), by using a sonicator for 30 min (1). This suspension was dispersed onto the commercially gas diffusion layer; the electrode was dried at 80°C for 30 min. The Pt loadings were 0.02, 0.05, and 0.1 mg/cm^2. The prepared electrode was hot pressed to better connection of catalyst layer and Nafion electrolyte (2).

Half cell fabrication

To study the effect of the catalyst, substrate and ionomer at the three phase interface and evaluate the oxygen reduction reaction, a homemade half cell test was used. The electrochemical half cell is used as ex-situ tools to evaluate electrode components. The half cell which made in the lab, has oxygen injection capability from one side and on the other side has proton conductivity from the solution to three phase interface. The part of half cell which is in contact with sulfuric acid, including nafion (for proton transfer of solution) and the other side consists of commercial gas diffusion layer to conduct the distribution of oxygen to the interface is three-phase (3).

Characterization of catalyst loading

The as-prepared electrodes were characterized using potentiostat– galvanostat (Biologic SP150). The I–V polarization measurements and electrochemical impedance spectroscopy were used. As shown in Fig. 1(a) the electrode with 0.1 mg/cm^2 Pt loading has the best I-V curve. The polarization resistance of electrodes decreased by increasing catalyst loading (Fig. 1(b)). As shown in Fig (c), resistance on high frequency indicates the ohmic resistance of electrodes. Electrode with 0.1 mg/cm^2 Pt loaded has the lowest ohmic resistance. As the result, Pt with 0.1 mg/cm^2 loaded was optimized value.



(a) (b) (c)

Fig. 3: (a) I-V polarization curve; (b) nyquist diagram of and (c) high frequency nyquist plot of different Pt loading= 0.02, 0.05, 0.1 mg/cm^2, Pcell = 0.2 barg,

Keywords: *Platinum nano particles, polymer electrolyte membrane fuel cell, half-cell, multi wall carbon nanotube*

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TBHQ analysis as an antioxidant food additive using modified CdO/CNTs ionic liquids carbon paste electrode

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Abstract

TBHQ is a highly effective antioxidant [1]. In foods, it is used as a preservative for unsaturated vegetable oils and many edible animal fats.[2] It does not cause discoloration even in the presence of iron, and does not change flavor or odor of the material to which it is added [1]. It can be combined with other preservatives such as butylated hydroxyanisole (BHA). As a food additive, its E number is E319. It is added to a wide range of foods, with the highest limit (1 gram/kg) permitted for frozen fish and fish products. Its primary advantage is enhancing storage life.

A novel CdO/CNTs modified carbon ionic liquid electrode (CILE) was fabricated and used to investigate the electrochemical behavior of TBHQ. Modified electrode was prepared by mixing hydrophilic ionic liquid, with graphite powder, CdO/CNTs, and liquid paraffin. The fabricated modified electrode showed great electrocatalytic ability to the oxidation of TBHQ. The electron transfer coefficient, diffusion coefficient, and charge transfer resistant (R_{ct}) of TBHQ at the modified electrode were calculated. Square wave voltammetry of TBHQ at the modified electrode exhibited linear dynamic ranges in the concentration range of 0.1 to 750.0 µM. The detection limit (3σ) of 0.06 µM TBHQ was achieved. The proposed sensor was successfully applied for the determination of TBHQ in food samples.

Keywords: *TBHQ, CdO/CNTs, Modified electrode, Food analysis*

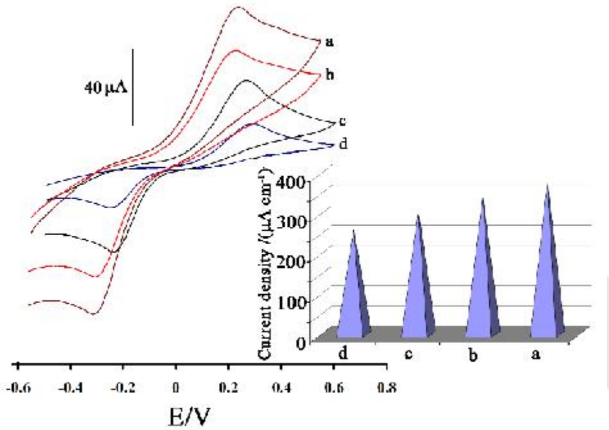

Figure 1: CV of TBHQ ate a surface of (a) CdO/CNTs ionic liquids paste electrode; (b) ionic liquid carbon paste electrode; (c) CdO/CNTs carbon paste electrode and (d) carbon paste electrode

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Application of RGO-Chitosan Nanocomposite for Fabrication Sensitive Aflatoxin B1 Electrochemical Aptasensor

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Abstract

Mycotoxins are the secondary metabolite product of fungi and molds which are created on the agricultural products prior to or after harvest and during transportation and preservation. Mycotoxins are categorized as the most cancerogenic materials according to the IARC categorization [1]. One type of mycotoxins are the aflatoxins. Main types of aflatoxins are G1, B2, B1 and G2 amongst which aflatoxins B1 are known as the most toxic aflatoxin. Detection of aflatoxins B1 has attracted the attention of many researchers because it is highly toxic and prevalent[2]. Therefore, in this work, a sensitive electrochemical aptasensor was developed for detection of aflatoxin B1. Various RGO-chitosan nanocomposites were synthesis and used for immobilization of aflatoxin B1 aptamer molecules on the surface of glassy carbon electrode (GCE). Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), Fourier transform infrared spectroscopy (FT-IR), scaning electron microscopy (SEM) and transmission electron microscopy were used for characterization of fabricated aptasensor. In the present work the effect of various variables such as glutaraldehyde linker concentration, glutaraldehyde incubation time, capture probe concentration, capture probe incubation time, aptamer probe concentration, aptamer probe incubation time and nanocomposite composition were investigated. In optimum conditions very sensitive aflatoxinB1 electrochemical aptasensor was fabricated. In the peresent work elctrochemical impedance spectroscopy was used for detection of aflatoxin B1. The fabricated impedimetric aflatoxinB1 aptasensor showed very good analytical parameter such as high sensivity, low detection limit, wide linear range and high selectivity. The resulted aptasensor can offer arsenic detection in environmental and other applications.

Keywords: *Redused Gerephene oxide, Aptasensor,AflatoxinB1, Electrochemical Impedance Spectroscopy, Electrode*

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Flower-like gold nanoparticles linked to gold DVD platform via L-cysteine self-assembly monolayer: A novel voltammetric sensor for detection of hydrazine

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Abstract

Hydrazine is a well-known carcinogenic substance with a high reducing property. It is a general-purpose chemical with wide-range applications in various industries, fuel cells, corrosion inhibiting and etc. The toxic nature of hydrazine as well as its high solubility in water raises the concerns about environmental pollution [1-3]. Therefore, development of simple, fast, accurate and sensitive sensors for monitoring of hydrazine in water, industrial, environmental and biological samples is of crucial importance today. Here, a novel disposable electrochemical sensor for detection of hydrazine is introduced based on gold nanoparticles (AuNPs) covered on a self-assembly monolayer of L-cysteine (SAM) over a gold digital versatile disc platform (DVD). The characteristics and morphology of AuNPs was characterized by UV-Vis spectroscopy, scanning electron microscopy and atomic force microscopy. Electrochemical impedance spectroscopy experiments in a ferri/ferrocyanide solution proved that AuNPs really act as an efficient electrocatalyst. Electrochemical behaviour of hydrazine on the AuNPs@SAM@DVD electrochemical sensor was investigated using cyclic voltammetry revealing the efficient electrocatalytic function of the sensor. This was confirmed by the decreased oxidation overpotentials and increased peak current response of the hydrazine. The quantitative measurements were carried out by differential pulse voltammetry after thorough optimization of influential operating conditions such as the amount of AuNPs and the pH and the concentration of supporting electrolyte. At last, the analytical performance of the sensor was demonstrated by determination of hydrazine in several environmental samples. The cheap disposable DVD platforms used as a replacement of expensive gold electrodes removes the concerns about the memory effects and tedious solid surface polishing.

Keywords: *Hydrazine, Gold Naopraticles, Self-assembly monolayer, L-cysteine, DVD, Electrochemical sensor*

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Excellent electrocatalytic activity of Au nano-flowers towards oxidation of sulfite: Application to electrochemical detection of sulfite in environmental samples

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Abstract

Today, development of nanotechnology has proved that noble metal nanoparticles show improved catalytic behaviour compared to their bulk materials due to their smaller size and the “nano-effect” [1]. This improved catalytic performance encourages the scientists to use these nanoparticles in the design of new electrochemical sensors. Sulfite is an anti-oxidant agent widely used as an additive to prevent from oxidation and bacterial growth during the storage of foodstuffs. However, due to its toxic effects, FDA has regulated limitations on the amount of sulfite in foodstuffs [2-3]. Therefore, detection of sulfite is of paramount importance in food quality control process.

In this work, electrocatalytic activity of flower-like Au nanoparticles towards electrochemical oxidation of sulfite has been investigated. Citrate stabilized Au nanoparticles (AuNPs) has been covered on a low cost and disposable gold DVD electrode via a self-assembly monolayer of L-cysteine (SAM) as linker. The characteristics of AuNPs were investigated using UV-Vis spectroscopy, particle size and scanning electron microscopy and the flower-like morphology of AuNPs was confirmed by atomic force microscopy. Electrochemical impedance spectroscopy experiments proved the electrocatalytic activity. Electrochemical oxidation of sulfite at the surface of the modified electrode was investigated using cyclic voltammetry showed the decreased oxidation overpotentials and increased current response of the sulfite compared to the bare Au and DVD electrodes. Square wave voltammetry is used for quantitative measurements after careful optimization of influential operating conditions such as the amount of AuNPs and the pH of the solution. The analytical applicability of the proposed electrode was demonstrated by determination of sulfite in water and beverages.

Keywords**:** Sulfite, Flower-like Au nanoparticles, Gold DVD, Voltammetry.

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An electrochemical sensor for voltammetric determination of ascorbic acid using modified carbon paste electrode

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Abstract

Ascorbic acid awater soluble vitamin is an extremely important substance which plays a unique redox andelectrochemical role. It is known as an antioxidant[1]. It is one form of vitamin C. Eating foods rich in vitamin C is important for your overall health, especially if you are at risk for high blood pressure, common cold, Alzheimer’s disease, mental illness, cancer, infertility andcancer [2].

Due to its importance, many analytical *techniques* have been developed and reported for the determination of ascorbic acid inpharmaceutical preparations, biological fluids, food and beverages. The methods are: chromatography,spectrophotometry,mass spectrometry,flow injection,chemiluminescence andelectrochemical methods[3]. Among them electrochemical approaches are used extensively for the especial and sensitive properties because other methods usually need samplepretreatment that is time-consuming and grinding. It is generally believed that direct redox reactionof this specie at bare electrodes such as carbon or those metallicones, Hg, Au, Pt require a high overpotential. Thus, there have been numerous attemptsto enhance the electrode kinetics using various CMEs [4]. In recent years, chemically modified carbon paste electrodes have received increasing attention due to their potential applications in various analyses and also due to their low background current (compared to solid graphite or noble metalelectrodes), high sensitivity, facility to prepare, low cost, stable response, large potential window and simple surface renewalprocess [5].

Since the discovery of carbon nanotubes (CNTs), great investigations were centralized on the studies of theirproperties and applications.Because CNTs possess several unique properties such as small size, high electricaland thermal conductivity, high chemical stability, high mechanicalstrength and high specific surface.Moreover, the subtle electronicbehavior of CNTs reveals that they have the ability to promoteelectron-transfer reaction and have a high

electrocatalytic effectwhen used as electrode materials. All these fascinatingproperties make CNTs as a suitable candidate for the modificationof electrodes [6].

In the present work, 2-Chlorobenzoyl ferrocene (2CBF) was synthesized and used to construct a modified carbon nanotube paste electrode. The electro-oxidation of ascorbic acid at the surface of the modified electrode was studied using cyclic voltammetry (CV), chronoamperometry (CHA), and square wave voltammetry (SWV). Under the optimized conditions, the square wave voltammetric peak currents of ascorbic acid increased linearly with ascorbic acid concentrations in the ranges of 1.0×10^{-7} to 7.0×10^{-5} M and detection limit of 64.0 nM was obtained for ascorbic acid. Finally this modified electrode was used for determination of ascorbic acid in real samples

Keywords: *Ascorbic acid, Carbone nanotube, Electrocatalytic, Carbon paste electrode, Modifier*

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Voltammetric analysis of diphenhydramine in pharmaceutical samples using a nanostructure based sensor

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Abstract

Diphenhydramine which is a first generation antihistamine has been mainly used for the treatment of allergies and itchiness, insomnia, motion sickness, and extrapyramidal symptoms. Additionally, Diphenhydramine has significant antitussive activity [1]. Therefore, determination of diphenhydramine is very important in pharmaceutical and biological samples.

A new room temperature ionic liquid modified CdO/SWCNTs carbon paste electrode had been fabricated by using hydrophilic ionic liquid 1-methyl-3-butylimidazolium chloride as a binder. In the first step, we synthesized CdO/SWCNTs using direct chemical precipitation methods and nanocomposite characterized with TEM method. Figure 1 shows a typical TEM for synthesized nanocomposite.

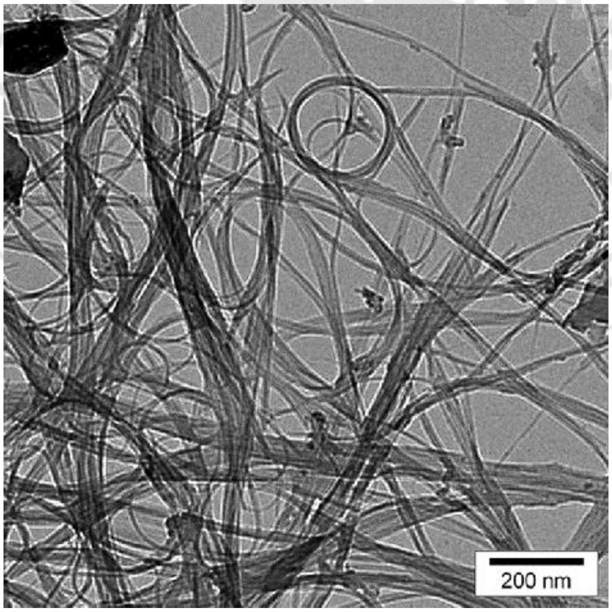

Figure1; TEM image of CdO/SWCNTs

The cyclic voltammogram showed an irreversible oxidation peak signal for diphenhydramine at a surface of modified electrode. Compared to bare carbon paste electrode, the electrochemical response was greatly improved for diphenhydramine electrooxidation. Detection limit of morphine was found to be 0.03 μM using square wave voltammetry (SWV) method. The proposed sensor was successfully applied for the determination of diphenhydramine in human urine and pharmaceutical samples.

Keywords**:** *Diphenhydramine, CdO/SWCNTs nanocomposite, Ionic liquids, Voltammetric analysis*

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Electrochemical sensor for isoproterenol based on a carbon paste electrode modified with carbon nanotube and modifier

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Abstract

Isoproterenol is a synthetic sympathomimetic amine that is structurally related to epinephrine but acts almost exclusively on beta receptors.It is a medication used for the treatment of pulmonary hypertension andallergic emergencies, bronchitis, cardiac chock and heartattack. It is also well known that isoproterenol generates free radicals leading to lipid peroxidation, which causeirreversible damage to the myocardium [1]. Increasein formation of reactive oxygen species (ROS) during ischemia/reperfusion andthe adverse effects of oxygen radicals on myocardiumhave been well established by both direct and indirectparameters. Thus, the excess of the drug causes loss of functionalintegrity and necrotic lesion in heart muscle [2], Therefore, fromhealth viewpoints, development of a sensitive analytical method for thedetermination of isoproterenol isvery important. Several methods have been described for the determination of isoproterenol such as spectrofluorimetry, spectrophotometry,liquid and gas chromatographic and electrochemical methods [3]. Among them electrochemical methods are practical and attractive because electrochemical instrumentation is usually fast, relatively inexpensive, simple, power efficient, accurate and highly sensitive.Moreover, thedevelopment of a rapid electrochemical method for isoproterenol determination that does not require sample pretreatmentis possible. It is known thatthe electrochemical oxidation of isoproterenol atbare electrode surfaces requires high-overpotential [4, 5].

Carbon paste is one of the most popular materials toprepare solid-state electrodes, with high applicability in electrochemistryresearch.The easeand speed of preparation and obtaining a new reproducible surface,low residual current, porous surface and low cost are advantages of carbonpaste electrodes (CPEs) over all other solid electrodes [6].

In the present work, 2-Chlorobenzoyl ferrocene (2CBF) was synthesized and used to construct a modified-carbon nanotube paste electrode. The electro-oxidation of isoproterenol at the surface of the modified electrode was studied using cyclic voltammetry (CV), chronoamperometry (CHA) and square wave voltammetry (SWV). Under the optimized conditions, the square wave voltammetric peak currents of isoproterenol increased linearly with isoproterenol concentrations in the ranges of 2.5×10^{-7} to 8.0×10^{-5} M and detection limit of 9.0×10^{-8} M was obtained for isoproterenol. Finally this modified electrode was used for determination of isoproterenol in real samples

Keywords**:** *Isoproterenol, Carbone nanotube, Electrocatalytic, Carbon paste electrode, Modifier*

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Vitamin C analysis in food and pharmaceutical samples using a nanostructure electrochemical sensor

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Abstract

Ascorbic acid (vitamin C, AA) plays an important role in human health. In one of its functions, it assists in the absorption of iron by promoting iron reduction to the ferrous state, which is necessary for the formation of collagen. Moreover, diets poor in AA lead to increased susceptibility to many kinds of infections and slow down the healing of wounds and fractures [1]. The direct electrochemistry of AA on a modified carbon paste electrode (CPE) was described. The electrode was modified with Zinc oxide (ZnO) nanoparticles and 1,3-dipropylimidazolium bromide as a binder. The oxidation peak potential of AA at the surface of the ionic liquid ZnO appeared at 550 mV, which was about 80 mV lower than the oxidation peak potential at the surface of the traditional carbon CPE under a similar condition. The linear response range and detection limit were found to be 0.1–400 μmol L^{-1} and 0.05 μmol L^{-1}, respectively. Other physiological species did not interfere in the determination of AA at the surface of the proposed sensor in the optimum condition. The proposed sensor was successfully applied for the determination of AA in real samples.

Keywords: *Ascorbic acid, ZnO nanoparticles, Modified electrode*

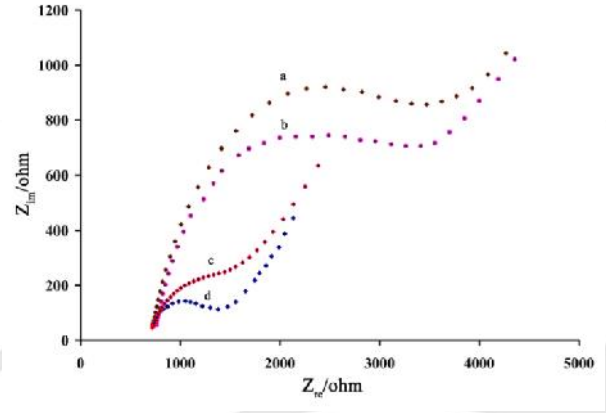

Figure 1: EIS of AA ate a surface of (a) ZnO/NPs ionic liquids paste electrode; (b) ionic liquid carbon paste electrode; (c) ZnO/NPs carbon paste electrode and (d) carbon paste electrode

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Determination of tryptophan in food and pharmaceutical samples using a nanostructure electrochemical sensor

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Abstract

Tryptophan (Trp) is a vital amino acid for humans and herbivores, they cannot live without consuming. This compound is a precursor for serotonin (a neurotransmitter), melatonin (a neurohormon), and niacin. It has been implicated as a possible cause of schizophrenia in people who cannot metabolize it properly. When improperly metabolized, it creates a waste product in the brain that is toxic, causing hallucination and delusions [1].

Ionic liquid/multiwall carbon paste electrode (IL/MWCNTs/CPE) has been used as a high sensitive sensor for the professional quantitative determination of tryptophan in food and pharmaceutical samples in aqueous solution. The propose sensor shows a better electrochemical response with lower over-potential and high sensitivity for tryptophan compared with unmodified carbon paste electrode using linear sweep voltammetry (LSV). The electro-oxidation of tryptophan occurred in a pH-dependent e− and H+ process, and the electrode reaction followed a diffusion-controlled pathway. Under the optimum conditions in square wave voltammetry (SWV), the voltammetric oxidation peak current of tryptophan showed linear dynamic ranges with a detection limit of 0.05 μM for tryptophan. The modified electrode was successfully used for the determination of the tryptophan in real samples with satisfactory result.

Keywords: *Tryptophan, Multiwall carbon nanotubes, Modified electrode*

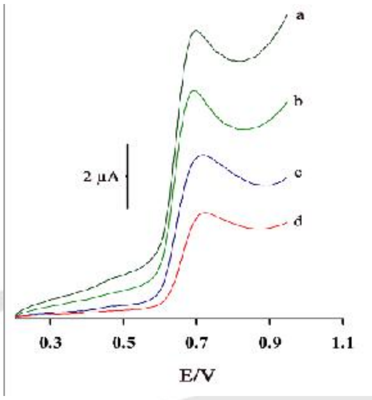

Figure 1: LSV of tryptophan ate a surface of (a) multiwall carbon nanotubes ionic liquids paste electrode; (b) ionic liquid carbon paste electrode; (c) multiwall carbon paste electrode and (d) carbon paste electrode

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WO_3 nanoparticles based electrochemical sensor for trace determination of theophylline by adsorptive stripping differential pulse voltammetry

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Abstract

Theophylline (1,3-dimethyl-3,7-dihydro-1H-purine-2,6-dione) is a kind of methyl xanthine derivatives which exists widely in nature. It was used in treatment of infant apnea, asthma and chronic bronchospasm of adults [1]. The most accepted range of effective theophylline plasma concentration in adults is between 5 and 20 mg mL^{-1}. Levels higher than 20 μg/mL can cause arrhythmia, fever, dehydration, insomnia, anorexia, coma, heartburn tachycardia and cardiac arrest. Because theophylline exists in many soft drinks, foodstuff and natural products, such as cocoa, tea and chocolate [2], it is important to develop a simple, accurate and rapid method for theophylline determination. The main reported procedure for the determination of theophylline in different samples is chromatographic methods. In spite of the high sensitivities of the chromatographic methods, they are very expensive; involve the use of complex procedures with several sample manipulations, require long analysis time and trained personnel.

In recent years, nanostructured metal oxides have been widely applied as sensing material in sensors and biosensors because of their high chemical stability, biocompatibility, structural flexibility, higher catalytic behavior and strong adherence to substrates [3]. In the present work, an electrochemical sensor for theophylline determination was prepared by the modification of a glassy carbon electrode (GCE) with the nano-composite of tungsten trioxide nanoparticles and multiwall carbon nanotubes (MWCNTs). Tungsten trioxide (WO_3) is an n-type semiconductor with a reported band gap of about 2.6–2.8 eV. The intrinsic conductivity arises from its non-stoichiometric composition giving rise to a donor level formed by oxygen vacancy defect in the lattice [4]. The WO_3 nanoparticles were synthesized by precipitation reaction between the sodium tungstate dihydrate and nitric acid.

The constructed sensor was applied for determination of theophylline by adsorptive stripping differential pulse voltammetry. Theophylline showed a well-defined oxidation peak at the modified electrode in sulfuric acid solution which the peak current is much higher than that at the bare GCE and MWCNT-modified GCE.

The results showed that the electrochemical oxidation of theophylline on the modified electrode was diffusion-controlled. The effects of scan rate, electrolyte solution, pH, accumulation condition and amounts of MWCNT and nanoparticles were optimized. Under optimized conditions, the calibration curve was linear in the concentration ranges of $2.0 \times 10^{-8} – 2.0 \times 10^{-5}$ M with a detection limit of 8.0×10^{-9} M. This modified electrode was used as a sensor for determination of theophylline in pharmaceutical formulation and blood serum samples with satisfactory results.

Keywords: *Tungsten trioxide, Theophylline, Glassy carbon electrode, Carbon nanotubes, Adsorptive differential pulse voltammetry.*

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Electrochemical Hydrogen Peroxide Sensing Based on Nano-Sized Byphenylic Ni Complex

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Abstract

In this project, we investigated a new non-enzymatic sensor for the measurement of hydrogen peroxide. The detection of hydrogen peroxide is important, since it is related to determination of numerous biological species, such as enzymes [1-3]. This sensor was prepared in the basis of Ni complex. The size of complex was characterized below 100 nm by the scanning electron microscopy. Moreover, the FT-IR spectroscopic studies of the complex confirmed the synthesis of the complex. Nickel complex was dispersed in ethanol and put on a glassy carbon electrode. The cyclic voltammetry and chronoamperometry were employed as electrochemical methods for monitoring the hydrogen peroxide detetion. Moreover, electrochemical impedance spectroscopy was utilized for the investigation of electrochemical behavior of the modified electrode. The study of cyclic voltammograms in different pH solution was performed. The pH=7 solution was considered for further studies due to the biological pH (pH=7.4). The potentials were chosen by the increasing effect of the H_2O_2 injection on the signals. The H_2O_2 injection represented the reduction potential around -0.3 V versus Ag/AgCl reference electrode. The potential scan rate indicated linear relationship between peak current and the root of scan rate because of diffusion mechanism of mass transform.

Keywords: *Byphenylic Ni complex, cyclic voltammetry, Chronoamperometry, Hydrogen peroxide*

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Simultaneous and sensitive determination of ascorbic acid and tryptophan on ionic liquid/nanocomposite modified carbon paste electrode

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Abstract

Ascorbic acid (AA), also known as vitamin C, is very popular for its antioxidant property, and present in the human diet as a vital vitamin. It is needed for many functions in the body, including helping the body use carbohydrates, fats, and protein [1]. Moreover, it is also used for the prevention and treatment of senility, the common cold, treating asthma, some mental illness, infertility, allergies, eye ulcers, blood clots, gum disease, pressure sores and AIDS. Tryptophan (Trp), as an essential amino acid for the human body and a vital constituent of protein biosynthesis of living organisms is important in nitrogen balance and the maintenance of muscle mass and body weight in humans [2]. It is well known that ascorbic acid and tryptophan are usually co-existing substances in biological matrixes and abnormal levels of these species will lead to several diseases and disorders. Therefore, to establish a simple, accurate, rapid and inexpensive method for simultaneous detection of AA and Trp in food, pharmaceutical products and biological fluids is very necessary. The room temperature ionic liquids (RTILs) modified carbon paste electrodes (CPEs) has shown higher electron rate transfer compared to that of bare CPE [3]. Moreover, RTIL has been shown to be suitable media for supporting biocatalytic processing. Nowadays, there is wide interest in the fabrication of nanocomposite particles with unparalleled and tailored properties for various applications in material science [4]. In this paper, MWCNT/Fe_3O_4@SiO_2 based electrochemical sensor was fabricated for the simultaneous determination of ascorbic acid (AA) and tryptophan (Try), which is very important in the clinical diagnosis. Electrochemical studies were carried out by using cyclic voltammetry (CV), square wave voltammetry (SVW) and chronoamperometry (CHA). The experiment results showed good linear response range for detection of AA and Trp and the detection limits were 0.1 µM and 5 µM (S/N=3). Moreover, the modified electrode exhibited excellent stability and reproducibility. The analytical performance of this sensor was

also demonstrated for the determination of ascorbic acid in commercial pharmaceutical samples such as tablets and injections of vitamin C. The applicability of this sensor was also extended in the determination of tryptophan in spiked samples.

Keywords**:** *Ascorbic acid, Tryptophan, Nanocomposite, Ionic liquid, Modified electrode.*

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Fabrication of NiO nanoparticle onto the surface of a modified screen-printed electrode for simultaneous determination of dopamine and uric acid

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Abstract

Dopamine, has been of interest to neuroscientists and chemists since its discovery in the 1950s. As the most important neurotransmitter in the mammalian central nervous system, the amount of DA distributed in organs has great influences on human movements and emotions. The abnormal low concentration level of DA can cause Tourette's syndrome, schizophrenia, Parkinson's disease, Huntington's disease, HIV infection and other similar neurological disorders. Therefore, the determination of DA for quality control analysis and for medical control is very important [1, 2]. Among various analytical methods, modern electrochemical techniques have attracted considerable interest due to the good simplicity, sensitivity, selectivity, stability and often do not require any pre-treatments or pre-separation [3]. Over recent years, various materials including polymer, nanocomposite and metal oxide nanoparticles have been employed for the modification of the electrode surfaces. Due to the unique properties of metal oxide nanoparticles, there is a major interest in the use of them such as ZnO, Co_3O_4, NiO and CuO to modify the surface of electrode. Among these nanoparticles, nickel oxide (NiO), a p-type semiconductor with a wide band gap of 3.7 eV in room temperature and a high isoelectric point (IEP) of about 10.7, has been studied intensely because of its high chemical stability, electrocatalysis, electron transfer capability and good biological compatibility [4, 5]. A disposable biosensor for determination of dopamine based on nickel oxide nanoparticles and the graphene nanosheets (GN) modified screen-printed carbon electrode (SPCE) was fabricated. The catalytic activity of the NiONPs/GN-SPCEs was demonstrated by the electrochemical measurements. The electrochemical behaviors of dopamine (DA), and uric acid (UA) were investigated by cyclic voltammetry (CV), differential pulse voltammetry (DPV) and chronoamperometry (CHA). The

separation of the oxidation peak potentials for DA–UA was about 145 mV, which allowed simultaneously determining dopamine, and uric acid. The electrochemical studies confirmed that the electrooxidation of dopamine at the modified electrode is a diffusion controlled electrochemical process. The DPV was employed for the determination of dopamine; under optimum conditions, the electrochemical oxidation signal of dopamine increased linearly from 0.1-500 µM. The proposed electrochemical biosensor was sensitive, rapid, disposable with low cost, fewer sample volume and easy preparation, which showed great promise for screen-determination of trace dopamine and uric acid in real samples.

Keywords*: *Nickel oxide nanoparticles, Graphene nanosheets, Screen-printed carbon electrode, Dopamine, Uric acid

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Construction of selective potentiometric sensor for Isoniazid by modified carbon paste electrode with Iron magnetic nanoparticles

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1. Introduction

Isoniazid (pyridine-4-carboxilic acid hydrazide or isonicotinic acid hydrazide) is a widely used drug alone in the prophylaxis and in combination with other anti tuberculars in the treatment of all forms of tuberculosis [1]. Several methods for the analysis of isoniazid are available in the literature. [2,8]. On the other hand, applications of potentiometric sensors in the field of pharmaceutical and biomedical analysis have been advocated [9]. Potentiometric detection based on ion-selective electrodes (ISEs), offers several advantages such as speed and ease of preparation and procedures, simple instrumentation, relatively fast response, wide dynamic range, reasonable selectivity, and low cost [10]. In this paper, we introduced new potentiometric sensors for selective determination of Isoniazid in pharmaceutical preparations and biological fluids.

Keywords: Isoniazid, Nanoparticles, CPE, ISEs, Potentiometric.

2. Experimental

2.1. Instrument and Materials:

All potentiometric measurements performed with potentiometer mode lPTR 79,that electrode Ag/AgCl was used as reference.Fe_3O_4 nanoparticles modified carbon paste electrode (Fe_3O_4–CME) was used as working electrodes .All materials were obtained from Merck, Germany. Double distilled water was used for the preparation of aqueous solutions.

3. Result

3.1.Affecting parameters:

Standard solutions of Isoniazid were used to find the optimum pH of the supporting electrolyte at CPE. Optimal condition for electrode such as amount of Fe3O4 nanoparticles, Graphite powder, mineral oil (Nujol) and interfering Ions effects, on electrode response were investigated.

3.2. Calibration Graph:

Relationship between concentration of isonizid and potential of modified electrode under optimized condition were studied. This electrode, in concentration rang of 10^{-5} to 10^{-10} M exhibits a liner response with 9/51 mv/dec nernstion slope and $3/09\times10^{-13}$ M detection limit.

4. Conclusion

Fe_3O_4 nanoparticles modified carbon paste electrode was developed as an effective and highly sensitive electrode for determination of Isoniazid by potentiometric method. This electrode gave a considerable enhancement insensitivity, improved detection limit, reproducibility and repeatability thereby being a promising electrode for the determination of trace amounts of Isoniazid in pharmaceutical and clinical preparations.

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Analysis of 4-chlorophenol in environmental samples using NiO nanoparticles ionic liquids carbon paste electrode

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Abstract

In this work we describe a novel NiO nanoparticles room temperature ionic liquid (RTIL) modified carbon paste electrode as a high sensitive sensor for voltammetric determination of 4-chlorophenol (4-CP) in environmental samples. The sensor exhibits an enhanced effectiveness for the electro-oxidation of 4-CP in aqueous solution. The oxidation peak potential for this matter at a surface of the ionic liquid (n-hexyl-3-methylimidazolium hexafluoro phosphate) NiO/NPs carbon paste electrode appeared at 610 mV that was about 90 mV lower than the oxidation peak potential at the surface of the traditional carbon paste electrode (CPE) under similar condition. The mechanism of the electro-oxidation process on the surface of the modified electrode was analyzed. Square wave voltammetry (SWV) was applied as a very sensitive electrochemical method for the determination of sub-micro-molar amounts of 4-CP. The prepared modified electrode shows several advantages such as simple preparation method, high stability, high sensitivity, and excellent catalytic activity, long-term stability and remarkable voltammetric reproducibility for eletrooxidation of 4-CP. The proposed sensor was successfully applied for the determination of 4-CP in environmental samples. The XRD pattern of NiO/NPs, in the 2θ range of 10–90°, is shown in Fig. 1A. Typical TEM micrograph of the NiO/NPs is shown in Fig. 1B.

Keywords: *4-chlorophenol; NiO nanoparticle, Ionic liquids, Voltammetric analysis*

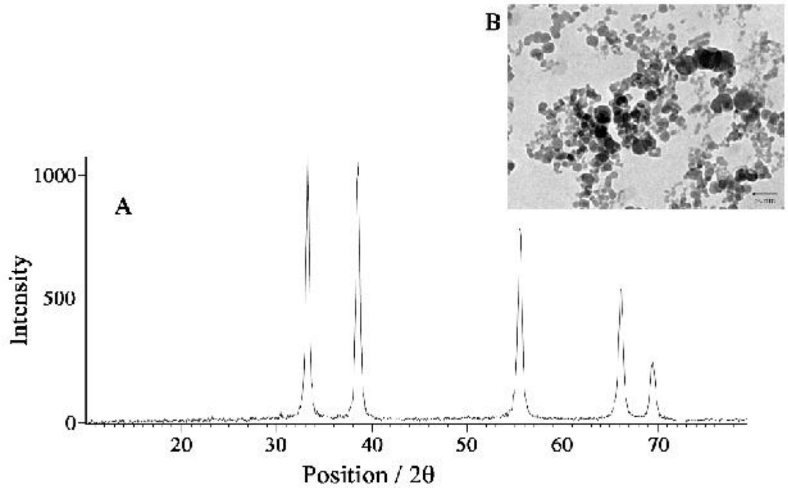

Figure 1: Fig. 1. A) XRD patterns of as-synthesized NiO/NPs. B) SEM images of NiO/NPs.

Determination of Ni (II) by carbon past electrode modified with clinoptilolite nanoparticles-dimethyl glyoxime (NClino-DMG)

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Abstract

Clinoptilolite was pretreated by mechanical ball-milling method to obtain nano particles and it was modified by DMG. The raw and modified samples were characterized by XRD, FT-IR, SEM, BET, TG-DTG and energy dispersive analysis X-ray spectroscopy (EDAX). The modified Clinoptilolite nano-particles with DMG (NClino-DMG) was used for the modification of carbon paste electrode (NClin-DMG-CPE). The modified electrode was then used for voltammetric determination of Ni(II) in aqueous solution. To determine the interaction of experimental parameters, response surface methodology (RSM) was used. The effects of some key operating parameters such as: zeolite particle size, nature and concentration of the supporting electrolytes, pH of solution, electrode ingredients and potential scan rate on the voltammetric behavior of the modified electrode were studied.

Keywords: *Clinoptilolite, Modified electrode, Voltammetric determination, RSM*

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The novel synthesis of Nb_2O_5 nanoparticles via surfactant free methods applicable for electrochemical energy devices

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Introduction

Niobium pentoxide (Nb_2O_5) has been studied extensively due to its application in Li-ion battery, additives for $BiTiO_3$ capacitors, electrochemical electrodes and etc (1-4).Nb_2O_5 nanostructures synthesized via different methods like solvo-thermal, hydrothermal, sol-gel, mechano-chemical and electrodeposition with different precursors (5). In this work we present a time-consuming and cost efficient method which not containing any surfactant to produce it.

Keywords: Nb_2O_5 nanoparticles, X-ray diffraction, Crystal growth, surfactant-free synthesis

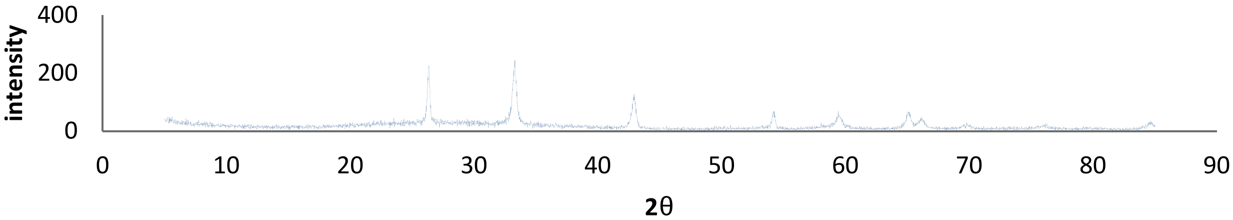
Experimental

At first 0.16 mg Nb_2O_5 powder dissolved in 10ml hydrofluoric acid (HF 40%). The heater temperature was fixed in 100^0c and uses a magnet for stirring the solution and fastening the procedure. After one hour Nb_2O_5 dissolved in HF completely and a transparent solution were obtained. Then it was diluted with distilled water to get 4g/l Nb_2O_5 solution. After that pH of solution was tuned to 9.0 by adding aqueous ammonia solution and a white precipitate were obtained. It was washed with deionized water and ethanol solution for several times to remove F^- ions. Then it was filtered with special paper and dried it with oven at 80^0c for 6h. Finally, the dried precipitate calcinated at 580^0c for 30 minutes and a white powder were obtained.

Results and discussion

X-ray diffraction of Nb_2O_5 powders were carried out by Philips (pw 3710). Figure 1 shows the XRD plot of Nb_2O_5 nanoparticles.

The crystalline structure is hexagonal and the average crystalline size was calculated by Scherrer formula,



$$D = \frac{k}{\beta}$$

With k = 0.9 and $\lambda_{k\alpha}$ (Co) = 1.78901.Major peaks was indexed as (100), (001), (101) and (102) which is referred to average size of 30.2 nm, 33.0 nm, 22.9 nm and 20.4 nm, respectively.

Conclusion

Nb_2O_5 nanoparticles were successfully synthesized via a chemical surfactant free method. The range of size of nanoparticles was from 20nm to 33nm, whose the highest peak is about 30.2nm.

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A High sensitive voltammetric sensor for bisphenol A using a nanostructure modified electrode

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Abstract

Bisphenol A is a chemical used in the manufacture of epoxy resins for the lacquer lining of metal food cans, as a monomer of polycarbonates, and the monomer of plastic used in the base paste of dental sealants [1]. But polycarbonate and epoxy resins, inner surface coating of food and beverage cans, from which BPA can leach into food and environment.

The electrochemistry of bisphenol A (BPA) was studied by voltammetric methods at a surface of carbon paste electrode modified by a ZnO/CNTs nanocomposite and room-temperature ionic liquid of 1,3-dipropylimidazolium bromide. The ratio of ZnO/CNTs and ionic liquid (IL) on the surface of the electrode has to be controlled carefully because the charging currents. The anodic peaks of BPA and Sudan I in their mixture can be well separated. At pH 7.0 the two peaks are separated ca. 0.47 and 0.70 V, respectively; hence BPA can be determined in the presence of Sudan I and more than 8.7 times current excess of BPA. The peaks current of square wave voltammograms (SWV) of BPA and Sudan I increased linearly with their concentration in the ranges of 0.002–700 µM BPA and 0.2–800 µM Sudan I. The detection limits for BPA and Sudan I were 9.0 nM and 80 nM, respectively. The modified electrode has been successfully applied for the assay of BPA in food samples. This study provides a simple and easy approach to selectively detect BPA in the presence of Sudan I.

Keywords**:** *Bisphenol A, ZnO/CNTs, Ionic liquids, Voltammetric analysis*

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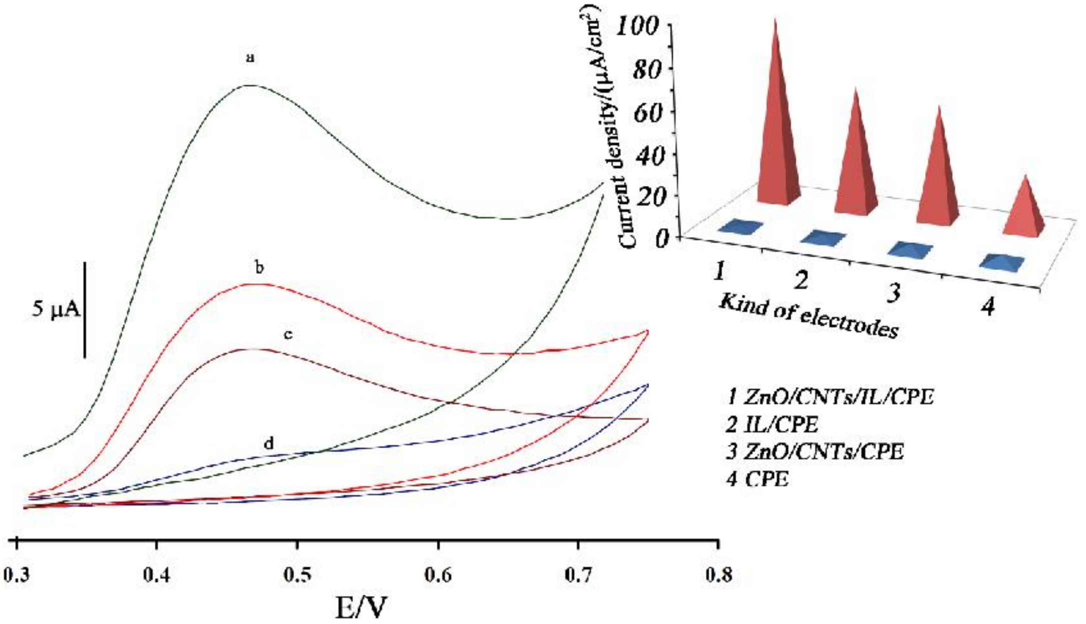

Fig. 1. Cycic voltammograms of a) ZnO/CNTs/IL/CPE, b) IL/CPE, c) ZnO/CNTs/CPE and d) CPE in presence of 300 µmol L^{-1} BPA at a pH 7.0, respectively. Inset: the current density derived from cyclic voltammograms responses of 300 µmol L^{-1} BPA at pH7.0 at the surface of different electrodes with a scan rate of 100 mV s^{-1}.

Ascorbic acid determination in food and pharmaceutical samples using modified carbon paste electrode

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Abstract

Ascorbic acid (AA), as a water soluble vitamin, is an effective reducing agent and a powerful antioxidant in food, preventing color changes and alterations of aroma and flavor as well as extending the storage time of the products. Although AA is naturally present in a wide range of foods, particularly fruits and vegetables, it has limited stability and may be lost from foods during storage, preparation and cooking [1].

In this study, a simple and rapid analytical method development for ascorbic acid (AA) determination in food samples by using square wave voltammetry (SWV) method on NiO nanoparticles ionic liquid modified carbon paste electrode. For this, several parameters, such as NiO/NPs, ionic liquid ratio, and pH, have been studied. The cyclic voltammogram showed an irreversible oxidation peak at 0.52 V (vs. Ag/AgClsat), which corresponded to the oxidation of AA. Compared to common carbon paste electrode, the electrochemical response was greatly improved. Under the optimized conditions, the oxidation peak current of AA showed linear dynamic range 0.08–380 μM with a detection limit of 0.04 μM, using the SWV method. The proposed sensor was successfully applied to the determination of AA in fresh vegetable juice, fruit juices and food supplement samples without previous preparation and was compared with a published electrochemical method. Figure 1 shows catalytic effect of recommend procedure at a optimum condition.

Keywords**:** *Ascorbic acid, NiO nanoparticles, Ionic liquids, Voltammetric analysis*

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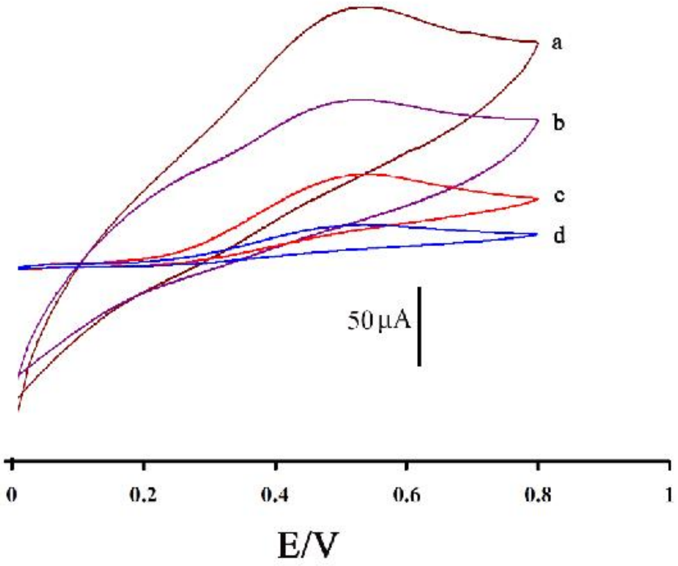

Figure 1: Cycic voltammograms of a) NiO/NPs/ILCPE, b) CP/ILE, c) NiO/NPs/CPE and d) CPE in presence of 500 µm AA at a pH 7.0, respectively.

Nickel nanoparticle supported on ZrO_2 nanotubes as a new high active electrodes for methanol electrooxidation

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Abstract

Fuel cells are attractive sources of electrical power since they realize the direct conversion of chemical into electrical energy. Considerable interest has been directed to the use of fuel cells in electric vehicle technology. One promising system is the direct methanol fuel cell (DMFC). Since it requires little additional equipment compared to the extensive gas process technology for methanol reforming, the fuel is best transported and converted into energy from the liquid state. In this research, we report the preparation and application of Ni/ZrO_2-NTs/Zr electrode formed by anodizing of the zirconium substrate to produce ZrO_2 nanotubes with subsequent cathodic deposition of nickel on these nanotubes. The electroactivity of the Ni/ZrO_2-NTs/Zr electrode for the methanol oxidation in alkaline solutions was studied by cyclic voltammetry. The results were compared with those of the pure nickel.

Fig. 1 shows cyclic voltammograms of (a) Ni/ZrO_2-NTs/Zr in the presence of 0.1 M methanol (b) Ni in the absence of methanol (c) Ni in the presence of 0.1 M methanol in 0.5 M NaOH solution at a potential sweep rate of 100 mVs^{-1}. It is observed from Fig. 1 that the presence of methanol in 0.5 M NaOH solution leads to the rapid increase in the anodic currents. The electrochemical oxidation of methanol at nickel electrodes can be represented by:

$$Ni(OH)_2 \rightarrow NiOOH + H^+ + e^- \quad (1)$$

$$NiOOH + \text{methanol} \rightarrow Ni(OH)_2 + \text{oxidation products of methanol} \quad (2)$$

The active NiOOH formed during the positive potential scan is consumed through Reaction 2. Subsequently, the formed Ni (OH) in Reaction 2 is again oxidized to NiOOH during the anodic potential sweep. The current densities for methanol oxidation on Ni/ZiO_2-NTs/Zr electrode are greater than that observed for flat nickel electrode. This implies that the Ni/ZrO_2-NTs/Zr electrodes exhibit higher catalytic activity compared with flat nickel electrodes. This can be attributed to the larger surface area of the Ni/ZrO_2-NTs/Zr electrodes.

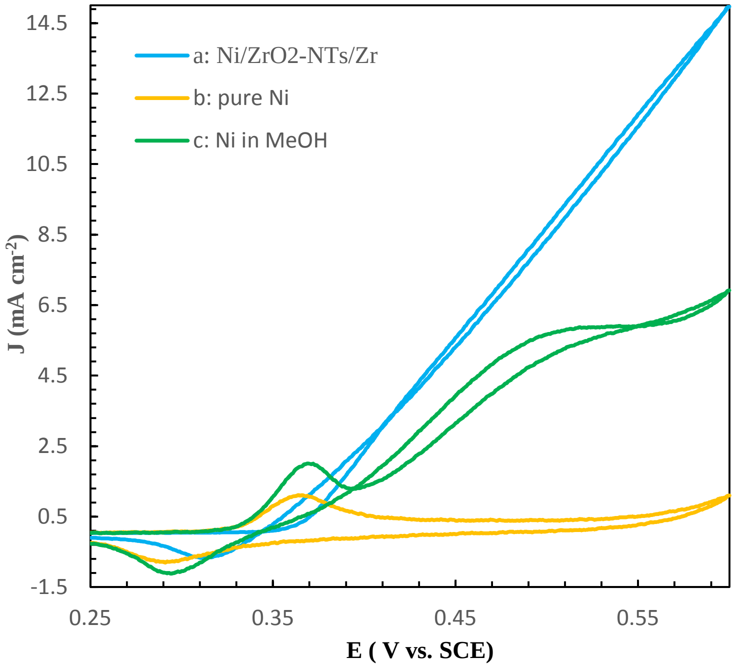

Fig. 1 Cyclic voltammograms in a 0.5 M NaOH solution at 25 °C with a Scan rate of 100 mVs^{-1} for (a) Ni/ZrO_2-NTs/Zr in the presence of 0.1 M methanol (b) Ni in the absence of methanol (c) Ni in the presence of 0.1 M methanol.

Keywords**:** *Ni/ZrO_2 NTs/Zr, Electrooxidation, Cyclic voltammetry, Methanol.*

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Electrocatalytic determination of isoproterenol, acetaminophen, tryptophan and thophylline using a carbon paste electrode modified with graphene and modifier

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Abstract

Isoproterenol is a sympathomimetic beta adrenergic agonistmedication. It had been used for bradycardia or heart block. By activating 1-receptors on the heart, it induces positive chronotropic, dromotropic, and inotropic effects [1]. Isoproterenol has positive inotropic and chronotropic effects on the heart. Acetaminophen is a widely used analgesic anti-pyretic drug. It is a suitable alternative for the patients who are sensitive to aspirin. However, overdoses will cause liver and kidney damage [1]. L-Tryptophan is one of the essential amino acids in protein biosynthesis of living organisms. Tryptophan concentration is a sensitive parameter to monitor the biochemical balance of the brain. It is very essential for people with sleep deprivation, anxiety and mood enhancement due to its ability to increase brain levels of serotonin and melatonin [2].

Theophylline is a kind of methyl xanthine derivatives which exists widely in nature. It has been reported that theophylline can cause various physiological effects, such as relaxation of bronchialmuscle, gastric acid secretion and stimulation of the central nervous system. Theophylline is one of the most commonly used medications for the treatment of the symptoms of chronicasthma [1].

Carbon paste electrodes (CPEs) are widely utilized to perform the electrochemical determinations of a variety of biological and pharmaceutical species owing to their low residual current and noise, ease of fabrication, wide anodic and cathodic potential ranges, rapid surface renewal, and low cost. Moreover, chemically modified electrodes (CMEs) can be easily prepared

by adding different substances to the bulk of CPEs in order to increase sensitivity, selectivity, and rapidity of determinations [1].

In the present work, a novel carbon paste electrode modified with graphene oxide nanosheets and a novel ferrocene derivative was fabricated. The electrochemical study of the modified electrode, as well as its efficiency for voltammetric oxidation of isoperoterenol, is described. It has been found that under optimum condition (pH 7.0) in cyclic voltammetry, the oxidation of isoperoterenol occurs at a potential about 120 mV less positive than that of an unmodified carbon paste electrode. The prepared modified electrode exhibits a very good resolution between the voltammetric peaks of isoperoterenol, acetaminophen, L-tryptophan and theophylline which makes it suitable for the detection of isoperoterenol in the presence of acetaminophen, L-tryptophan and theophylline in real samples.

Keywords: *Isoperoterenol, Acetaminophe, L-Tryptophan, Theophylline, Graphene, Modified electrode*

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Voltammetric determination of levodopa, acetaminophen and tyrosine using a carbon paste electrode modified with graphene and modifier

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Abstract

Parkinson´s disease (PD) is believed to be related to low levels of dopamine in certain parts of the brain. Levodopa (LD) is considered the most effective treatment available for Parkinson_s disease. Paracetamol or acetaminophen (AC) is a widely used over-thecounter analgesic (pain reliever) and antipyretic (fever reducer). It is commonly used for the relief of fever, headaches, and other minor aches and pains, and is a major ingredient in numerous cold and flu remedies [1]. L-Tyrosine is an important amino acid which is considered nonessential because the human body can make it from another amino acid called phenylalanine. In the human body, L-Tyrosine is used to make catecholamines. L-Tyrosine plays a crucial role in biological systems as it is a predecessor of hormones as well as of neurotransmitters such as thyroxin and dopamine respectively, in addition to other physiologically essential biomolecules [2].

The chemical modification of inert substrate electrodes with mediators offers significant advantages in the design and development of electrochemical sensors. In operations, the redox activesites shuttle electrons between a solution of the analyte and the substrate electrodes often along with a significant reduction of the activation overpotential. A further advantage of chemically modified electrodes is that they are less prone to surface fouling and oxide formation compared to inert substrate electrodes [1].

In the present work, a novel carbon paste electrode modified with graphene oxide nanosheets and a novel ferrocene derivative was fabricated. The electrochemical study of the modified electrode, as well as its efficiency for voltammetric oxidation of levodopa, is described. It has been found that under optimum condition (pH 7.0) in cyclic voltammetry, the oxidation of levodopa occurs at a potential about 250 mV less positive than that of an unmodified carbon paste electrode. The

prepared modified electrode exhibits a very good resolution between the voltammetric peaks of levodopa, acetaminophen and L-tyrosine which makes it suitable for the detection of levodopa in the presence of acetaminophen and L-tyrosine in real samples.

***Keywords**: Levodopa, Acetaminophen, L-Tyrosine, Graphene, Modified electrode*

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Hydroquinone analysis in liposome carrier using a voltammetric sensor

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Abstract

Hydroquinone (HQ) has a variety of uses principally associated with its action as a reducing agent that is soluble in water. It is a major component in most black and white photographic developers for film and paper where, with the compound Metol, it reduces silver halides to elemental silver. There are various other uses associated with its reducing power. As a polymerization inhibitor, hydroquinone prevents polymerization of acrylic acid, methyl methacrylate, cyanoacrylate, and other monomers that are susceptible to radical-initiated polymerization. This application exploits the antioxidant properties of hydroquinone [1].

An ionic liquid-modified NiO nanoparticles paste electrode has been fabricated as a voltammetric sensor. . This electrode showed enhanced electrochemical response and strong analytical activity towards the direct electrochemical oxidation of HQ. The electron transfer coefficient, α, and diffusion coefficient of HQ at the modified electrode were calculated. Under optimal conditions at pH 7.0, the anodic peak currents increased linearly with the concentration of HQ in the range of 50.0–400 μM with a detection limit of 30.0 μM (3σ). The interferences of foreign substances were investigated. Cyclic voltammetry was used to check the applicability of the proposed sensor to the determination of HQ in real samples with satisfactory results. Figure 1 shows catalytic effect of recommend procedure at an optimum condition.

Keywords**:** *Hydroquinone, NiO nanoparticles, Ionic liquids, Voltammetric analysis*

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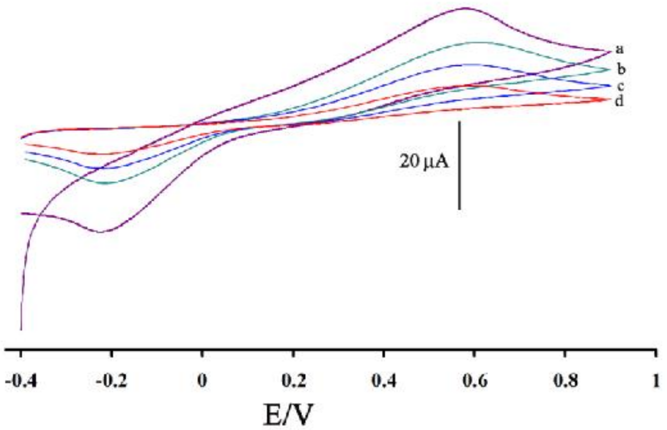

Figure 1: Cycic voltammograms of a) NiO/NPs/ILCPE, b) CP/ILE, c) NiO/NPs/CPE and d) CPE in presence of 500 µm HQ at a pH 7.0, respectively.

Kojic acid determination in pharmaceutical samples using NiO nanoparticles ionic liquids carbon paste electrode

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Abstract

Kojic acid is a chelation agent produced by several species of fungi, especially Aspergillus oryzae, which has the Japanese common name koji. [1] Kojic acid is a by-product in the fermentation process of malting rice, for use in the manufacturing of sake, the Japanese rice wine. [1] It is a mild inhibitor of the formation of pigment in plant and animal tissues, and is used in food and cosmetics to preserve or change colors of substances. It forms a bright red complex with ferric ions. A chemically modified electrode was constructed and applied to the electro-oxidation of the kojic acid (KA). The oxidation peak potential of the KA at a surface of NiO/NPs ionic liquid carbon paste electrode (NiO/NPs/IL/CPE) appeared at 950 mV. The NiO nanoparticle (NiO/NPs) was characterized with different methods such as transmission electron microscope (TEM) and x-ray diffraction (XRD). Under optimized (pH 6.0), linear calibration curves were obtained in the range of 10.0–400 µM for KA, which shows adequate for the quantification in real samples. The proposed method was successfully applied to the determination of KA in both pharmaceutical and urine samples.

Keywords**:** *Kojic acid, NiO nanoparticles, Ionic liquids, Voltammetric analysis*

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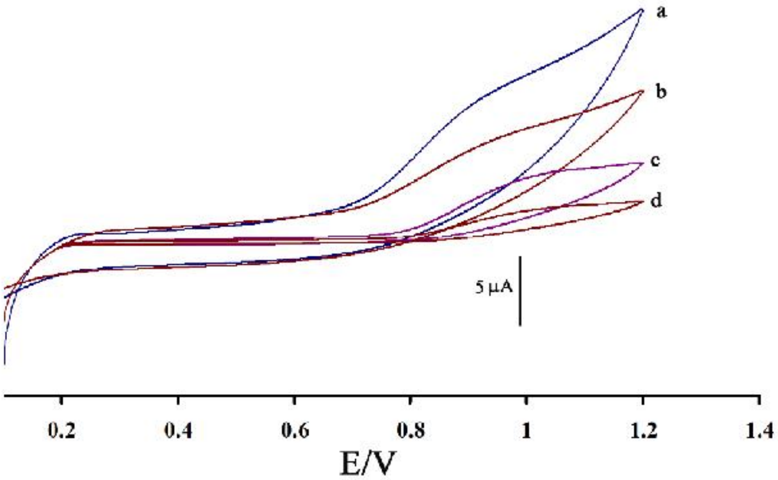

Figure 1: Cycic voltammograms of a) NiO/NPs/ILCPE, b) CP/ILE, c) NiO/NPs/CPE and d) CPE in presence of 500 μM KA at a pH 6.0, respectively.

Introduction of New Electrochemical Biosensor for Detection of DNA Hybridization

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Abstract

The development of DNA biosensors has recently attracted significant attentions in connection with research efforts directed at gene analysis, tissue matching, the detection of genetic disorders and forensic applications [1, 2]. To date, various sensing strategies for DNA detection such as fluorescence [3], quartz crystal microbalance [4], surface plasmon resonance spectroscopy , surface-enhanced Raman scattering and electrochemical have been employed. In this work, we introduced a novel electrochemical DNA sensor for the detection of DNA hybridization. The new electrochemical biosensor was fabricated by modifying a screen printed graphite electrode (SPE) with gold nanoparticles decorated on graphene (AuNPs/G). The whole DNA biosensor fabrication process was characterized by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) techniques. The probe DNA immobilization and its hybridization on the modified electrode were further studied with CV and differential pulse voltammetry (DPV). Under optimum conditions, the developed biosensor showed a good linear relationship between the current value and logarithm of the target DNA concentration ranging from 0.5 fM to 0.05 nM with a detection limit of 3.64×10^{-16} M. Moreover the biosensor could effectively recognize the complementary target DNA from single base mismatched and non complementary target sequences.

Keywords: *Screen printed electrode, Graphene nanosheets, DNA hybridization, and Differential pulse voltammetry*

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Electrochemical immunoassay based on a 96-well screen-printed ELISA plate

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Abstract

In this work, a novel electrochemical based-immunoassay for the specific detection of biomarkers employing a 96-well screen-printed microplate as the transducer surface, was developed. The capture element of the proposed sandwich immunoassay was efficiently immobilized onto the surface of the 96-well array and different concentrations of biomarkers, within a range of clinical interest, were assayed. The detection of the analyte of interest was accomplished by using alkaline phosphatase (AP) as the enzymatic label. The analytical signal was obtained by using two AP enzymatic substrates: 3-indoxyl phosphate/silver ions (3-IP/Ag^+) [2] and the new hydroquinone diphosphate/silver ions (HQDP/Ag^+), which results were compared, namely in terms of sensitivity. In both cases, a biometallization process, where the enzymatic reaction gives rise to a compound that reduces silver ions in solution into a metallic deposit, took place. Thus, the silver enzymatically deposited on the electrode surface was detected through the oxidation peak of the silver when an anodic stripping scan was carried out. Moreover, different methodologies for the modification, in a reproducible manner, of this 96-well screen-printed electrochemical array, were studied. Therefore, the ELISA plate surface was modified with carbon nanotubes (CNTs), gold nanoparticles (GNPs) and with a hybrid conjugation of these carbon-metal nanomaterials (CNTs-GNPs). The reproducibility, stability and biofuncionality of these nanostructed transducer surfaces were also evaluated. The electrochemical behaviour of this immunosensor was carefully evaluated assessing aspects as sensitivity, non-specific binding, limits of detection and reproducibility and the analytical figures of merit were obtained.

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Non-enzymatic ethanol sensor based on a nanostructured disposable screen-printed electrode

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Abstract

The determination of ethanol is of great importance in food and beverage industries which need fast, simple and economic analytical methods to control fermentation processes and the quality of products [1]. A variety of methods (e.g., gas chromatography, liquid chromatography, refractometry, spectrophotometry, among others) had been reported for the determination of this analyte [2]. These methods need bulky instrumentation and are relatively expensive and complex to perform. For that reason, the development of alternatives to perform *in situ* determination of ethanol is demanded. Electrochemical sensors (ES) appears as promising methods for the development of simple, fast, cost effective and portable platforms for *in situ* analysis. Among ES, several enzymatic ethanol sensors have been developed in recent years. However, aspects such as the chemical and thermal instabilities intrinsic of the nature of enzymes, as well as the tedious fabrication procedures, appear as important disadvantages of these enzymatic sensors [3]. Therefore, in order to surpass these drawbacks, great attention is being paid to metal nanomaterials, which can be useful for catalytic and analytical applications. The excellent catalytic properties of platinum nanoparticles (Pt-NPs) for the oxidation process of alcohols have already been described [4, 5].

Herein, a simple and sensitive method for the electrocatalytic detection of ethanol using disposable screen-printed carbon electrodes modified with Pt-NPs is presented. The electrochemical results obtained revealed that Pt-NPs can effectively enhance the electron transfer between the analyte of interest and the electrode. The content of ethanol was assayed in different alcoholic beverages such as beer, wine and spirituous drinks; moreover alcohol-free beverages were also analyzed. The electrochemical behaviour of this screen-printed enzymatic-free ethanol sensor was carefully evaluated assessing aspects such as sensitivity, limits of detection and reproducibility and the analytical figures of merit were obtained.

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Application of ZnO nanoparticles ionic liquids modified electrode as a sensor for determination of promazine

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Abstract

Promazine is a medication that belongs to the phenothiazine class of antipsychotics. An older medication used to treat schizophrenia; it is still prescribed, alongside newer agents such as olanzapine and quetiapine. It has predominantly anticholinergic side effects, though extra pyramidal side effects are not uncommon either. The monitoring of promazine is significant for quality assurance in the pharmaceutical industry and for obtaining optimum therapeutic concentrations in body fluids to minimize the risk of toxicity [1]. Therefore, determination of this drug is important in biological compound such as urine and drug.

In this work we describe the first report for determination of promazine using a nanostructure modified ionic liquid carbon paste electrode in the aqueous solution. For this goal, a novel modified carbon paste electrode with ZnO nanoparticle and 1-methyl-3-butylimidazolium bromide as a binder (ZnO/NPs/ILs/CPE) was fabricated. The oxidation peak potential of promazine at the surface of the ZnO/NPs/ILs/CPE appeared at 685 mV, which was about 65 mV lower than the oxidation potential at the surface of CPE under similar conditions. Also, the peak current was increased to about 4.0 times at the surface of ZnO/NPs/ILs/CPE compared to CPE. The linear response range and detection limit were found to be 0.08–450 and 0.04 µmol/L, respectively. The modified electrode was successfully used for the determination of promazine in real samples with satisfactory results. The XRD pattern of ZnO/NPs, in the 2θ range of 10–90°, is shown in Fig. 1A. Typical SEM micrograph of the ZnO/NPs is shown in Fig. 2B.

Keywords: *Promazine; ZnO nanoparticle, Ionic liquids, Voltammetric analysis*

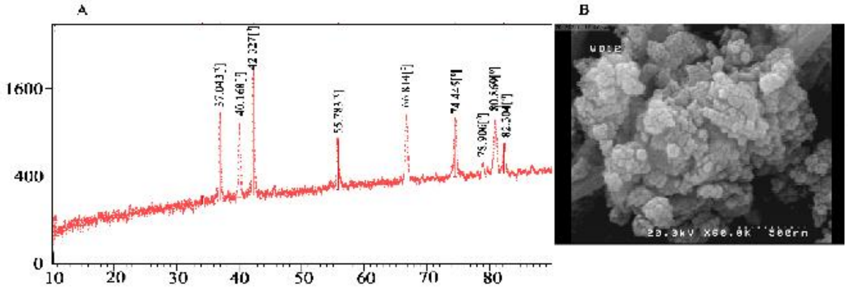

Figure 1: Fig. 1. A) XRD patterns of as-synthesized ZnO/NPs. B) SEM images of ZnO/NPs.

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Synthesized of MgO nanoparticles and its application in preparation of electrochemical sensor in vanillin analysis

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Abstract

Vanillin is a phenolic aldehyde, which is an organic compound with the molecular formula $C_8H_8O_3$. Its functional groups include aldehyde, hydroxyl, and ether. It is the primary component of the extract of the vanilla bean [1].

A carbon paste electrode modified with MgO/NPs and room-temperature ionic liquid, n-hexyl-3-methylimidazolium hexafluoro phosphate was prepared. Figure 1 shows the XRD pattern for MgO nanoparticles synthesized in this work. The electrochemistry of vanillin at the surface of the modified electrode was studied using cyclic voltammetry, chronoamperometry, and electrochemical impedance spectroscopy (EIS). The cyclic voltammogram showed an irreversible oxidation peak at 0.6 V (vs. Ag/AgClsat), which corresponded to the oxidation of vanillin. Compared to common carbon paste electrode, the electrochemical response was greatly improved. Under the optimized conditions, the oxidation peak current of morphine showed two linear dynamic ranges (in 0.08–600 µmol L^{-1}) with a detection limit of 0.02 µmol L^{-1}, using differential pulse voltammetry. The proposed sensor was successfully applied for the determination of vanillin in food samples.

Keywords: *Vanillin, MgO nanoparticles, Ionic liquids, Voltammetric analysis*

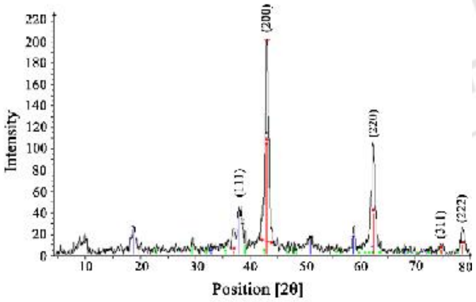

Figure 1: XRD pattern for MgO nanoparticles

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A nanostructure based sensor for determination of BHA in food samples

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Abstract

Butylated hydroxyanisole (BHA) is an antioxidant consisting of a mixture of two isomeric organic compounds, 2-tert-butyl-4-hydroxyanisole and 3-tert-butyl-4-hydroxyanisole. It is prepared from 4-methoxyphenol and isobutylene. It is a waxy solid used as a food additive with the E number E320. The primary use for BHA is as an antioxidant and preservative in food, food packaging, animal feed, cosmetics, rubber, and petroleum products.[1] BHA also is commonly used in medicines, such as isotretinoin, lovastatin, and simvastatin, among others.

A sensitive and selective electrochemical method for the determination of BAH was developed using CdO nanoparticles (Fig. 1) and a room temperature ionic liquid (i.e. 1-butyl-3-methylimidazolium hexafluoro phosphate. This modified electrode is a very good alternative to previously described electrodes because the electrocatalytic effect is achieved without any electrode modification. The electrochemical parameters such as diffusion coefficient and charge transfer resistance were determined using cyclic voltammetry and electrochemical impedance spectroscopy. Under the optimized conditions, the peak current was linear to BHA concentration over the concentration range of 1.0 to 550 μmol L^{-1} using square wave voltammetry. The detection limit was 0.06 μmol L^{-1}. The proposed method was successfully applied to the determination of BHA in food samples.

Keywords: *BHA, CdO nanoparticles, Ionic liquids, Voltammetric analysis*

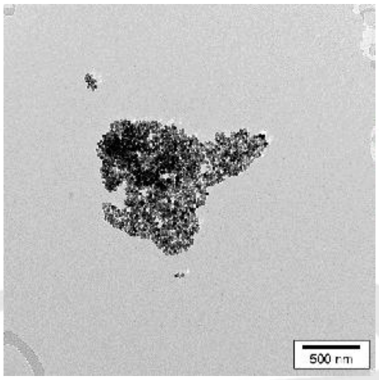

Figure 1: Tem image of CdO nanoparticles

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Reference

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11th Annual Electrochemistry Seminar of Iran

Tarbiat Modares University 18-19 Nov, 2015

Synthesize and functionalization of Mesoporous Silica Nanoparticles for drug delivery to cancer cells

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Abstract

Aim: Nowadays cancer is one of the main reasons for mortality, so scientists try to find new methods for drug delivery.[1] Nanoparticles are promising carriers to overcome lots of problems in this area.[2] Among different types of nanoparticles, Mesoporos Silica Nanoparticles (MSNs) show several attractive features for anticancer drug delivery.[3]

Methods: In this study we prepared MSNs with different functional groups including amine-modified MSNs, phosphonate-modified MSNs, PEGylated MSNs, MSNs functionalized with polyethyleneimine-polyethylene glycol (MSN-PEI-PEG) and unmodified MSNs by using co-condensation method. The nanoparticles were characterized with Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), BET surface area, particle size analyzer, Thermogravimetric Analysis (TGA) and Elemental Analysis (CHN). These nanoparticles were loaded with anticancer drug, epirubicin hydrochloride (EPI). Cytotoxicity of MSNs loaded with EPI were evaluated with MTT assay on C26 cancer cell line and the in-vivo antitumor activity of MSNs loaded with EPI were evaluated in BALB/c mice bearing C26 colon carcinoma.

Results: The TEM images show spherical and porous nanoparticles (Fig. 1). Phosphonated MSNs had the highest drug loading. Drug release from MSNs was pH- and time-dependent. In vitro drug release in Phosphate Buffer Saline with pH 7.4 was slow whereas in acetate buffer with pH 5.5 was rapid. In-vivo antitumor activity of MSN-PEI-PEG loaded with epirubicin was better than the other formulations.

Conclusion: The results indicated that MSNs could be an effective nanocarriers for anti-tumor therapies

***Keywords**: Mesoporous silica, Epirubicin, Drug delivery, Cytotoxicity, Cancer, Nanoparticle*

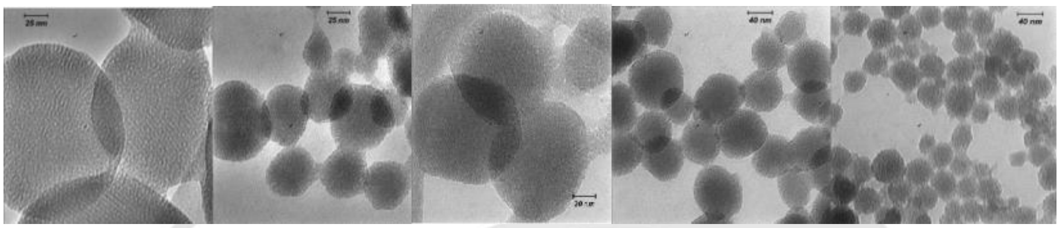

Fig.1. TEM images of unmodified-MSN, amine-MSNs, phosphonate-MSNs, PEGylated MSNs, MSN-PEI-PEG from left to right respectively.

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Electrochemical behavior of sulphydryl compounds at surface of carbon paste electrode modified with ferrocene/carbon nanotubes

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Abstract

During the past few years, considerable research efforts have been devoted to the synthesis, modifications, and applications of carbon nanotubes (CNTs), due to their appealing uniform and high specific surface area and unique physical and chemical properties (1-3). In this work, we report a simple and effective strategy for functionalization of the carbon nanotubes by ferrocene. Then carbon nanotubes functionalized by ferrocene (FC-CNTs) were studied by scanning electron microscopy (SEM), energy dispersive X-ray (EDAX) and voltammetry methods. In order to study electrocatalytic properties of carbon nanotubes functionalized with ferrocene, carbon-paste electrode modified with carbon nanotubes functionalized with ferrocene (FC-CNTs/CPE) was prepared and electrochemical behavior of this modified electrode was investigated in absence and presence of sulphydryl compounds. The results showed that sulphydryl compounds oxidation was catalyzed by carbon nanotubes functionalized with ferrocene in carbon paste and due to anodic current increase according to concentration of sulphydryl compounds.

Keyword: *Ferrocene, Carbon nanotubes, Sulphydryl compounds, Carbon paste electrode*

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Electrochemical behavior of silver nanoparticles synthesized at different temperatures

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Abstract

Nanocatalysis has recently been a rapidly growing field which involves the use of nanoparticles as catalysts for a variety of organic and inorganic reactions (1). Ag nanoparticles show excellent catalytic and electrocatalytic activities. For the past few years, various rapid chemical methods have been developed for the synthesis of silver nanoparticles (2). Reduction of $AgNO_3$ by reductants such as citrate, ascorbic acid, or borohydride, is among the most used methods for the preparation of silver nanoparticles in aqueous solution (3).

In this work, first silver nanoparticles were synthesized in the presence of gelatin as reductive and stabilizer in aqueous media at temperature of 500, 600, 700 and 800 °C. The synthesized silver nanoparticles were studied by XRD, SEM, EDAX and voltammetry methods. XRD results of silver nanoparticles have shown 28, 25, 22 and 18 nm in size approximately, respectively at temperature of 500, 600, 700 and 800 °C. In order to study the catalytic properties of silver nanoparticles, carbon paste electrodes modified with silver nanoparticles synthesized at different temperatures were prepared and electrochemical behavior of these modified electrodes were investigated in the presence of sulfuric acid. The results showed that the reduction of hydrogen ion was catalyzed by silver nanoparticles, leading to increase cathode current.

Keyword: *Silver nanoparticles, Gelatin, Catalyst, Hydrogen evolution reaction*

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The impact of nanomaterials on signal amplification in a miRNA electrochemical sensor

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Abstract

Circulating miRNAs have been becoming as one of the most important biomarkers for cancer early detection (1). Biosensors are the attending class of miRNA quantification methods due to their great specificity and selectivity. The electrochemical biosensors are the most attractive method, because of their inexpensive, fast and precise detection (2). Additionally, nanobiosensors are the biosensors which are using nanomaterials for signal amplifying and improving the sensitivity of the detection system (3). Many of nanomaterials have been synthesized with different elements, shapes, structures, aspect-ratios and functionalization scheme, based on their goal application. In this research, graphene oxide and gold nanorods applied in an electrochemical nanobiosensor for miRNA quantification (4). The graphene oxide used for expanding the active area of electrode surface, and the gold nanorods attaching to the graphene oxide sheet to provide a media for attachment of thiolated single strand probes (SS-probe) (5-6). The probe was designed to specifically and selectively hybridize to the target miRNA. Additionally, Oracet blue used as an electroactive label which can intercalates with double strand oligonucleotide and the reduction signals of OB is measured by differential pulse voltammetry (DPV). The results showed that application of graphene oxide and gold nanorods are very effective in signal amplification and the current for nanobiosensor is much higher compared to the method that not used nanomaterials (Fig 1). In the optimization of experiments which is shown in the Fig 2, the maximum current for the nanobiosensor was achieved at the concentration of the graphene oxide and gold nanorods, 1.0 mg/mL and 100µg/mL, respectively.

In conclusion, the application of nanomaterials, graphene oxide and gold nanorods, have extensively improved the electrochemical signals, succeeded the better sensitivity and lower detection limit.

Keywords: nanomaterial, Graphene oxide, Gold nanorods, Nanobiosensor

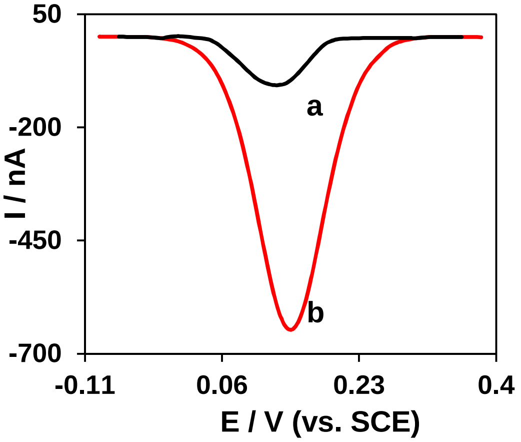

Fig 1. The difference of DPVs (a) without nanomaterials, (b) with nanomaterials

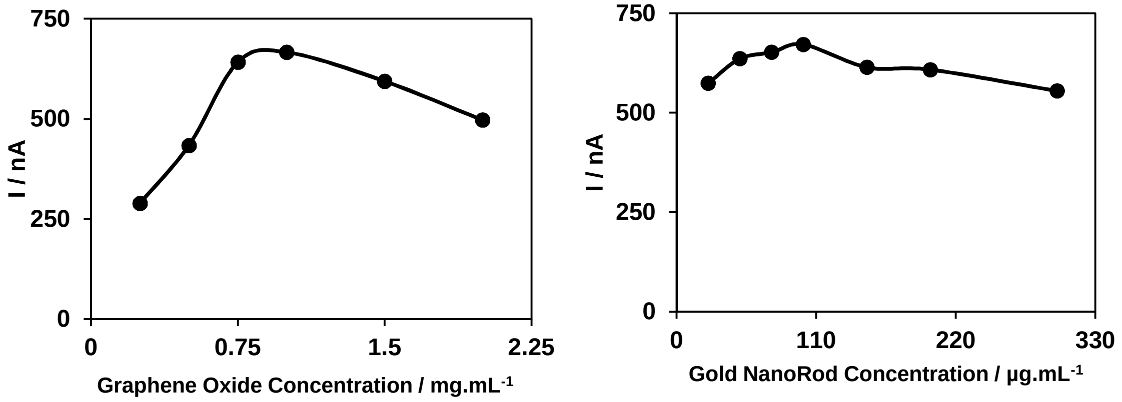

Fig 2. The optimization of nanomaterial concentrations to achieve maximum signal amplification

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A modified ZnO/CNTs nanocomposite ionic liquid carbon paste electrode as a sensor for nitrite determination

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Abstract

The presence of nitrite in groundwater and atmosphere is an essential precursor in the formation of nitrosamines, many of which have been proven to be powerful carcino- gens [1, 2]. The increase in nitrite concentration in the blood causes a decrease in oxygen transport by the blood causing methemoglobinemia, better known as the “blue baby syndrome” reaction of nitrite with Fe (II) forming hemoglobin to methemoglobin, HbFe (III) [3]. For these reasons, determination of nitrite has received consider-able attention.

A fast and simple voltammetric method based on the use of ZnO/CNTs nanocomposite/ionic liquids carbon paste electrode is proposed for the determination of nitrite. In the first step, we describe synthesis and characterization of ZnO/CNTs nanocomposite with different methods such as transmission electron microscopy (TEM) (Fig. 1). In the second step, application of the synthesis ZnO/CNTs nanocomposite describes for the preparation of carbon paste electrode modified with ionic liquids as a binder for voltammetric determination of nitrite in food samples. The peaks current of square wave voltammograms (SWV) of nitrite increased linearly with their concentration in the ranges of 0.1–900 μM. The detection limits for nitrite was 0.07. The modified electrode has been successfully applied for the assay of nitrite in food samples. The obtained data was check with F and t tests.

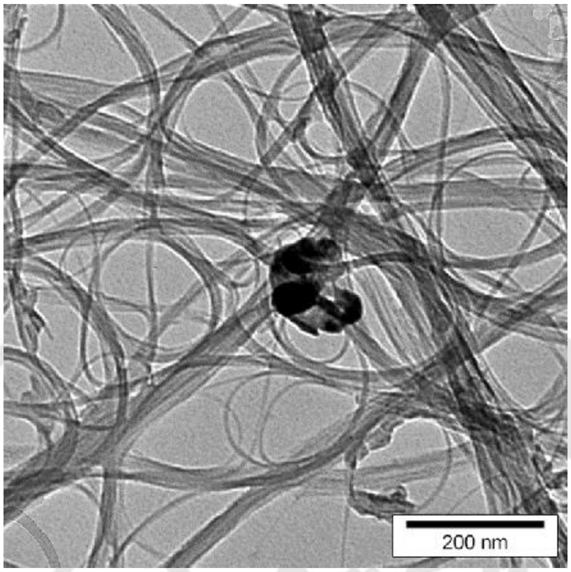

Figure 1: TEM image of ZnO/CNTs

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Keywords**:** *Nitrite, ZnO/CNTs nanocomposite, Ionic liquids, Voltammetric analysis*

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Determination of vanillin in food samples based on an ionic liquid/$CuFe_2O_4$ nanoparticle carbon paste electrode

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Abstract

Vanillin (VAN)(4-hydroxy-3-methoxybenzaldehyde) is the major component of natural vanilla. The desirable flavor and aroma properties of vanillin have led to its widespread application in confectionery, beverage, pharmaceutical, and food and perfumery industries [1].

In this work, a simple and high sensitivity electrochemical sensor was developed to determine VAN based on $CuFe_2O_4$ nanoparticles ionic liquid modified carbon paste electrode ($CuFe_2O_4$/ILCPE) using cyclic voltammetry, electrochemical impedance spectroscopy (EIS) and square wave voltammetry (SWV) methods. The novel sensor exhibited an obviously catalytic activity towards the oxidation of VAN, which can be confirmed by the increased oxidation peak current and the decreased oxidation peak potential when compared with the bare carbon paste electrode (CPE). The electron transfer coefficient (a), diffusion coefficient (D), and charge transfer resistance (R_{ct}) of VAN at the modified electrode were calculated. The linear response range and detection limit were found to be 0.1–700 µM and 0.07 µM, respectively (Fig. 1). Other species did not interfere with the determination of VAN at a surface of propose sensor in the optimum condition. The proposed sensor was successfully applied for the determination of VAN in food samples with satisfactory results.

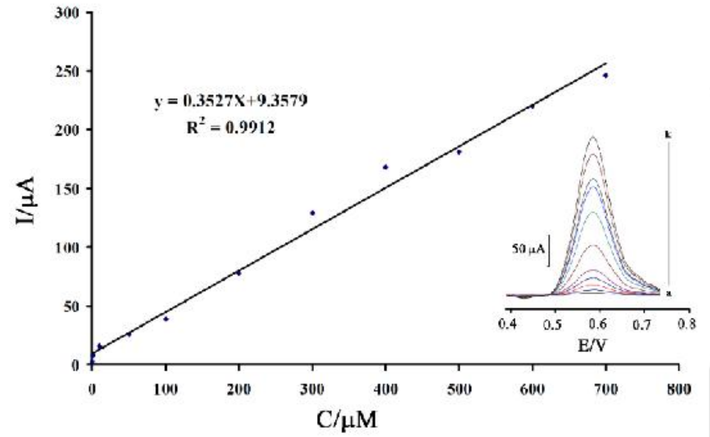

Figure 1: The plots of the electrocatalytic peak current as a function of VAN concentration. Inset) SWVs of $CuFe_2O_4$/ILs/CPE in 0.1 M PBS (pH 7.0) containing different concentration of VAN in µM.

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***Keywords*:** *Vanillin, $CuFe_2O_4$ nanoparticles, Ionic liquids, Voltammetric analysis*

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Sol-gel electrode modified with carbon nanotubes as a novel sensor for the voltammetric determination of gallic acid

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Abstract

Gallic acid ($C_7H_6O_5$) is one of the natural phenolic antioxidants found in black tea, grapes, sumac, saffron and some other plants. Due to the effects of gallic acid in human health, antioxidant and anticancer activities the development of robust and sensitive methods for the determination of this component gains more importance [1]. Recently many techniques have been employed for the determination of GA including spectrophotometry [2], chromatography [3], flow injection [4], resonance light scattering [5] and electrochemical methods [6]. In comparison with other methods electrochemical techniques are simple to perform, rapid, reasonably inexpensive and are appropriate alternative to other methods [7].

At the present study electrochemical behavior of gallic acid at sol-gel electrode modified with carbon nanotubes was investigated using cyclic voltammetry and cronoamperometry. Differential puls voltammetry as a sensitive technique was used for the determination of gallic acid at trace amounts. Some effective parameters such as pH, and concentration and type of supporting electrolyte were optimized.

Obtained results showed linear ranges of 0.05 – 2.2 mM and 1.6 – 99 µM and detection limits of 13 and 0.96 µM for cyclic voltammetry and differential puls voltammetry respectively. Developed sensor successfully used for the determination of gallic acid at tea sample.

***Keywords**: Gallic acid, Sol-gel electrode, Carbon nanotubes, Voltammetry*

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Amperometric sensing of anti-HIV drug, Nevirapine, on nanocomposite modified glassy carbon electrode

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Abstract

This work describes the synthesis of silver nanoparticles functionalized with 11-mercaptoundecanoic acid and thiosemicarbazide that covalently attached to the multi wall carbon nanotube (MWCNT) on the surface of glassy carbon electrode. The modified glassy carbon electrode was used to electrochemical oxidation study and determination of antiretroviral drug Nevirapine (NEV). NEV is the first member of the non-nucleoside reverse transcriptase inhibitors that licensed for the treatment of AIDS [1]. Various techniques have been developed for the analysis of NEV. In spite of the great success of these methods, their high costs, time-consuming and complicated operations, limit their applications in routine laboratories. Only a few electrochemical methods has been presented for determination of NEV [2,3].

Hence, the aim of this work was to construct of a novel electrochemical sensor for determining the concentration of NEV in human serum samples and dosage forms. The proposed sensor’s respond showed good accuracy and reproducibility to NEV and exhibited excellent characteristics by amperometry such as a wide linear range from 4 to 80 µM, a low detection limit of 200 nM, high sensitivity.

These results showed the efficient catalytic property of the AgNPs-TSC/MWCNTs nanocomposite modified glassy carbon electrode toward NEV determination.

Keywords: *Nevirapine, anti-HIV drug, Ag nanoparticles, MWCNTs, modified glassy carbon.*

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PEDOT:PSS-Graphene-Nickel Nanoparticles Composite as Electro catalyst for urea oxidation

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Abstract

A facile two-step strategy was used to preparation Nano composite of reduced graphene oxide doped conducting polymer poly (3,4-ethylenedioxythiophene) decorated with nickel nanoparticles (NiNPs) onto a glassy carbon electrode (GCE). Composites of poly (3,4-ethylenedioxythiophene):poly (styrene sulfonate) (PEDOT:PSS) and reduced graphene oxide (RGO) have been prepared by solution mixing and have been fabricated as an beneficial support for Ni nanoparticles on a GCE. NiNPs were electrodeposited on PEDOT+RGO support by applying constant potential to nickel ions solutions. Then, NiNPs/PEDOT+RGO/GCE applied as efficient electro catalyst for electro oxidation of urea.

The electro catalytic properties of NiNPs/PEDOT+RGO modified glassy carbon electrode toward the oxidation of urea were analyzed by cyclic voltammetry (CV) and chronoamperometry (CA). Cyclic voltammograms indicated the high electro catalytic activity of NiNPs/PEDOT+RGO is mainly described to the good electrochemical activity of PEDOT+RGO composites and the well-dispersed Ni nanoparticles on the surface of PEDOT+RGO composite. Images of scanning electron microscope also was used to checking the changes on the surface of the electrode after modification. The composite exhibits a good stability after 1000 s and causes a noticeable intensification electrochemical effective surface area of modified electrode. The electrochemical effective surface area of four modes of electrode including the bare GCE, NiNPs/PEDOT/GCE, PEDOT+RGO/GCE and NiNPs/PEDOT+RGO/GCE were calculated 0.28, 0.71, 0.81, 0.98 Cm^2 respectively.

The urea electrochemical oxidation process in alkaline media is described below:

$$CO(NH_2)_2(aq) + 6OH^- \rightarrow N_2(g) + 5H_2O(l) + CO_2(g) + 6e^- \quad (1)$$

$$6H_2O(l) + 6e^- \rightarrow 3H_2(g) + 6OH^-(aq) \quad (2)$$

Reaction (1) occurs at the anodic compartment of the urea electrolyzer, while reaction (2) occurs at the cathodic compartment of the cell.

Hence the NiNPs/PEDOT+RGO catalyst is promising material for urea removal/decomposition from urea-rich wastewater, as well as for hydrogen production.

***Keywords*:** *Poly (3, 4-ethylenedioxythiophene), Reduced graphene oxide, Nickel nanoparticles, Electro catalyst, Urea.*

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Simultaneous determination of epinephrine and acetaminophen concentrations using a modified glassy carbon electrode prepared by Graphene and NiO nanoparticles

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Abstract

Based on the outstanding properties of graphene (GR) and nickel oxide nanoparticles (NiO NPs), modified electrode was prepared by casting GR solution and then electro deposition of NiO NPs on the glassy carbon electrode (GCE) surface. GR was obtained by chemical reduction of graphite oxide (GO) and characterized by scanning electron microscope and infrared spectroscopy. The electrochemical effective surface area of two modes of electrode including the NiO/GR/GCE and NiO/GCE were calculated 0.038 and 0.029 cm^2 respectively.

The electro catalytic properties of NiO/GR modified glassy carbon electrode toward the oxidation of epinephrine (EP) were analyzed by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). In CV studies, in the presence of EP, NiO/GR composite modified electrode shows a significantly higher current response for epinephrine oxidation.

At the pH of 7.0 in a 0.1M phosphate buffer solution, the DPV anodic peak currents showed a linear relationship versus EP concentrations in the range of 1.0–100µM and 100-1800.0 µM. The detection limit of 0.84 µM with the linear detection range from 1 µM to 100µM was obtained.

The modified electrode exhibits an efficient electro catalytic behavior together with well-separated oxidation peaks for EP and acetaminophen (AC). The diffusion coefficient ($D = 6.56\times10^{-5}\ cm^2\ s^{-1}$), and the kinetic parameters such as electron transfer coefficient, ($\alpha = 0.33$) and catalytic rate constant, ($k'_h = 8.7\ cm\ s^{-1}$) for EP were also determined using electrochemical approaches.

Finally, the resulting sensor was used to detect EP and AC simultaneously in blood plasma samples. The results were explained using the theory of electro catalytic reactions at chemically modified electrodes.

Keywords: *Graphene, Nickel oxide nanoparticles, Electro catalysis, Epinephrine, Acetaminophen.*

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A $CuFe_2O_4$ nanoparticle ionic liquids carbon paste electrode as a sensor for uric acid analysis

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Abstract

Uric acid is a metabolism product of purine in human body [1]. The uric acid concentrations in urine and serum are in certain ranges for healthy persons. Therefore, the determination of UA concentration is helpful for the diagnosis of the some diseases such as gout, hyperuricaemia and Lesch-Nyhan syndrome.

In this work, a new room temperature ionic liquid modified $CuFe_2O_4$ carbon paste electrode had been fabricated by using hydrophilic ionic liquid 1-methyl-3-butylimidazolium bromide as a binder. In the first step, we synthesized $CuFe_2O_4$using co-precipitation methods and nanoparticles characterized with TEM method. Figure 1 shows a typical TEM for synthesized nanoparticles.

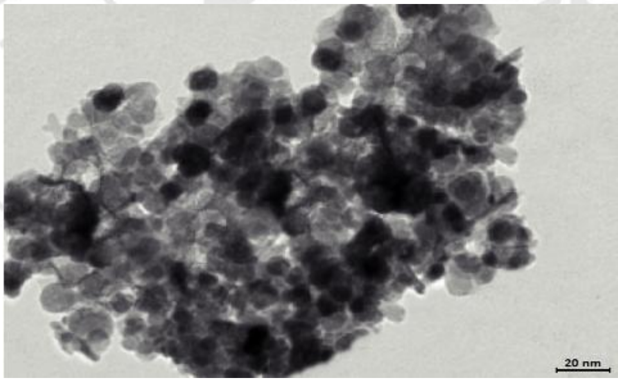

Figure1; TEM image of $CuFe_2O_4$

The cyclic voltammogram showed an irreversible oxidation peak signal for UA at a surface of modified electrode. Compared to bare carbon paste electrode, the electrochemical response was greatly improved for UA electrooxidation. Detection limit of UA was found to be 0.06 μM using square wave voltammetry (SWV) method. The proposed sensor was successfully applied for the determination of UA in human urine samples.

Keywords: *Uric acid, $CuFe_2O_4$, Ionic liquids, Voltammetric analysis*

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A nanostructure based electrochemical sensor for determination of epinephrine

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Abstract

Epinephrine (EP) or adrenaline is an important hormone produced by the adrenal glands during exciting situations or high stress in human body. On the other hand, adrenaline is one of the important parts of the human body's acute stress response system, also called the "fight or flight" response. The mechanism of response for adrenaline describe by stimulating the heart rate, contracting blood vessels, and dilating air passages, all of which work to increase blood flow to the muscles and oxygen to the lungs. In addition, adrenaline is used as a medical treatment for some potentially life-threatening conditions including anaphylactic shock [1, 2]. This paper describes the development of 1,3-dipropylimidazolium bromide ionic liquid-$CuFe_2O_4$ nanoparticle modified carbon paste electrode for the voltammetric determination of EP in real samples. We describe the synthesis and characterization of $CuFe_2O_4$with different methods such as transmission electron microscopy (TEM); energy-dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD). The electrochemical oxidation of EP occurred in a pH-dependent $2e^-$ and $2H^+$ process, and the electrode reaction followed a diffusion-controlled pathway. The oxidation peak potential of EP on the modifed appeared at 340 mV, which was about 115 mV decrease of the overpotential compared to that obtained on the traditional carbon paste electrode (CPE). The electrochemical parameter such as charge transfer coefficient was calculated.

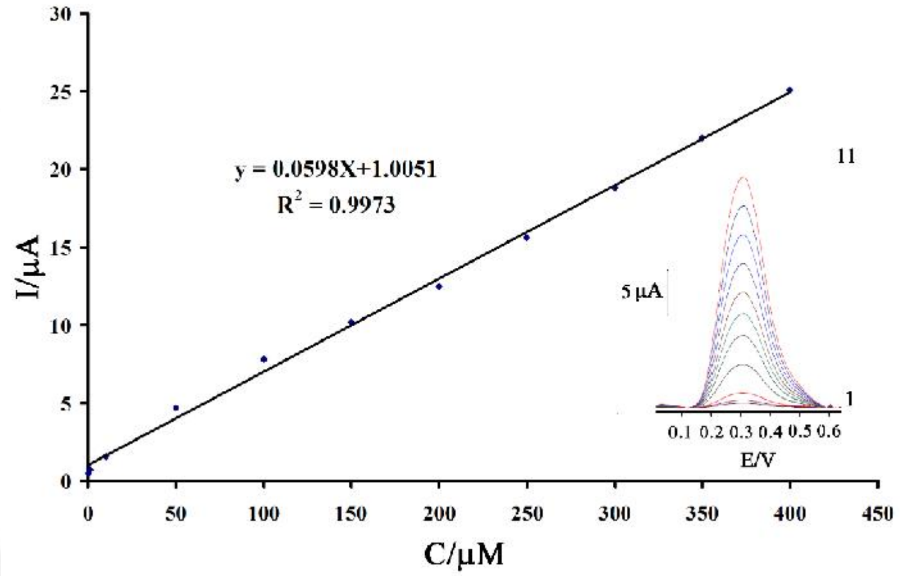

Figure 1: The plots of the electrocatalytic peak current as a function of adrenaline concentration. Inset) SWVs of $CuFe_2O_4$/ILs/CPE in 0.1 M PBS (pH 7.4) containing different concentration of adrenaline in µM.(1-11): 0.1; 1.0; 10.0; 50.0; 100.0; 1550.0; 200.0; 250.0; 300.0; 350.0 and 400 µM.

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The linear response range and detection limit were found to be 0.1–400 µmol L^{-1} and 0.07 µmol L^{-1}, (Fig. 1) respectively using the square wave voltammetry method. The results showed that the proposed sensor is highly selective, sensitive with a fast response for Ep analysis.

Keywords: *Epinephrine, $CuFe_2O_4$ nanoparticles, Ionic liquids, Voltammetric analysis*

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Electrochemical characterizations of Iron oxide/Au core/sell nano particles by embedding of them on GCE/MWCNTs electrode surface

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Abstract

In this work a novel method for electrochemical characterization of Iron oxide/Au core/shell nano particles was reported. Co-precipitation method was used for synthesizing Iron oxide core following by citrate reduction for preparing Au shell. A glassy carbon electrode was modified by dropping a suspension of oxidized multi walled carbon nano tubes on its surface. After drying of CNT layer, some dispersion of Iron oxide/Au core/shell nano particles was embedded on CNT layer. The electrochemical studies using CV technique showed very sharp picks related to Au shell. The absence of Iron oxide peaks verified full coating of them by Au shell.

Keywords: *Electrochemical characterization, Iron oxide/Au core/shell nano particles, Glassy carbon electrode, Multi walled carbon nano tubes*

Introduction

Nowadays, Iron oxide/Au core/shell nano particles have been considered as interesting materials in many research areas such as biosensing, drug delivery and cancer therapy [1]. Since the full coating of Iron core is necessary for protecting of it from degradation and achieving acceptable performance in all applications, various microscopy and spectroscopy methods and recently electrochemical techniques have been reported for characterization of these materials. Mohammad and Arfine studied the electrochemical behavior of Iron oxide/Au core/shell NPs by CV technique. They used compression of NPs in a cylindrical Pt electrode to study them. Very weak peaks were observed for Au [2]. Carla et al. used a graphite paste electrode modified by core/shell $CoFe_2O_4$/Au nano particles for electrochemical characterization of NPs [3]. In this study, a high sensitive and novel method was described for electrochemical characterization of iron oxide/Au core/shell NPs using by glassy carbon electrode modified by oxidized Multi walled carbon nano tubes.

Experimental

Electrochemical experiments were performed using AUTOLAB PGSTAT 30 electrochemical analysis system. A three-electrode system was used that consists of GCE/MWCNTs, a saturated calomel electrode as reference electrode and platinum wire as auxiliary electrode. The iron oxide NPs were synthesis by co-precipitation method. Then, Au shell was formed using by reduction of Au^{3+} ions by citrate [4]. The Au NPs were also prepared by citrate reduction of Au^{3+} ions.The MWCNTs were undergo acid treatment by nitric acid and sulphuric acid. The GCE/MWCNTs was prepared through dropping of 2 µl of MWCNT dispersion (dispersed in DMF, 6 mg/ml) on electrode surface and subsequent drying in room temperature. For embedding of MNPs or Au NPs or Fe_3O_4 NPs on electrode surface, a 2 µl of dispersion of them (10 mg/ml for Iron oxide/Au and 1 mg/ml for Au NPs) dropped on modified electrode surface and left to dry at room temperature.

Results and discussion

The shape and size of the nanoparticles were determined by SEM. The nanoparticles appeared nearly spherical and had an average diameter of about 20 nm and 30 nm for Fe_3O_4 and Fe_3O_4/Au ones respectively. The increase in the diameter of the some nanoparticles could be not only due to gold coating, but also to the aggregation of several Fe_3O_4 nanoparticles coated by the same gold shell. The EDS spectra also confirmed the composition of nanoparticles and demonstrated the presence of Au, Fe and O elements with 5.33 % wt of Au in Fe_3O_4/Au NPs.

The electro-chemical redox properties of Fe_3O_4/Au NPs was studied employing cyclic voltammetry in the applied potential range of 0.0 to +1.5 V recorded at 50 mVs-1 in the presence of phosphate buffer solution (pH 7.0, 0.05 M) and KCl (0.5 M). For identifying of observed peaks, CVs for GCE/MWCNTs, GCE/MWCNTs-Fe_3O_4 and GCE/MWCNTs-AuNPs was recorded, too. As shown in Fig. 1 an oxidation peak in 0.9 was observed for GCE/MWCNTs-AuNPs in which for GCE/MWCNTs- Fe_3O_4/AuNPs a similar peak in higher potential, 1.1 was observed too that related to Au oxidation. Similar reduction peaks were observed for these two cases that shows reduction of Au NPs for GCE/MWCNTs-AuNPs and Au shell for GCE/MWCNTs- Fe_3O_4/AuNPs.

The presence of a weak reduction peak at 0.9 V for GCE/MWCNTs may be related to Iron impurities in MWCNTs. This peak has low intensity for GCE/MWCNTs-AuNPs and GCE/MWCNTs-Fe_3O_4/AuNPs that shows well formation of Au shell on Fe_3O_4 cores. A same peak with higher intensity was observed for GCE/MWCNTs-Fe_3O_4, which confirms that the reduction peak at 0.9 was related to Iron.

Conclusions

The electrochemical studies using GCE/MWCNTs and CV technique showed very sharp picks related to Au shell of Fe_3O_4/Au core/shell NPs and absence of peak related to Iron oxide core that provides a simple and cheap method for electrochemical characterization of nano materials.

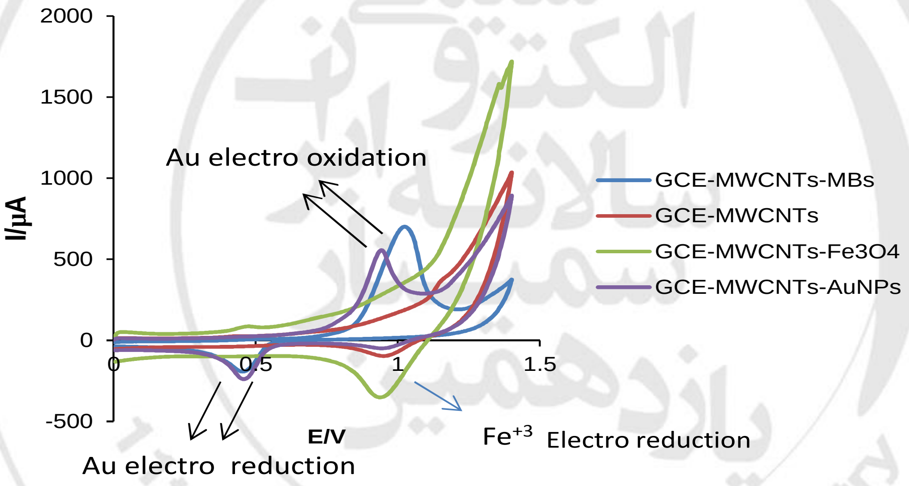

Fig. 1 CVs for different modified form of GCE.

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Preparation of epoxy-zeolite nanocomposite coating and investigation of immersion time effect on its corrosion protection on mild steel in NaCl media

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Abstract

Mild steel used in nearly every type of product created from steel, it is weldable, very hard and although it easily rusts, very durable. This type of steel is able to be magnetized and used in almost any project that requires a vast amount of metal. Due to its poor corrosion-resistance, it must be protected in order to prevent rust from damaging it.

The application of polymer coatings to metals and alloys is the oldest means of corrosion control and dates back to antiquity. Most modern barrier systems are based on thermosetting polymers, such as epoxies [1]. Epoxy systems are widely used, for example, in building and civil engineering sectors, due to an excellent combination of mechanical properties, chemical stability, corrosion and wear resistance as well as adhesiveness to most metals and alloys [2]. Barrier and corrosion protection properties of organic coating systems may be improved by addition of fillers. Smaller filler particles may increase polymer–fillerinteractions and also improve barrier properties of the host polymericcoating. Hence, nano-sized particles with very fine grain sizeand high boundary volume, provide enhanced barrier properties incomparison with conventional fillers [3]. Indeed, such nanocomposite coatings have shown improved corrosion protection and barrier properties.

In this work, Epoxy-zeolite nanocomposite coatings were prepared. The synthesized coatings were characterized by Scanning Electron Microscopy (SEM) and XRD techniques.Corrosion performance of coated mild steel panels was investigated using EIS, Polarization techniques and immersion test. The immersion test show that nanocomposite can improve the protection ability

of epoxy coatings, so that tafel polarization and impedance curves in immersion tests, show that the protection efficiency of coated mild steel panels, during 43 days immersion in 3.5% NaCl electrolyte is 99%.

Keywords**:** Nanocomposite, Resin epoxy, Corrosion, Electrochemical Impedance Spectroscopy, Polarization, Mild steel, Immersion test

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Development of a New Electrochemical Imprinted Sensor Based on Poly-pyrrole, Sol-gel And Multiwall Carbon Nanotubes for Tramadol Analysis

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Abstract

Tramadol (1RS, 2RS)-2-[(dimethylamine)-methyl]-1-(3-methoxy-phenyl)-cyclohexanol hydrochloride) is a centrally acting analgesic that is widely used for the treatment of moderate to severe pain (including postoperative) throughout the world. Tramadol is extremely useful in treating somatic and visceral pain, and may also be of value in the treatment of neuropathic pain [1]. A new electrochemical sensor based on a glassy carbon electrode (GCE) modified with functionalized multiwall carbon nanotubes and molecularly imprinted polymer (MIP) composed from Polypyrrole and sol-gel for determination of tramadol was developed. The integration between functionalized multiwall carbon nanotubes, conductive polymers and sol-gel technology is a way to take advantage of the properties of all materials [2,3]. The fabrication process of the sensor was characterized by cyclic voltammetry and electrochemical impedance spectroscopy. The electrode was applied to the simple, rapid, highly selective and sensitive determination of tramadol using square wave voltammetry. The experimental parameters that affect the performance of the MIP sensor were optimized. Under the optimized conditions calibration curve of the imprinted sensor had two linear concentration ranges from 0.2 to 2.0 nM and 2.0 to 20.0 nM, with the limit of detection (LOD) of 0.25 nM. The effects of potentially interfering substances on the determination of tramadol were investigated and it was found that the electrode is highly selective. Furthermore, the proposed method was successfully applied for determination of tramadol in real samples.

Keywords: *Imprinted Sensor, Tramadol, , Molecularly Imprinted Polymer, Sol-gel, Polypyrrole.*

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Developments on the modification of graphite electrodes with nanoparticles

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Abstract

The surface structure of common graphite electrodes are suitable for electrochemical detection of various analytes due to their favorable properties such as good conductivity and resistance to environmental. The material of the graphite electrodes (GEs) is low in cost, easily maintained, displays strong adsorption properties, low background current, and good electrocatalytic properties toward some electroactive molecules, and displays a wide potential window .The modification of GPEs, using a suitable electrocatalyst such as nanomaterials, is crucial to the fabrication of sensitive electrochemical sensors. Modifying graphite electrodes with nanoparticles has attracted lots of attention due to their unique characteristics. In this article we investigated on the application of modified graphite electrodes with nanomaterials.

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Deposition of ZnS thin film and modyfing optical properties by Ag nanoparticles

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Abstract

Recent years In spite of scientist have concentrated on using solar energy as a clear and renewable source of energy, using this kind of energy depend on economical justification. For this purpose, most researches have been done on efficiency and low price raw materials. Among the materials with semiconductor properties, ZnS thin film is a kind of n semiconductor with 3.65eV band gap that raw materials for deposition is low cost. Zns thin film could be used as solar cell window. Firstly In this research we focused on impressive parameters of ZnS thin film electrodeposition by direct current and pulse current and secondly on influence of Ag nanoparticles doptant on optical properties of ZnS thin film. Result showed us that good enough optical properties in ZnS thin film deposited by pulsic current method and dopted by Ag nanoparticles.

Key words: pulse electrodeposition, ZnS thin film, Ag nanoparticles, optical properties.

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Sensetive electrochemical immunosensor for human chorionic gonadotropin based on gold nanoparticle/graphene-ionic liquid-chitosan nanocomposite film modified glassy carbon electrode

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Abstract

A novel and highly sensitive electrochemical immunosensor was developed to detect human chorionic gonadotropin (hCG) based on immobilization of hCG–antibody (anti-hCG) onto robust nanocomposite containing Graphene (Gr), Chitosan (Chit), 1-methyl-3-octyl imidazolium tetra fluoro borate as ionic liquid (IL) (Gr-IL-Chit) and then Gold nanoparticles (AuNPs) were used as a linker to immobilize hCG antibody onto the modified electrode. The amine groups of the antibody are covalently attached to an AuNPs/Gr-IL-Chit nanocomposite. Cyclic voltammetry (CV), impedance spectroscopy (EIS) and scanning electron microscopy (SEM) were employed to characterize the assembly process and the performance of the immunosensor. Differential pulse voltammetry (DPV) and EIS studies demonstrated that the formation of antibody–antigen complexes decreased peak current and increased Rct of $[Fe(CN)_6]^{3-/4-}$ redox pair at the AuNPs/Gr-IL-Chit/GCE. The optimization of the pH of supporting electrolyte and the incubation time were studied in details. Because of the synergistic effect of IL, Chit and Gr and the unique properties of AuNPs, the obtained immunosensor exhibited a wide linear response to hCG in two ranges from 0.005 to 1.484 and 1.484 to 411.28 (mIU/mL). A relatively low detection limit of 0.0016 mIU/mL (S/N =3) was calculated from DPV. Satisfactory results were obtained for determination of hCG in human serum samples. Moreover, this immunosensor has dramatic stability and repeatability.

Keywords: *Electrochemical immunosensor; Human chorionic gonadotropin; Nanocomposite; Differential pulse voltammetry, Impedance spectroscopy.*

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Effect of Applied Potential on Removal of Cobalt from Polluted Water

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Abstract

The separation of a wide range of contaminants in surface water and groundwater has become a critical issue worldwide, due to population growth, rapid development of industrialization, and long-term droughts [1]. Heavy metals in wastewater are one of the severe environmental concerns. Due to the harmful effect of heavy metals in wastewater, it is necessary to find a good method to treat wastewater containing toxic metals to remove their hazardous effects on human health and ecology. In order to minimize the health risks of toxic heavy metals many methods have been suggested by different research groups to remove toxic heavy metal ions from wastewaters such as chemical precipitation, ion-exchange, membrane filtration, adsorption, electrochemical treatment, and so on. Although all of these techniques can be employed to remove heavy metals from wastewater, they also have some inherent advantages and limitations [1-3]. Electrochemical treatment technique for removal of heavy metal from wastewater is a process consisting electrodissolution of soluble anodes, usually made of iron or aluminum. The generation of metallic cations takes place at the anode, due to the electrochemical oxidation of the iron or aluminum, whereas at the cathode the production of hydrogen typically occurs. Electrocoagulation process involves many chemical and physical phenomena, such as anodic oxidation, cathodic reduction, coagulation, electrophoretic migration, and adsorption. This method is regarded as a rapid and well-controlled method that requires fewer chemicals, provides good reduction yields and produces less sludge. Although all above techniques can be employed for the wastewater treatment, it is important to notice that the selection of the most suitable treatment techniques depends on some factors such as the initial metal concentration, the component of the wastewater, capital investment and operational cost, plant flexibility, reliability and environmental impact [4]. In this study, we attempt to remove cobalt from water electrochemically by applying different potential. The applied potential is an important

parameter in all electrochemical systems. The electrochemical cell contains 200 mL of polluted water (~100 ppm cobalt) and two iron sheets as sacrificial anode and cathode. The reaction was conducted with an applied potential ranging from 8 V to 30 V, for half an hour. The concentration of cobalt in water before and after treatment was determined. The obtained results show that the concentration of cobalt in water after treatment is in the range ~8 ppm to ~44 ppm, depending on the applied potential. In fact increasing the voltage can help to increase the electrochemical reaction rate and produce more precipitate in the electrochemical cell. Based on our results it is possible to reduce the concentration of cobalt in water from ~100 ppm to about 8 ppm, using electrochemical method. We suggest this method as an easy and promising technique for removal of heavy metals from aqueous medium.

Keywords*: Cobalt, Polluted Water, Electrochemical Treatment, and Potential.*

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Influence of Applied Voltage on Electrooxidation of Iron in the Cell Containing -cyclodextrine

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Abstract

Synthesis of functionalized iron oxide nanostructures has recently been attracting increased interest for many biomedical and biological applications [1]. It is a technological challenge to control size, shape, stability, and dispersibility of nanoparticles [2-4]. Iron oxide nanoparticles possess high surface energies due to their large surface to volume ratio. Consequently, they tend to aggregate so as to minimize the surface energies. Also, they have high chemical activity. Therefore, providing proper surface coating and developing some effective protection strategies to keep the stability of magnetic iron oxide nanoparticles is very important. The present report focuses on the synthesis of functionalized magnetite nanoparticles with β-cyclodextrine molecules by applying different voltages. Here, magnetite nanoparticles were synthesized electrochemically using a chronoamperometric technique. Two purified iron plates of 1cm × 4cm and 1cm ×1cm were used as cathode and sacrificial anode, respectively. The electrodes were polished mechanically by fine grain emery paper and then ultrasonically cleaned with ethanol and dried. The cleaned electrodes were mounted in an electrolytic bath containing 200 ml of 0.25 M Na_2SO_4 and β-cyclodextrine as organic additive. In order to study the effect of applied voltage on structure and magnetic properties of the particles, a group of samples prepared by applying 5 V, 8 V, 11 V, and 14 V, keeping concentration and temperature at 0.03 M and 60°C. To understand the effect of β-cyclodextrine on the properties of Fe_3O_4 nanoparticles, one reference sample was prepared in the electrolytic bath without any organic. The reaction time was chosen as 1800 s and electrolyte temperature was controlled using a thermostatic water bath. After applying appropriate potential difference the solution went through several color changes. After a few hundred of seconds the solution became black and the particles started to precipitate. The

black precipitates washed several times with deionized water and then dried. X-ray diffraction, FT-IR spectroscopy, and electron microscopy were used to characterize the samples. X-ray diffraction patterns showed the formation of the spinel phase of Fe_3O_4. FT-IR spectra confirm the presence of organic molecules at the surface of particles. Electron microscope images showed the mean particle size is in the range 20-90 nm. The experimental parameters play significant role in determining the morphological and structural properties of the products. Based on these images we found that tuning the growth conditions has a strong effect on particle size and morphology. High resolution transmission electron microscope images showed the aggregation of very fine crystallite with different orientations. The results suggest that the particles have polycrystalline structures in nature.

Keywords*: Magnetite Nanoparticles, -cyclodextrine, Voltage, Electron Microscopy*

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Synthesis and characterization of NaX nanozeolite using stem sweep and application of Ag-modified nanozeolite in electrocatalytic reduction of H_2O_2

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Abstract

Hydrogen peroxide (H_2O_2) has a significant role in diverse fields such as synthesis of various organic compounds, food and agricultural, pharmaceutical, biological, clinical, environmental and chemical industry and fuel cells. Therefore, it is worthwhile to make efforts to develop a rapid, simple, accurate and reliable method for determination of H_2O_2 [1]. Electrochemical methods have been used for determination of H_2O_2 due to their inexpensive, effective, simple and high sensitivity nature. However, the direct oxidation or reduction of H_2O_2 at bare electrode has drawbacks like slow electron transfer kinetics and high overpotential for redox reactions. Metal particles, such as Ag as a typical noble metal particles show excellent catalytic activity for H_2O_2 reduction because they not only have common characteristics of noble metal particles but also have unique properties of biocompatibility, availability, catalysis and low toxicity [2]. Zeolite is one of the nanoporous materials that have a high potential application in the various fields such as catalysis, sensing, ion exchange and absorption for separation of various chemical species. Recently, exceptional attention has been paid to synthesis of nanocrystalline zeolites. Nanocrystalline zeolites are materials with dimensions of less than 100 nm with special properties. In the electrochemical fields, zeolites have been applied in construction of electrochemical sensors and Electrocatalysis. Zeolite-modified electrodes (ZMEs) are a subcategory of the so-called chemically modified electrode, which are electrodes based on the ion exchange ability of zeolite between electroactive and nonelectroactive cations in the surface located zeolite particles [3]. In the present work we synthesized template-free NaX nano-zeolite from SSA as silica source by the hydrothermal method. NaX was modified through the replacement of Na^+ with Ag (I). In order to prepare the modified carbon paste electrode (Ag/X-CPE), zeolite and graphite powder (30:70 w/w) were hand-mixed in diethyl ether. Afterward, 2 to 3 drops of paraffin was added and this mixture was thoroughly mixed. The resulting carbon

paste was packed in the bottom of glassy tube (internal radius of 1.5 mm) and copper wire was inserted through another end of the tube to create electrical contact. Prior to each experiment, constructed electrode (NaX-CPE) was immersed in 0.1 M $AgNO_3$ solution for 10 min. Finally, the silver ions were electrochemically reduced at -1 V vs. Ag| AgCl for 5 min. The Ag/X-CPE electrode was used for electrochemical determination of H_2O_2. The synthesized nanoparticles were characterized using X-ray diffraction, scanning electronic microscopy, Brunauer–Emmett–Teller (BET) and FT-IR techniques. The synthesized nanozeolite is used incorporating Ag (I) ions for preparing modified carbon paste electrode (Ag/X-CPE) as an electrochemical sensor for the reduction of H_2O_2. Electrochemical results demonstrate that nanozeolite provides a promising platform for the development of electrochemical sensors in biosensing and Ag/X-CPE electrode possesses the remarkable catalytic activity toward the H_2O_2 reduction. Amprometric results show that this sensor could detect H_2O_2 in linear ranges of 20 mM to 1.76 mM and 1.76–11.76 mM with a detection limit of 9.1 mM at a signal-to-noise ratio of 3 and a response time of 2 s. Furthermore, this sensor exhibited good anti-interference and selectivity. The prepared nonenzymatic H_2O_2 sensor indicated a remarkable analytical performance, including wide linear range, low detection limit, rapid response and high sensitivity toward the detection of H_2O_2 because of the existence of silver active sites in the pores of zeolites at the surface of modified carbon paste electrode.

Keywords: *Stem sweep, Ag particles, NaX nanozeolite, modified electrode, Hydrogen peroxide*.

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Preparation of bimetallic nanozeolite-supported Pt-Cu nanoparticles modified carbon paste electrode for enhanced formaldehyde electrooxidation

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Abstract

Fuel cells are being considered as an attractive electricity generation technology, which supplies very effective and direct conversion of chemical energy into electricity. To develop fuel cells, the anodic catalysts have been an important challenge. Therefore, some research fields have been dealing with the challenges to synthesis of cost effective and highly active catalyst for oxidation process of fuel in the fuel cells [1]. Formaldehyde fuel cells have been extensively considered because formaldehyde is an intermediate in the methanol oxidation. Also, it has practical application for metallizing non-conducting surfaces, especially in production of printed circuit boards [2]. Pt-based electrocatalysts are regarded as ideal catalyst for formaldehyde oxidation due to their prominent properties in the catalytic processes. However, Pt is one of the noble metals and high cost of noble metals can restrict their wide applications. Therefore, it is worthwhile to decrease the required amount of Pt in the electrocatalysts. The addition of a secondary element, in oxidized form or metallic form, into Pt catalyst is an effective way to reduce the amount of Pt. Also, bimetallic catalysts can improve the activity and stability of Pt-based catalysts due to change of Pt-Pt bond distance, d-band center shift, and Pt skin effect which result into lattice shrinking or lattice strain [3]. In the bimetallic systems like monometallic systems, the use of supporting material such as zeolite has various advantages such as stabilizing the nanoparticles against aggregation and achieving the highest possible electrode surface area which results in remarkable catalytic activity and efficiency. In this work, we synthesized NaX nanozeolite and used it for the first time for preparation of bimetallic X nanozeolite-supported Pt-Cu nanoparticles modified carbon paste electrode (Pt-Cu-XNZ/CPE). SEM image of Pt-Cu-XNZ/CPE indicated the layer of irregular flakes of graphite powder and dispersed white nanoparticles which this uniform dispersion can be assigned to presence of

nanozeolite on the electrode surface. The Cyclic voltammogram of Pt-Cu-XNZ/CPE was recorded in 0.5 M H_2SO_4 solution at 0.05 Vs^{-1}. The characteristic peaks of Pt surface (Pt-H redox peaks) at potential range of -0.2-0 V are assigned to atomic hydrogen adsorption on Pt surface. Appearance of these peaks confirm that platinization of the Cu nanoparticles surface has been achieved. The electrocatalytic activity of as-prepared Pt-Cu-XNZ/CPE toward formaldehyde oxidation was studied in an aqueous solution containing 1.5 M formaldehyde and 0.5 M H_2SO_4 at a scan rate of 0.05 $V.s^{-1}$ using cyclic voltammogram. It can be seen that formaldehyde oxidation exhibits the double voltammetry peaks that appear in the forward scan (Peak I) with peak potential of 0.72 V and reverse scan (peak II) with peak potential of 0.46 V. In summary, we prepared nanozeolite-supported Pt-Cu-XNZ/CPE for the first time with galvanic replacement method without using any reagent. This electrode indicated remarkably catalytic activity including decreasing oxidation overpotential and increasing oxidation peak currents toward formaldehyde oxidation.

Keywords**:** *Bimetallic, Electrooxidation, Formaldehyde.*

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A voltammetric sensor for determination of curcumin in food samples using nanostructure based electrochemical sensor

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Abstract

Curcumin can be used for boron quantification in the curcumin method. It reacts with boric acid to form a red-color compound, rosocyanine [1]. The curcumin determination in food industrial has great attention in the recent years. Functional foods (natural or synthetic) obtained by addition of nutrients to foods and drinks to cover dietetic recommendations 1, 2 are main group of food and human diets. Some synthetic colorants at extra level may be pathogenic, while diverse category of additive in different foods of various countries [2]. Therefore, we focus for determination of curcummin in food samples.

In this research we describe a novel CdO/NPs room temperature ionic liquid modified carbon paste electrode as a high sensitive sensor for voltammetric determination of curcumin in food samples. The synthesized CdO nanoparticles were characterized with different methods such as transmission electron microscopy (TEM) and X-ray diffraction (XRD). Figure 1 shows a typical TEM for synthesized CdO/NPs.

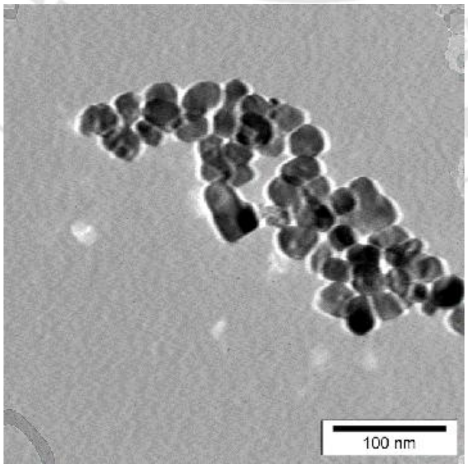

Figure 1: Tem image of CdO nanoparticles

The sensor exhibits an enhanced effectiveness for the electro-oxidation of curcumin in the optimum condition. The oxidation peak potential for curcumin at a surface of the ionic liquid (n-hexyl-3-methylimidazolium hexafluoro phosphate) carbon paste electrode appeared about 100 mV lower than the oxidation peak potential at the surface of the unmodified carbon paste electrode. The mechanism of the electro-oxidation process on the surface of the suggestion sensor was analyzed. Square wave voltammetry (SWV) was applied as a very sensitive electrochemical method for the analysis and determination of curcumin. The linear response range and detection limit were found to be 0.1 to 500.0 µM. The proposed sensor was successfully applied for the determination of curcumin in food samples.

Keywords: *Curcumin, CdO nanoparticles, Ionic liquids, Voltammetric analysis*

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Trace Amount Detection of Glucose Based On CoOx/CdS/rGO Photoelectroctrochemical Sensor

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Abstract

Facile and sensitive detection of glucose still is a challenge for analysts. Enzymatic and non-enzymatic electrochemical methods using graphene based modified electrodes are simple, available and general technique for glucose measurement (1). Enzymatic glucose sensors are popular due to their high sensitivity and selectivity toward glucose detection. Complicated immobilization procedures, long-term stability and high cost of enzymes are disadvantageous this kind of biosensors. Furthermore, glucose enzyme sensors can be easily affected by humidity, temperature and pH (2). As a result, more attempts focused on advance the non-enzymatic glucose biosensors based on transition metal, alloys, metal oxides and their composites with graphene (3). The current work describe the photoelectrocatalytic detection of glucose based on Finny Ball nanostructure (FBNs) of cobalt oxide (CoOx) which have been electrodeposited on cadmium sulfide nanoparticles /reduced graphene oxide composite (CdS/rGO). When the prepared sensor is exposed under visible light, cadmium sulfide (QD) significantly improve the sensitivity and limit of detection (4). The proposed CoOx/CdS/rGO hybrid composite is well characterized by scanning electron microscopy (SEM) and Energy Dispersive X-ray analysis (EDX) (Figure 1), and electrochemical impedance spectroscopy was used for measuring the electron transfer resistance. Those results confirm the integration of cadmium sulfide and cobalt oxide on the graphene substrate. Glucose sensing was investigated by both cyclic Voltammetry (CV) and amperometry techniques (Figure 2). The linear dynamic range and limit of detection were 1-10 and 10-1030 µM and 0.33 µM, respectively. This methodology can be used for developing glucose optical sensors with improved sensitivity.

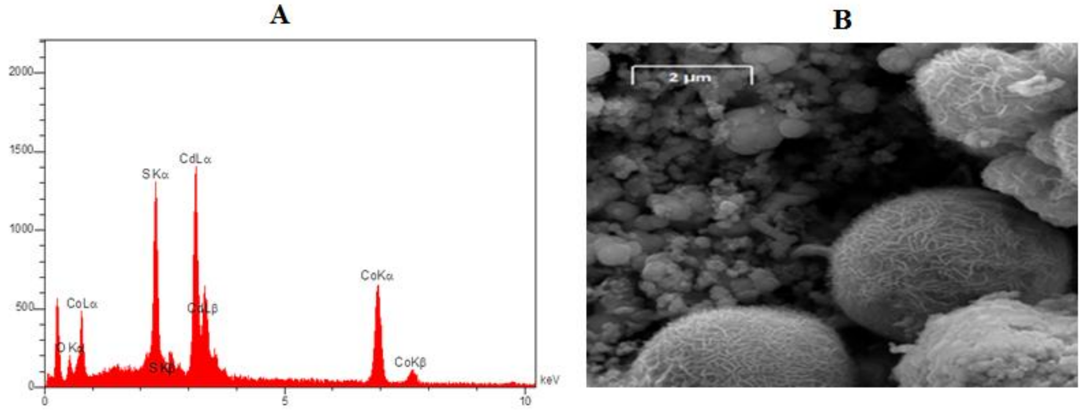

Fig.1. (A) EDX and (B) SEM image of the electrodeposited cobalt oxide on glassy carbon modifwith CdS/rGO composite.

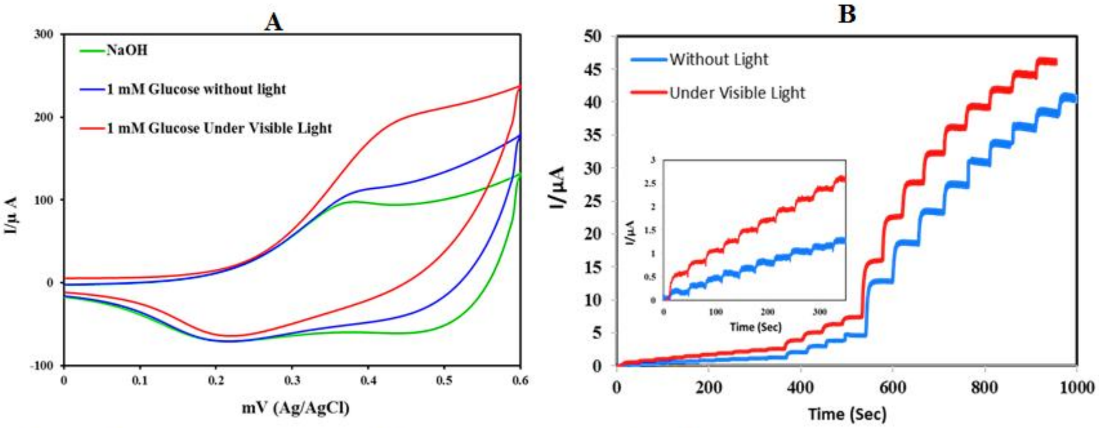

Fig.2. (A) Cyclic voltammetry response of GC electrode modified with CoOx/CdS/rGO hybrid composite in pH 12 buffer solutions at scan rate of 50mVs−1. (B) Amperometric response at rotating modified GC electrode (rotation speed 1000 rpm) held at 0.4V in pH 12 for successive addition of 1 µM and 30 µM and 0.3 mM of glucose in three levels.

Keywords: Electrodeposition; Cobalt oxide; Glucose detection; CdS Quantum Dots

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Fabrication of a new nanosensor based on PVC membrane for determination of ammonium ions

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Abstract

Ion-selective electrodes (ISE) are useful devices for determining the different cationic and anionic species because of high speed, low cost, simple preparation, a wide dynamic range and finally no requirement for the sample pretreatment [1]. In addition of using ISEs for direct determination of the investigated species they can be also used for indirect determination of other species [2]. Excess ammonia in the breeding pool may cause massive death of fish and other aquatic organisms due to eutrophication and depletion of the dissolved oxygen [3]. Furthermore, bacteria can convert ammonia into nitrite, which is a potent carcinogen [4]. Therefore, measuring ammonia content in water is important for aquaculture, drinking water and environmental monitoring. Traditional methods for measuring ammonia content were based on Nessler's reagent colorimetry, indophenol, Ophthaldialdehyde (OPA) and N-acetyl-cysteine (NAC) reagent, and titration. These methods are commonly cost and need the primary preparation steps.

In this research, a new nanosensor were prepared by incorporating sytosine amino acid as a ionophore with together a modified magnetic nano particles into a plasticized poly(vinyl chloride) matrix. The general procedure used to prepare the PVC membrane was mixing thoroughly optimised amounts of 30 mg of powdered PVC, 60 mg plasticizer DBP, 5 mg additive KTpClPB, 5 mg magnetic nano particles Fe_3O_4 modified and 2 ml of dry freshly distilled THF into a glass dish of 2 cm diameter. To this solution for the fabrication of the ammonium-selective membran 5 mg of sytosine as an ionophore was added and mixed very well. The solvent was evaporated at the room temperature. After 2 h the polymer membrane could be easily removed from the plate. Then the transparent PVC membrane was taken up from the plate and attached to the end of a glass tube with a diameter of 1 cm and height of 5 cm by means of PVC-THF viscose solution. The NH_4^+-selective electrodes were each time backfilled

with NH_4Cl internal filling solution of 0.01 mol dm^{-3} conditioned. Then the electrodes were conditioned in 0.01 mol dm^{-3} solution of MgCl for 48 h.

Calibration plots with Nernstian slopes (59.6 ± 0.8 mV/decade) for ammonium ion were observed over a linear range of concentration (1.0×10^{-6} to 1.0×10^{-1} mol dm^{-3}, at 25 ^{o}C). This electrode revealed a lower limit of detection of 3.9×10^{-7}. It has a short response time about 15 second. The influence of membrane composition, the pH of the test solution, the interfering ions on the electrode performance and the effect of temperature on the electrode response are investigating.

Keywords: Ammonium selective, PVC membrane, Nano particles, Potentiometric method

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Modified carbon paste electrode by multi-walled carbon nanotubes for Potentiometric determination of alprazolam in pharmaceutical formulations, human plasma and urine

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Abstract

For the first time a novel derivatized multi-walled carbon nano tubes-based on alprazolam carbon paste electrodes is reported. At optimum values of variable conditions, the proposed electrodes responded toward alprazolam linearly in the range of 5.0×10^{-10}-5.0×10^{-4} mol L^{-1} with slope of 19.71±0.2 mVdecade^{-1} of alprazolam concentration and detection limit of 1.3×10^{-9} mol L^{-1} for ALP/MWCNTs-CPE (electrode (VIII)). The electrode response is independent of pH in the range of 2–8, with a fast response time (8 s) at 25 ^{o}C for electrode (VIII). Moreover, the electrodes also showed high selectivity and long life time (more than 10 weeks) for electrode (VIII). The electrodes showed good selectivity for alprazolam toward wide variety of species. The proposed sensors were successfully applied for the determination of alprazolam in pharmaceutical formulations, human plasma and urine as indicator electrodes.

Keywords: Potentiometry, Alprazolam determination, multi-walled Carbon nanotube, carbon paste electrode, Pharmaceutical formulations.

Sensitive electrochemical determination of 4-hydroxybenzoic acid at the surface of a new nano ceramic modified electrode

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Abstract

4-Hydroxybenzoic acid is primarily known as the basis for the preparation of its esters, known as parabens, are widely used as bactericides and preservative agents in cosmetic, pharmaceutical and personal care products, as well as in processed food and beverages, for inhibiting the development of microorganisms and therefore prolonging products’ shelflife [1].

But human exposure to p-hydroxybenzoic acid esters is a concern, owing to adverse health effects of these compounds [2].

In the present work, the electrochemical oxidation of 4-Hydroxybenzoic acid has been studied using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) techniques at the surface of a nickel nanoparticles modified carbon paste electrode. The characterization of the modified electrode was studied using different methods such as scanning electron microscopy (SEM), electrochemical impedance spectroscopy (EIS) and CV. Also for electrochemical studies of paraben various electrochemical techniques such as chronoamperometry, chronocoulometry and linear sweep voltammetry (LSV) were applied. The modified electrode exhibited excellent electrocatalytic activity towards the oxidation of paraben. After optimizing the experimental conditions, the anodic peak current of paraben showed a linear correlation to its concentration in a broad linear dynamic range (0.7-1000.0 µM) with low limit of detection (62.0 ηM). Also the modified electrode presented a good stability and repeatability toward the determination of paraben. The results indicated that the nanostructured modified electrode could be employed for the determination of paraben in real samples with satisfactory results.

Keyword: 4-Hydroxybenzoic acid, Parabens, Nickel nanoparticles, Carbon paste electrode, electrochemical studies.

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Fabrication of an Electrochemical Sensor Based On Single-Walled Carbon Nanotubes Modified Gold Electrode for Determination of Ascorbic Acid

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Abstract

Since the discovery of carbon nanotubes (CNT) in 1991, research on CNT has progressedrapidly, and has became one of the most attractive part of nanotechnology [1]. Carbon nanotubes are molecular-scale wires with high electrical conductivity, high chemical stability, and extremely high mechanical strength and modulus [2]. There have been many new applications due to their unique chemical, electronic and mechanical properties. Recently, electrochemical studies suggested the ability of CNT to promote certain kindsofelectron-transferreactions[3]Nanotubes are categorized as single-walled carbon nanotubes (SWCNT) and multi-walled carbon nanotubes (MWCNT). Single-walled carbon nanotubes are constructed of a single sheet of graphite of diameter 0.4-2.0 nm while multi-walled carbon nanotubes consist of multiple concentric graphite cylinders of increasing diameter of 2-100 nm [4],In this experimental research , the electrochemical manner of ascorbic acid was investigated based on modified gold electrod using single- wall carbon nanotube (SW CNT/AuE) as an electrochemical sensor. At first, ascorbic acid was measured at the level of non modified and modified gold electrode with single- wall carbon nanotube; cyclic voltametric technique was used for determination of ascorbic acid. Ascorbic acid effectively accumulates on the (SW CNT/AuE) and causes redox peak (V.S Ag/AgCl) in a solution of ascorbic acid 300 µm with scan rate0.05 v/s .The height of redox peak become significantly higher than (AuE). And there was no peak on the AuE , before modification. the electrochemical parameters including : PH , kind of acid , concentration of acide , nanotube Scale. and scan rate have been optimized. Under the optimized conditions, the peak current was linear with the concentration of ascorbic acid in the range of 10 to 650µm with a detection limit 2.951µm. The proposed method was successfully used for the determination of ascorbic acid in the samples of blood serum.

Keywords: Ascorbic acid, Electrochemical Sensor, Single- wall carbon nanotube (SW CNT) and Cyclic voltammetry.

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Electron transfer rate and electrocatalytic performance of ionic liquid/graphene quantum dots nanocomposite modified electrode

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Abstract

Graphene is a new class of 2D carbon nanomaterials with one atom thickness. Graphene quantum dots (GQDs), are graphene sheets that are smaller than 100 nm and has been emerged as a significant research area in recent years (1). Recently some organic and inorganic materials have been utilized for the stabilization of GQDs on the electrodes surface for sensing and biosensing purposes (2). In this study 1-butyl-3-methylimidazolium hexafluorophosphate was used as an ionic liquid (IL) for the stabilization of GQDs on the electrode surface. The resulted ILs/GQDs modified electrode was studied with cyclic voltammetry and electrochemical impedance spectroscopy (EIS) techniques. The electron transfer rate and electrocatalytic performance of the prepared electrode was compared with GQDs and ILs modified electrodes. The results was shown that the ILs/GQDs modified electrode have better electron transfer rate and electrocatalytic performance than GQDs and ILs modified electrodes. Due to the unique electron transfer ability of ILs and GQDs, and also stability of the fabricated ILs/GQDs modified electrodes, it can be used in various electroanalytical purposes.

Keywords: *Graphene quantum dots; Ionic liquids; modified electrode*

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Direct Electrosynthesis of Polyaniline–Zeolite Nanocomposite Coatings on 304 Stainless Steel and Their Corrosion Protection Performance

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Abstract

Corrosion of metals is an enormous problem throughout the world. Several techniques have been used to protect metals from corrosion. Among them, polymer coatings may be the most widely used technique. Conducting polymer coatings such as polyaniline on 304 Stainless Steel electrodes can be obtained electrochemically and these coatings provide important protective properties against corrosion [1]. Several strategies have been used to increase the effectiveness of polyaniline as an anticorrosive coating on metals. The utility of various nanoparticles, such as ones made from inorganic materials, natural fibers, graphite, and zeolite as additives to enhance the mechanical and barrier performance of polymers has been established [2].

Polyaniline–zeolite nanocomposite coatings were electrosynthesized on 304 stainless steel using the galvanostatic polarization method. These coatings in current densities viz. 1, 2.5, 5 and 10 mA.cm^{-2} for duration of time of 100 s were tested. The deposition times viz. 50, 70, 150 and 200 s were applied for the current density of 2.5 mA.cm^{-2} and the corresponding potential transients were recorded. The synthesized coatings were characterized by UV–Vis absorption spectrometry, fourier transform infrared spectroscopy, X-ray diffraction patterns and scanning electron microscopy. Corrosion properties of these coatings were investigated by the potentiodynamic polarization and electrochemical impedance spectroscopy techniques.

The potentiodynamic polarization and EIS studies revealed that the polyaniline-zeolite nanocomposite acts as a corrosion protective layer on 304 stainless steel in 0.5 M HCl solution. The corrosion rate was found to be about 53 times lower than that observed for uncoated steel and also the corrosion current values decreased from 83.03 µA.cm^{-2} for uncoated steel to 1.55 µA.cm^{-2} for nanocomposite-coated steel under optimal conditions (i=2.5 mA.Cm^{-2}, t=100s).

Keywords**:** *Electrosynthesis, 304 Stainless Steel, Polyaniline, Nanocomposite coatings, Corrosion*

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Square Wave Voltammetric determination of Sulfadiazine in pharmaceutical formulation using Ceria NPs decorated graphene nanocomposite carbon paste electrode

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Abstract

Sulfonamides are among the most widely employed antibacterial agents in both human and veterinary medicine for prophylactic and therapeutic purposes due to their low cost and efficiency in the treatment of bacterial diseases. However, the widespread use of sulfonamides can lead to problems in terms of human health, taking into consideration that allergic and toxic reactions have been observed in patients treated frequently with sulfas. Therefore, methods which are accurate, simple and economical in terms of both time and cost for drug residue monitoring need to be developed (1). Chemically modified carbon paste electrodes (CCPEs) have been widely used because of their advantages such as renewability of their surface, stable response and low ohmic resistance (2). CeO_2 (called Ceria) nano particles have attracted a lot of attention due to its high catalytic activity (CeO_2 to Ce_2O_3) and biocompatibility (3). Recently, the decoration of RGO with different nanoparticles has received intense interest for producing a new type of hybrid materials with properties that are variant from those of the individual components (4). In this study, a nano composite carbon paste electrode which contained 5% Ceria NPs decorated RGO NPs was used as working electrode. The electrochemical behavior of sulfadiazine at bare and ceria NPs decorated graphene nano composite carbon paste electrode was investigated by cyclic voltammetry and the results are shown in Fig.1 (A). The surface morphology of a bare and CeO_2 NPs decorated on RGO NPs modified carbon paste electrode are represented in Fig.1 (B and C) respectively. As it can be seen in FE-SEM image (C), a large number of CeO_2 nanoparticles have been attached to the RGO surface with a good dispersion, indicating a good combination between nanoparticles and RGO. The study was carried out by using Fast Fourier Transfer Square Wave Voltammetry (FFT SWV) was applied as detection

technique. The proposed nanocomposite electrode showed two linear responses to sulfadiazine concentrations from 3 to 10 µM and 30 to 700µM (R^2 = 0.9956 & 0.9948, respectively). In order to show the applicability of the proposed electrode, it was successfully used in determination of sulfadiazine in pharmaceutical products with acceptable 5% relative errors.

Keywords: Sulfadiazine, Nanocomposite, Carbon paste electrode, Ceria NPs, Square wave voltammetry

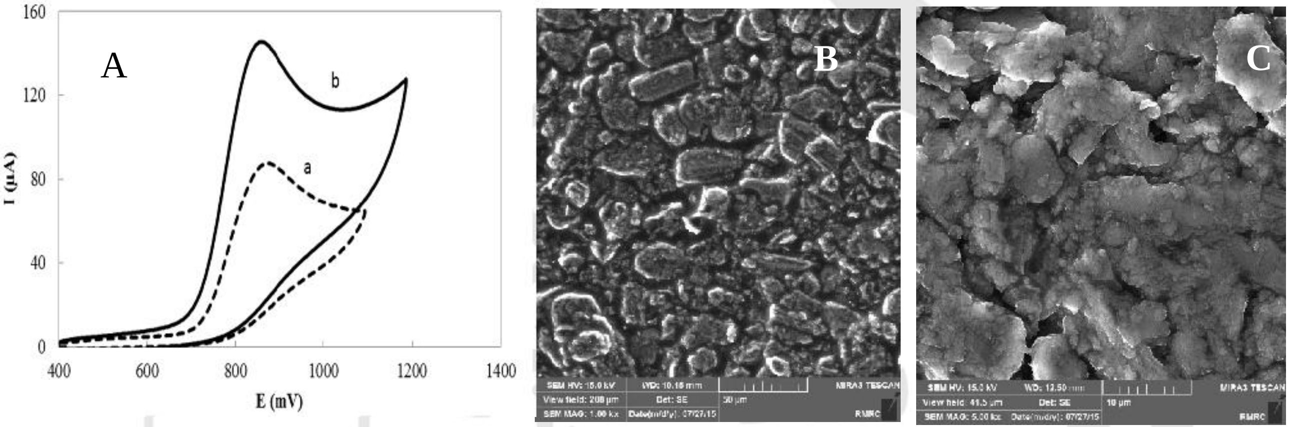

Figure.1 (A) Cyclic voltammograms of 1.0 mM sulfadiazine at bare(a) and CeO2 NPs decorated on RGO NPs modified carbon paste electrods (b), FE-SEM image of bare (B) and CeO2 NPs decorated on RGO NPs carbon paste electrods (C)

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Preparation and characterization of a novel nanosensor based on iron oxide nanoparticles for electrochemical studies of epinephrine

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Abstract

Epinephrine or 4-(1-hydroxy-2-[methylamino]ethyl)-1,2-benzenediol hydrochloride (Epi), belongs to the family of catecholamine neurotransmitters, which is widely distributed in the mammalian central nervous system for message transfer process. It is as an important chemical mediator for conveying nerve impulse in the mammalian central nervous systems. Furthermore, Epi can be used to treat cardiac arrest and bronchodilator for asthma patients [1]. Therefore, a quantitative determination of Epi is quite helpful for developing research in disease diagnosis, pharmacological research and life science. Epi shows an electroactive nature [2], so electrochemical methods along with modified electrodes can be useful for its sensitive detection. In the present study, a simple strategy for determination of Epi based on iron oxide nanoparticles modified carbon paste electrode is reported. The iron oxide nanoparticles displayed high effective surface area, high porosity, more reactive sites and excellent electrochemical catalytic activity toward the oxidation of Epi. The characterization of the modified nanosensor was carried out by different techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV). The electrochemical oxidation of Epi has been studied using CV and differential pulse voltammetry (DPV) techniques at the surface of the modified electrode. After optimizing the experimental conditions, the anodic peak current of Epi showed a linear correlation to its concentration in a broad linear dynamic range (0.4-270µM) with low limit of detection (19 nM). Also the modified nanosensor presented a good stability and repeatability toward the determination of Epi. Finally, the proposed method was successfully applied for the determination of Epi in real samples.

***Keywords**: Epinephrine, Iron Oxide Nanoparticles, Nanostructured Modified Sensor, Electrochemical Studies.*

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Voltammetric Citalopram Nanosensor

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Abstract

In this work, electrochemical behavior of Citalopram (CTP) was studied. Because of simplicity, rapidity, high sensitivity and selectivity, vaoltammetric nanosensors are very important in the drug determination. CTP is an antidepressant drug of the selective serotonin reuptake inhibitor class that is used for the treatment of severe depressive disorders [1-3]. Silver nanoparticles and 1, 4-Dihydropyridines were used to fabricate a modified carbon paste electrode as an electrocatalyst and organic selective agent, respectively. 1, 4-Dihydropyridines represents an important class of compounds that arises in many biological products such as vasodilators, anti-tumor and anti-diabetic agents. Silver nanoparticles with the general characteristics of nanoparticles such as catalytic properties, conductivity, high surface area, strengthening and so arises as a good option to modify carbon paste electrodes. The effects of various experimental factors such as pH, supporting electrolyte and potential scan rate have been investigated. The limit of detection and the linear range were found to be 1.50×10^{-5} and 1.0×10^{-2} to 1.0×10^{-4} M of CTP, respectively. Finally, the proposed nanosensor was applied for determination of CTP in biological specimen and pharmaceutical products, successfully.

Keywords: *Citalopram, Silver nanoparticles, 1, 4-Dihydropyridines, cyclic voltammetry*

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Electrochemical Approach for Preconcentration and Determination of Anti Cancer Drug Capecitabine by a Novel Organic Solvent Mediated HF-PGE electrode

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Abstract

Capecitabine, chemically 5'-deoxy-5-fluoro-N4-pentyloxycarbonyl-cytidine [1], represents the first-line treatment for colorectal and breast cancers [2]. The aim of this study was to design a new sensitive single-use electrode to CPT preconcentration and measurment simultaneously for use in a three-electrode voltammetry system. This electrode was designed by modifing pencil graphite electrode with a new combination of functionalized polyurethane foam and MWCNT supported by hallow fiber, with using organic solvent instead of ionic liquid for the first time. The space between the nanocomposite deposited on pencil and covered hallows fiber filled with air molecules. Linear response range was 7.70×10^{-6} to 1.42×10^{-4}M, LOD and LOQ was obtained and finally was used for real analyt biological samples of urine and nail.

***Keywords**: Capecitabine, DPV, Polyurethane Foam, Hallow Fiber, One-use Electrode*

2. Methode

At first for nanocomposite synthesis, shaved commercial polyurethane foam (PUF) was soaked in HCl 3M for 24h, then was washed with distilled water and placed into HCl 0.1 M solution, cooled in an ice bath and then ethyliodide was added drop wise to PUF with strong stirring and left for 24 h in the fridge [3], then blended in a agate mortar. Beside multiwalled carbon nano tube was functionalized by sonication in mixture of nitric and sulfuric acid (30:70) for 6 h. Finally PUFIX and functionalized CNTMW were added to ethanol and refluxed for 6 h at 55 ^{0} C. the black powder CNTMW-PUFIX was washed with water and acetone and the air-dried. CNTMW-PUFIX was blended in a agate mortar. Successive stages of nanocomposite synthesis was confirmed by FT-IR spectroscopy and SEM imaging. MWCNT twisting around the foam nanoparticles (r ≈ 53), creating the perfect platform for analyte capture and increase extraction.

For fabrication electrode, segments of 15.0 mm polypropylene hollow fiber was cleaned with distilled water and acetone and directly dried in air.

Synthesized nanocomposite was dispersed in organic solvent, graphite pencils rod placed for 8 min at it, then was inserted carefully into the hallow fiber segment and was placed at apparatus as working electrode for LSSME procedure. The standard solution of CPT in phosphate buffer pH 7 was added to cell and the voltage scanning in the range of + 0.5 to + 1.5 volt, was started.

3. Rsult and discussion

The studies at Robinson buffer, phosphate buffer and $NaClO_4$ was carried out by DPV technique. The peak obtained in phosphate buffer 0.05 M was so sharper. Then the range of pH 2 to 12 was investigated. The pH of solution is an important factor that it is affect on the peak current. The highest peaks was observed at pH 7.0. In next step, the influence of nanocomposite concentration was investigated. For this purpose, 1 to 20 mgr of nanocomposite in 2 ml octanol was dispersed and checked. Most extraction yield, was accured in the presence of 10 mgr of nanocomposite. For review the effect of organic solvent, acetone, 1-butanol, cyclohexanol, 2-decanol and 1-octanol were investigated. The octanol showed the best peak with the lowest background.

The effect of scan rate for CPT peak current was studied. Scan rates 10 to 100 mVS -1 was checked, results at more scan rates was showed the negative impact on the efficiency of extraction. The reason, can be to give more time for the preconcentration and extraction process.

Finally studies was continued by investigation of chitosan and triton x-100 addition affect. Different volumes of 10 % W/V chitosan and 10^{-3} M solution of triton x-100 solution, was added to 10 ml of buffer solution containing 10^{-4} M CPT in the voltammetry cell. Overall addition of both showed a positive effect on extraction efficiency and peak current. The best voltammogram was obtained at 1.0 ml for chitosan and 2.0 ml for triton x-100.

4. Conclution

Mentioned electrode with regard to the proposed method, is fast and need to very low level of organic solvents, also has satisfactory LOD and LOQ. Small amounts of analayt in biological matrices nails and urine was determined easily with 93% and 98% efficient. These results indicated that designed electrode by the developed method could be used for anti-cancer drug analysis with acceptable reproducibility.

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Selective electrochemical sensor based on graphene nanoplatelets modified platinum electrode for determination of sunset yellow as a food coloring

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Abstract

Food coloring, or color additive, is any dye, pigment or substance that imparts color when it is added to food or drink. Food coloring is used both in commercial food production, domestic, pharmaceuticals and medical devices [1]. Food dyes were originally synthesized from coal tar, but now they are synthesized from petroleum. These dyes are used because they are cheaper and brighter than most natural food colorings. Food dyes are not pure chemicals, they can contain up to 10% of impurities that are in chemicals from which dyes are made or developed in the manufacturing process. Sunset Yellow (SY) is a petroleum-derived orange azo dye used in food, cosmetics, and drugs. [2-3] For example, it is used in candy, desserts, snacks, sauces, and preserved fruits. Sunset Yellow is often used in conjunction with E123, amaranth, to produce a brown coloring in both chocolates and caramel.

Graphene nanoplatelets (GNPs) represent a new class of carbon nanoparticles with multifunctional properties. Each particle consists of several sheets of graphene with an overall thickness of about 5 to 25 nm. This unique size and platelet morphology makes these particles especially effective at providing barrier properties, while their pure graphitic composition makes them excellent electrical and thermal conductors. Their thermal conductivity and mechanical properties are similar to carbon nanotubes (CNTs) but their aspect ratios are higher than CNTs. GNPs have been thus widely applied as the electrode materials in many fields [4,5], e.g. for sensing applications, loading catalysts and constructing batteries and supercapacitors.

In this study, a highly sensitive electrochemical sensor for the determination of sunset yellow as a food coloring was fabricated using graphene nanoplatelets modified platinum electrode. Cyclic voltammetry studies shows that the modified electrode has higher sensitivity for oxidation/reduction of SY with a pair of well peaks at 0.708 and 0.625 V (versus Ag/AgCl) in Britton Robinson buffer (pH 3.0, 0.1 M). Some parameters such as kind of supporting

electrolyte, pH, volume of coated graphene nanoplatelets and scan rate have been optimized to get higher sensitivity. The fabricated electrochemical sensor can be successfully applied to the determination of SY as a coloring additive in drinks and foods.

Keywords: *Graphene nanoplatelets, Platinum electrode, electrochemical sensor, Sunset Yellow*

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Reviewing the structure of modern nano-electrodes and their application in electrochemistry

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Abstract

Main materials used to make an electrochemical cell include two electrodes and an electrolyte. Electrodes are conductive structures that electrochemical processes would happen in their interface with electrolyte material. The purpose of present research is to review some current developments in making nano-electrodes and their application. Recently, this electrode attracted most attention due to its positive features. A great attention has been paid to various kinds of materials used to make these electrodes, especially naturals. No doubt, applying natural nano-electrodes play an important role in the development of electro chemistry knowledge. Also, these materials are recyclable, finally, they haven't caused any damage to our environment.

Keywords: *Electrode, Electrolyte, Nano-Electrode, Structure, Application*

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Stripping Voltametric Determination of Vitamin B6 Using Modified Glassy Carbon Electrode with β-Cyclodextrin Functionalised Graphene Nano Sheets

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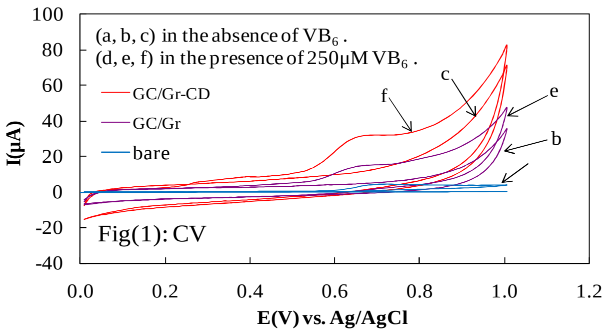
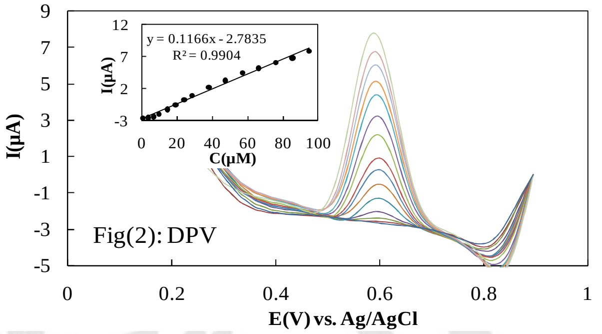
Abstract

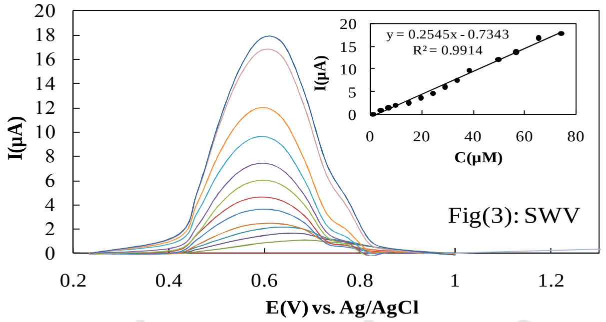
Vitamin B_6 (VB_6) helps the body to make antibodies, transmit signals in the brain, maintain normal nerve function, make haemoglobin and keep blood sugar in normal ranges. β-Cyclodextrin (β-CD) is a very stable oligosaccharide that is composed of seven glucose units linked with each other by α-(1,4)-glycosidic linkage. The CDs have a truncated cone-resembled shape with a hollow cavity. The depth of the hollow cavity is 0.78 nm for all three types (α, β and γ) of CDs. Thus, a variety of guests can be encapsulated into the cavity via the host-guest interaction in aqueous conditions and even in the solid state. On the other hand Graphene with a unique two-dimensional structure, is predicted to be an excellent electrode material for energy storage and conversion system due to its large surface area, high electrical conductivity, flexibility, and mechanical strength. Therefore β-Cyclodextrin functionalised graphene is able simultaneously possessing unique properties of graphene and β-Cyclodextrin. In this study fabricated modified glassy carbon electrode with β-yclodextrin functionalised graphene (GC/Gr/β-CD) and applied for electrochemical measurement of VB_6. Cyclic voltammetry was employed to evaluate the electrochemical performance of modified electrode and compare its electrochemical performance with modified glassy carbon with graphene (GC/Gr) and bare electrode. As can be seen of fig (1) GC/Gr/β-CD is capable in VB_6 oxidation than other two electrodes. After optimization all effective parameter in measurment such as pH, instrumental parameter we obtain calibration curve for VB_6 determination By methods of differential pulse voltammetry (DPV), square wave voltammetry (SWV) and linear sweep voltammetry (LSV) that shown in Fig (2) to (4). In Table (1) show the results obtain from calibration curves and Compared with other works. To examine the predominant type of mass transport a study was

carried out using cyclic voltammetry on scan rate effect and the result shows electrooxidation reaction is an adsorption controlled process.

Keywords: *graphene, cyclodextrin, modified electrode, stripping voltammetry, vitamin B$_6$.*







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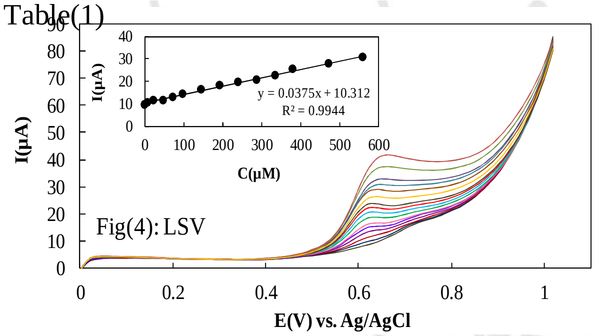

Analyt	**Linear range**	**LOD**	**Method**	**Reference**
VB$_6$	0.2 – 4 mg.L^{-1}	0.060 mg.L^{-1}	Spectrophotometry	1
VB$_6$	0.49 - 19 μM	0.37 μM	Spectrofluorimetry	2
VB$_6$	2.4 – 17 μM	0.013 μM	HPLC, Electochemical detection	3
VB$_6$	2.5 – 100 μM	1 μM	Amperometry	4
VB$_6$	450 – 3300 μM	37 μM	Linear sweep voltammetry (LSV)	5

VB_6	1.2 – 690 µM	0.410 µM	Cyclic Voltammetry (CV)	6
VB_6	1.3 – 13 µM	0.350 µM	Cyclic Voltammetry (CV)	7
VB_6	2.5 – 75 µM	0.8 µM	Differential pulse voltammetry (DPV)	8
VB_6	0.5 – 100 µM	0.2 µM	Differential pulse voltammetry (DPV)	9
VB_6	0.3 – 100 µM	0.1 µM	Differential pulse voltammetry (DPV)	10
VB_6	1 – 74 µM	0.114 µM	Square wave voltammetry (SWV)	This work
VB_6	1 – 100 µM	0.470 µM	Differential pulse voltammetry (DPV)	This work
VB_6	10 – 600 µM	7.9 µM	Linear sweep voltammetry (LSV)	This work

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Novel multi walled carbon nanotubes/ionic liquid based carbonpaste electrode for potentiometric determination of analapril in pharmaceutical and biological fluids

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Abstract

For the first time a novel derivatized multi-walled carbon nanotubes/ionic liquid-based on analapril carbon paste electrodes is reported. At optimum values of variable conditions, the proposed electrodes responded toward analapril linearly in the range of 1.0×10^{-9} - 5.0×10^{-3} mol L^{-1} with slope of 59.58±0.2 $mVdecade^{-1}$ of analapril concentration and detection limit of 2.0×10^{-9} $molL^{-1}$ for ANAL/MWCNTs/I.L-CPE(electrode(17). The electrode response is independent of pH in the range of 2–8, with a fast response time (10 s) at 25 ◦C for electrode (17). Moreover, the electrodes also showed high selectivity and long life time (more than 8 and 9 weeks) for electrode (17). The electrodes showed good selectivity for enalapril toward wide variety of species. The proposed sensors were successfully applied for the determination of enalapril in pharmaceutical and biological fluids and as indicator electrodes.

Keywords: *Potentiometry, enalapril determination, multi-walled Carbon nanotube, ionic liquid, carbon paste electrode, Biological fluids*

Abbreviations: ANAL, enalapril; PTA, phosphotungestic acid; MWCNTs, multi-walled carbon nanotubes; I.L ionic liquid; CPE, carbon paste electrode;

Electrochemical Determination of Anti Cancer Drug Imatinib, Using Nickel Nanopararticle Modifide Carbon Paste Electrode

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Abstract

Imatinib is one of the newest anticancer drugs in the market and was one of the first drugs to be pushed through Food and Drug Administration's (FDA) fast track designation for approval [1]. Till now, the commonly employed techniques for the determination of this drug in bulk form, pharmaceutical formulation, and biological fluids are based on HPLC [2-4] and spectroscopy [1,5] methods .the problems encountered using such methods are need for time-consuming extraction procedures and expensive instrumentation so the use of simpler, faster, cheaper and also sensitive techniques can be interesting alternatives, especially those based on electroanalytical techniques. Electrochemistry has many advantages, making it an appealing choice for pharmaceutical analysis [6, 7] .The usefulness of modified carbonpaste electrodes (MCPEs) in the electroanalytical chemistry has been widely demonstrated and their development for analysis applications is still of great interest [8] .Nowadays, it is important to develop new materials capable to change the electrode surface with better analytical properties, includinggraphene, nanoparticles, and carbon nanotubes. Among them, nanosized metal particle modified electrodes have emerged as a promising alternative for the electroanalysis of organic and inorganic compounds. [9, 10].

In this work for the first time, the electrocatalytic oxidation of Imatinib was carried out by nickel nanoparticles modified carbon paste electrode (Ni-NP/MCPE) using cyclic voltammetry and chronoamperometry methods. At first, nickel nanoparticles were synthesized by non-aqueous polyol method and then these nanoparticles were mixed with graphite powder to form modified carbon paste electrode. Resulting modified electrode was characterized by SEM images. In the presence of 0.1 M NaOH a good redox behavior of the Ni(III)/Ni(II) couple at the surface of electrode can be observed. Imatinib was successfully oxidized at the surface of this modified electrode. The electrocatalytic oxidation peak current of this drug was linearly depending on its

concentrations in range of 7×10^{-6} - 6×10^{-4} M. The proposed sensor exhibited a high sensitivity and was successfully applied for determination of Imatinib in some real samples.

Keywords*: *Electrocatalytic oxidation, Nickel nanoparticles, Non-aqueous polyol method, Imatinib

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Synthesis and Characterization of Metal Organic Framework UiO-66 and using in NCPEs in the Lithium Battery

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Abstract

In recent decades, development of Li-Battery technology is due to the transition from traditional liquid electrolytes to solid state electrolytes. In this study, a porous and stable metal organic framework (MOF) is synthesized and utilized as a filler in a nanocomposite. MOF materials, having porous structure, exhibit high surface area which gives them a variety of applications in storage of gases, catalysis, adsorption and removal of heavy metals and dyes, drug delivery and etc. These days, MOFs are extensively used in batteries and super-capacitors (1).

A Nano-composite polymer electrolyte (NPCE) is prepared via cast-solution method by which MOF (Zr- BDC, UiO-66) and LiTFSI are used as fillers for PMMA polymer matrix. These polymer electrolytes react well in electrochemical reactions and MOF will increase the ionic conductivity of the nano-composite electrolyte therefore the charge/discharge efficiency will be enhanced. To identify MOF and nanocomposite of PXRD, SEM and dynamic light scattering (DLS) measurements. Thermo gravimetric analysis (TGA), FT-IR, The surface areas were determined by N2 sorption measurements and calculated with the BET model (2).

***Keywords:** Li-Battery, nanocomposite, PMMA, charge/discharge, MOF, cast-solution, electrolyte.*

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Synthesis and Characterization of Metal Organic Framework (cu-dub-BDC) and Study in the nanocomposite Polymer Electrolytes

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Abstract

Porous materials have been widely used in batteries and super capacitors attribute to their large internal surface area(usually1000-6000 m^2. g^{1-}) and porosity that can favor the electrochemical reaction, interfacial charge transport ,and provide short diffusion paths for ions. Huge surface area high porosity, Low density, controllable structure and tunable pore size (1). In this study, a new filler : metal-organic framework (MOF)(cu-dub-BDC) , via mechanical method (ball- mille) which is successfully prepared and incorporated in poly(methyl methacrylate) (PMMA) and lithium bis trifluoro methane sulfonylimide (LiTFSI) based nano composite polymer electrolyte (NCPE) by cast solution for improving electrochemical properties in lithium ion battery. The control of crystal and particle size is proven by powder XRD, SEM and dynamic light scattering (DLS) measurements. Thermo gravimetric analysis (TGA) and Ar sorption experiments show that the materials from modulated syntheses can be activated and that they exhibit high specific surface areas (2).

Keywords: *Li-Battery, Nanocomposite, MOF(cu-dub-BDC), Solid electrolyte.*

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Preparation and characterization of ZnO/PVA hybrid film for application in electrochemical sensing

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Abstract

Semiconductor based transducers play an important role in electrochemical sensing [1]. In this study, zinc oxide/polyvinyl alcohol nanostructured hybrid film were prepared by electrochemical deposition method on the F-doped SnO_2 conductive glass (FTO/ZnO/PVA). Nanostructured ZnO is found to exhibit unique properties including high specific surface area, high catalytic efficiency, strong adsorption ability, biocompatibility and high electron communication features [2]. Nanostructured ZnO can be prepared using sol-gel, electrophoresis, RF sputtering, hydrothermal, and molecular beam epitaxy techniques. Among these, electrochemical deposition of ZnO yields controlled morphology and thickness by adjusting electrochemical parameters such as current or potential. Besides, higher deposition rates can be easily obtained [4,5]. PVA selection criteria was based on its water solubility, affording further electrical conductivity to the ZnO–polymer hybrid film transducer, and controlling the growth and crystallization of ZnO by tuning PVA content in electrodeposition bath.[6] Surface of the ZnO–polymer hybrid film characterized by field emission-scanning electron microscopy (FE-SEM). Monitoring of sensor fabrication was performed using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) techniques. The fabricated sensor can be applied for electrochemical sensing.

Keywords: *Electrochemical deposition, hybrid film, Polyvinyl alcohol, Electrochemical sensing*

Reference

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Application of anodic stripping voltammetry to sorption performance assess of soluble eggshell membrane protein/MWCNT nonocomposite for heavy metal removal

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Abstract

Exposure to heavy metals, even at trace level, is believed to be a risk for human beings. Nowadays, numerous methods have been proposed for efficient removal of heavy metal from waters. Adsorption is one of the most important techniques for heavy metal removal from water samples (1).

In this study, multi-walled carbon nanotube was doped in soluble eggshell membrane protein (SEP/MWCNT) matrix to removal arsenic ions from aqueous solution (2). To assess the absorption mechanism and gain parameters involved in the absorption process, anodic stripping voltammetry (ASV) technique was used. ASV method consisted of two steps, including preconcentration of the analyte at the electrode surface by reduction, and stripping the preconcentrated analyte at the electrode surface by oxidation. Maximum Arsenic sorption was observed to be in acidic media (pH 1.7). According to the experimental results, Freundlich isotherm is considered for the absorption of Arsenic on the SEP/MWCNT nonocomposite.

Keywords: *Anodic Stripping Voltammetry, MWCNT, Heavy Metal*

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Anodic stripping voltammetry and analysis of Hg(II) in water samples after preconcentration with rGO doped soluble eggshell membrane protein

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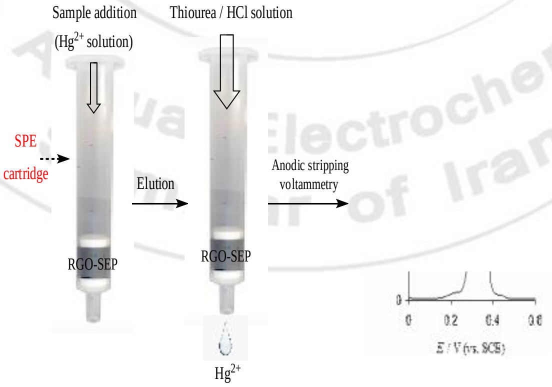
Abstract

Graphene, a new class of 2D carbon nanomaterials with one atom thickness, has attracted considerable attention in recent years (1). Eggshell membrane is cheap, green and easily achieved biopolymers which have been used frequently in analytical science (2). In the present study, reduced graphene oxide is doped efficiently into the soluble eggshell membrane protein (RGO-SEP) and the resultant biocomposite is introduced as a novel and effective nano-sorbent in SPE for the preconcentration of Hg^{2+}. In order to increase the sensitivity and detection limit of the developed method, anodic stripping voltammetry (ASV) technique was used as a detection method. The scheme of the preconcentration and determination process was shown in scheme 1.

Here Hg^{2+} was preconcentrated in two steps:

first in SPE process which Hg^{2+} preconcentrated according to enrichment factor; second in ASV technique which Hg^{2+} accumulates on the electrode surface. Thus the developed method is very sensitive, cost effective, and green in comparison with other reported techniques.



Keywords*: *Anodic Stripping Voltammetry; Eggshell Membrane; Mercury Analysis

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Electron Microscopy of Samples in Liquid and Applications in Electrochemical Studies

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Abstract

The necessity of vacuum for protecting electron gun and decreasing the scattering are main limitations in study of liquids with high vapor pressure. So in different types of electron microscopy, including scanning, transmission or scanning transmission, there has been some attempts to modify the liquid environment with vacuum. First open chambers and differential pumping has been implemented. Liquid cells are other option in which liquid is capsulated in an electron transparent material such as TiN or Graphene. Developments in thin film technology are improving equipment in this area, but there are some drawbacks also. Most important limitations in studies are change in liquid thickness, electron- sample interaction, depth of focus in transmission methods, bubble formation and heating. These studies could help materials science and biological sciences. Combining electrochemical equipment and studies with electron microscopy has also been interest in this field studies. With mounting working, counter and reference electrode in liquid area and combing electrochemical instruments with microscopy further investigation of electrochemical reactions has become possible. In this article, fundamentals of electron microscopy in liquids and different types of sample chambers will be reviewed briefly and some electrochemical and microscopic studies will be stated.

Keywords*: *Electron Microscopy, Liquid Samples, SEM, TEM, STEM, In-Situ, Electrochemical.

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Investigating the Effect of Thickness on the Performance of ZnO-based DSSC by Electrochemical Impedance Spectroscopy Technique

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Abstract

Due to the unique properties of ZnO nanostructures, they are widely used as photoanode substrate in dye sensitized solar cells (DSSCs). In the present study, a composite of ZnO nanoparticles paste was synthesized by sonochemical method. The composite was made using two different nanoparticles approximately 35 and 350 nanometers particle sizes considering the respect ratio of 3:1 involving the main and scattered layers. To investigate the cell performance, different ZnO film thicknesses of photoelectrodes were prepared to obtain efficient performance. The cells were fabricated *using N719 ruthenium dye* and all photovoltaic parameters *such as* short circuit current density (J_{SC}), open circuit voltage (V_{OC}), fill *factor (FF) and conversion efficiency (η) measured as well.* Electrochemical impedance spectroscopy (EIS) as a powerful technique was employed to determine an appropriate equivalent circuit for studying the electron lifetime, charge transport and transfer resistances in all fabricated cells where the EIS results show appropriate agreement with the measured device performance parameters. The results demonstrate the ZnO thickness is a critical parameter for providing sufficient resistance to suppress the charge recombination process and transporter electrons. Consequently the highest overall power conversion efficiency (3.61%) was obtained where the thickness of photoelectrode was optimized around 21-µm-thick by doing three times Dr. Blade deposition method.

Keywords**:** *ZnO-based DSSC, Electrochemical impedance spectroscopy, Electron lifetime, Nanocomposite, Sonochemical method.*

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Alumina nanoparticles Modified carbon paste electrode as a new voltammetric sensor for determination of Dopamine

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Abstract

In this work, a new dopamine sensor based on Alumina nanoparticles modified carbon paste electrode (Al_2O_3NPsCPE) was studied, for the first time. The electrochemical performance of the Al_2O_3NPsCPE for detection of dopamine was investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The morphology of Al_2O_3NPsCPE was investigated by scanning electron microscopy (SEM).

Keywords: *Alumina nanoparticles, modified carbon paste electrode, dopamine, DPV*

Introduction

Dopamine (DA) is a typical important neurotransmitter that belongs to the catecholamine group and plays a significant role in central nervous, renal, hormonal and cardiovascular system [1,2]. The research on the carbon paste modified electrodes has been rather intense which is mostly due to special properties of carbon paste electrodes such as wide potential windows, low cost and low electrical resistances [3].

Results and Discussion

In this study, the influence of some experimental variables such as carbon paste composition, working solution pH, scan rate and possible interferences were studied. Fig.1. exhibits the cyclic voltammograms obtained for the electrochemical response of 1.0 mM DA at the modified CPE (solid line) and bare CPE (dashed line) in 0.1 M phosphate buffer solution pH 8.0. At bare CPE, the anodic and cathodic peaks appear at 203 mV and 93 mV (vs. Ag/AgCl), respectively. We studied the electrochemical behavior of DA in buffered solutions with different pH values ($2 \leq pH \leq 12$) at the surface of Al_2O_3NPsCPE using cyclic voltammetry .The maximum peak currents of DA occurred at pH 8.0. Thus, it was chosen as the optimal pH for next experiments. The electrooxidation of DA was studied in 0.1M phosphate solution pH 8.0 at the surface of Al_2O_3NPsCPE using DPV technique. The results show that DPVs of DA oxidation at the surface of the Al_2O_3NPsCPE were linearly dependent on the DA concentrations, over the range of 8.0 to 330.0 µM .

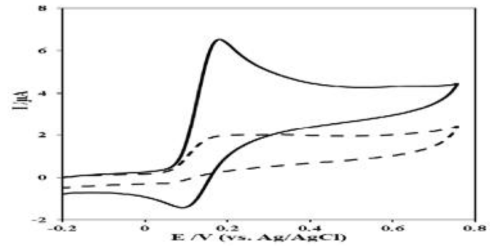

Fig.1. Cyclic voltammograms obtained for CPE (dashed line) and Al_2O_3NPsCPE (solid line) in 0.1M phosphate buffer solution of pH 8.0 containing 1.0 mM DA. Scan rate 0.1 V s^{-1}.

Conclusion

In this paper, we demonstrated determination of DA using Alumina nanoparticles modified CPE in 0.1 M phosphate buffer (pH 8.0) solution for the first time. The proposed sensor exhibited a high sensitivity, an excellent reproducibility, good selectivity.

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Synthesis of polypyrrole / TiO_2-Fe_2O_3 nanocomposite and use it to identify drug fexofenadine hydrochloride

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Abstract

In This study the nanocomposite of PPy/TiO2_Fe2O3 is synthesized by chemical polymerization. The modified carbon paste electrode by the nanocomposite was used as an indicator electrode for the determination of fexofenadine that is an antihistamine. The electrochemical behavior of fexofenadine was studied by cyclic voltammetry on the electrode. The electrochemical behavior of fexofenadine and effective factors such as pH, buffer, potential scan speed has been optimized. The results showed that the electrode has stability, high sensitivity and good electrochemical response to the fexofenadine in concentration ranges of 1.07*10-4-1.96*10-5 M in buffer solution of pH =7. The use of this nano-composite in the preparation of electrode improves the sensitivity and detection limit of the sensor and used successfully for determination of fexofenadine in real samples of pharmaceutical tablets.

Keywords: nanocomposite, polypyrrole / TiO2 - Fe2O3, nanosensor, conducting polymer

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Preparation of polyoxometalate/graphene nanocomposites with covalent interaction

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Absteact

polyoxometalate (POM) anions represent a large class of inorganic compounds that, because of their topological and electronic versatilities, have found applications in fields as diverse as catalysis, biology, medicine, and materials science.(1) The POMs exhibit the unique structure and redox properties, which could serve as ideal candidates for electrochemical applications.(2) Due to the fact that the POM salts have negligible conductivity, they are unsuitable for direct use in electroctalysis, storage and conversion of energy.(3) An approach for solving these problems is to attach POMs nanostructures directly on carbon based conductive materials through covalent or non-covalent interactions.(4) However, preparation of nanocomposites consisting of nanopolyoxometalate and nanocarbon based substrates such as graphite, carbon nanotube, and graphene with direct covalent bonding between its components is still a challenge in this research field.

In this work, we report the use of amine-modified graphenes for the synthesis of covalent attachment and highly dispersed nanopolyoxometalates on graphene nanosheets. The nanocomposites were characterized by several techniques including Fourier transform infrared spectroscopy (FT-IR), X-ray powder diffraction (XRD), scanning electron microscopy (SEM).

Keywords: *Polyoxometalate, graphene, covalent interaction, nanocomposite.*

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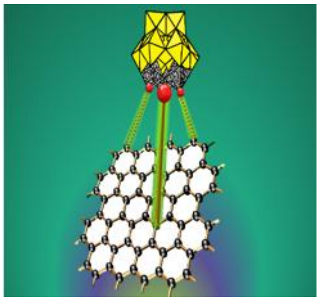
Scheme 1: The direct covalent bonding between POM and amine-modified graphene



Fabrication of an electrochemical sensor based on graphene nanoplatelets modified platinum electrode for study the molecular interaction between sunset yellow and DNA

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Abstract

Graphene nanoplatelets (GNPs) are the stack of graphene sheets with an overall thickness of about 5 to 25 nm. They have "platelet" morphology with a diameter ranging from 0.5 to 25 μm, resulting in high aspect ratios up to the thousands. Their thermal, conductivity and mechanical properties are similar to carbon nanotubes (CNTs) but their aspect ratios are higher than CNTs. GNPs have been thus widely applied as the electrode materials in many fields [1–3], e.g. for sensing applications, loading catalysts and constructing batteries and supercapacitors.

In this study, a platinum electrode was modified by graphene nanoplatelets using drop casting method for sensitive electrochemical oxidation/reduction of sunset yellow (SY) as a food coloring. The cyclic voltammetry study of SY on the surface of modified electrode showed a pair of well peaks at 0.708 and 0.625 V (versus Ag/AgCl) in phosphate buffer at pH = 7.4. The redox peak currents of SY decreased gradually upon titration with calf thymus DNA and the anodic peak potential shifted to negative direction due to the formation of more stable adduct between SY and DNA in oxidized form. Moreover, the mode of SY–DNA interaction was estimated from the variation in formal potential. In general the negative shift (anodic shift) in formal potential was caused by the electrostatic interaction of the small molecules with DNA [4].

***Keywords**: Graphene nanoplatelets; Electrochemical sensor; Sunset Yellow; DNA; Interaction*

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Evaluation and optimization of the factors affecting the performance of glucose biosensor

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Abstract

The fast and accurate determination of glucose has profound applications since glucose concentration is a crucial indicator in many diseases, such as diabetes, endocrine metabolic disorder. In recent years, many efforts have been made to develop reliable glucose biosensors using electrochemical [1], chemiluminescence [2], or other methods [3]. Among all the methods, enzyme-involved electrochemical glucose biosensor has been intensively studied because of its simplicity, high selectivity and relative low cost [4-6]. Recently, zinc oxide (ZnO) nanostructures have drawn many attentions in the fabrication of biosensors with many advantages, including nontoxicity, biological compatibility, fast electron transfer rates and easy preparation. ZnO thin film was prepared via electrodeposition method and its surface morphology was studied by scanning electron microscopy (SEM). Charactrization of GOX adsorption on ZnO thin film surface was performed using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) techniques. The impedimetric results were explained for glucose detection.

***Keywords**: Glucose oxidase, ZnO nanostructure, Glucose biosensor*

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Surface modification and functionalization for dopamine and ascorbic acid detection

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Abstract

Dopamine (DA) is a monoamine neurotransmitter found in brain and is essential for the normal functions of the central nervous system and plays a significant role in the function of human metabolism. It is important to develop sensitive sensor for the determination of dopamine by decreasing the interference of ascorbic acid [1, 2]. In this study, zinc oxide/polyvinyl alcohol nanostructured hybrid film were prepared by electrochemical deposition method on the F-doped SnO_2 conductive glass (FTO/ZnO/PVA). Zinc oxide (ZnO) has been recently used as transducer for fabrication of sensors due to its unique ability to promote electron transfer, non-toxicity, biological compatibility, enhanced analytical performance, easy manufacture and low cost [3-5]. PVA selection criteria was based on its water solubility and controlling the growth and crystallization of ZnO by tuning PVA content in electrodeposition bath.[6] Surface of the ZnO–polymer hybrid films were characterized by field emission-scanning electron microscopy (FE-SEM). Monitoring of sensor fabrication was performed using cyclic voltammetry (CV). The fabricated sensor was used to determine dopamine by differential pulse voltammetry technique.

Keywords: *Thin film; Dopamine sensor, Electrodeposition, Zinc oxide*

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Preparation and electrochemical characterization of ZnO/Polymer hybrid film

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Abstract

Electrochemical deposition as a reliable, cost-effective, mild physicochemical method has been an important issue for preparation of nanostructured hybrid metal oxides [1]. In this study, electrochemical deposition method was chosen for ZnO thin film deposition onto fluorinated thin oxide (FTO) layer as a biosensor transducer [2,3]. Surface characterization of the nanostructured ZnO film by scanning electron microscopy (SEM) exhibited porous surface areas as an excellent platform for enzyme immobilization. Monitoring of biosensor fabrication was performed using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) techniques. The results were explained the ZnO metal oxide as an efficient transducer for electrochemical biosensing.

***Keywords**: Electrochemical deposition, ZnO–polymer nanostructured hybrid film, Polyvinyl alcohol, Impedimetric sensing.*

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A novel electrochemical nanosensor for sensitive detection of paracetamol based on multivariate optimization methodology

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Abstract

Paracetamol (PCT) is commonly applied to control mild-to-moderate pain or to reduce opioid exposure as part of multimodal analgesia, and is the only compound recommended to treat fever in neonates [1]. PCT has low toxicity when used at the recommended doses. Nevertheless, the ease with which the general public can access this compound makes it frequently associated with overdoses, in this situation causing serious or even fatal hepatic damage [2,3]. So it is very important to create a sensitive, fast, accurate and simple method for PCT detection. In the present work, an electrochemical nanosensor for PCT was fabricated based on iron oxide nanoparticles by modification of carbon paste electrode surface. At first, iron oxide nanoparticles were synthesized and then used for preparation of an iron oxide nanoparticles modified carbon paste electrode (ION/CPE). The characterization of iron oxide nanoparticles was carried out through different methods such as X-ray diffraction (XRD), scanning electron microscopy (SEM) and voltammetry. The oxidative behavior of PCT was investigated by different voltammetric techniques at the surface of ION/CPE. Other novelty of the wok is application of multivariate optimization methodology for sensitive detection of PCT. Using the proposed method, the ION/CPE showed an excellent electrocatalytic activity for the oxidation of PCT, and accelerated electron transfer between the electrode and PCT. Under the optimal experimental conditions, the differential pulse peak current was linear with the concentration of PCT in the range of 0.01-250.0 μM with a detection limit of 2.0 nM. The proposed electrode revealed good stability and reproducibility. Moreover, the proposed method was successfully applied for the determination of PCT in real biological samples.

Keywords: *Iron Oxide Nanoparticles, Paracetamol, Multivariate Optimization, Electrochemical Methods.*

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Sensitive electrochemical analysis of carbendazim as a benzimidazol fungicide on a nano-structured modified electrode

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Introduction

Carbendazim, a powerful antifungal compound, can interfere in the pathogen formation during mitosis leading to bacteria destruction. The fungicidal activity of carbendazim against moulds, rots and blight has been established for more than four decades. Its protecting role against apple scab, powdery mildew was confirmed which leading to citrus fruits decay [1]. Notably, in spite of their good antifungal effect, accumulation of fungicides in the environment due to their long life time, have been the international community's concern. Serious health problem may be raised of indiscriminate use of pesticides in agriculture and so increasing the pesticide residue in fruits crops, such as various juice or edible oil that are routinely used in daily life [2]. Thus, an efficient quantificational technique for the pesticide residue analysis in agro-processing products is needed. Various analytical methods have been employed for carbendazim analysis such as high-performance liquid chromatography (HPLC) [3], UV–visible spectrometry [4], mass spectrometry [5], voltammetry [6] and surface enhance Raman scattering [7] have been developed for the detection of carbendazim in divers environmental matrices. In the presence study, a nano-structured modified electrode using carbon nanoparticles (CNPs) composite was fabricated as a sensitive electrochemical sensor for carbendazim.

*Preparation of the Modified GCE:*Before modification, the GCE was polished with 0.05 µm alumina slurry on a polishing cloth, rinsed thoroughly with water and sonicated in water for 5 min.The modifier suspension was prepared in deionized water under ultrasonic agitation for 30 min. A desired volume (1µL in optimum value) of the suspension was cast on the pretreated GCE surface and dried in an oven at 50 ^{0}C.

Results and discussion: here the modification procedure improved colloidal dispersion of CNPs in water, affording uniform and stable thin film for altering the surface properties of the working electrode. The electrochemical behavior of carbendazim at the bare and modified electrode was investigated. The results indicated that compared to bare electrode, the prepared modified electrode significantly enhanced the oxidation peak current of carbendazim. Experimental parameters, such as scan rate, pH, accumulation conditions and amount of modifier used on the GCE surface were optimized by monitoring the cyclic, differential pulse and square wave voltammograms toward carbendazim. Under the optimal conditions, the modified electrode showed a wide linear response to the concentration of carbendazim in the range of 0.04-1µM. The modified electrode showed high sensitivity, long-term stability and significant voltammetric reproducibility in response to carbendazim. These excellent properties make the prepared sensor suitable for the accurate determination of trace amounts of carbendazim for analytical studies in agriculture and toxicology in environmental studies.

In conclusion, in this study, the CNP composite has been applied to prepare a new sensitive electrochemical sensor. The modified electrode has remarkable electrochemical advantages, such as antifouling behavior, good reproducibility and acceptable repeatability. Therefore, we believe that this sensor has potential to be used for an accurate determination of carbendazim.

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Investigation of potentiometric Behavior of Amoxicillin by Ion-Selective Electrode with Nano Clinoptilolite Doped with Cu2+Ion

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Abstract

The objective of this work is study the potentiometric behavior of amoxicillin (AMX) at nano zeolite-modified ion selective electrode dopped with copper(II) ions (Cu2+) . Zeolite that used is clinoptilolite that made it into nano particales with ball-mill method. One of the properties of zeolites is ability to ion exchange and applied here for making modifier [1]. Cu2+ work as catalyst to oxidize AMX with nano clinoptilolite this aim increase because nano particles have better ratio surface to volume. Modifier that applied in electrode identify by XRD method and SEM.

In this work for preparation ion selective electrode and mixed dioctyl phthalate and Cu(II)-NC and poly vinyl chloride and tetrahydrofuran. Then glassy pipes with a diameter of 2 mm inserted in mixture and drying in room temperature reviewed the electrodes response in absent and present of AMX by potentiometric method. By using this electrodes experimental parameters affecting on the efficiency including solution pH, temperature and modifier percent were examined and optimized. β-lactamic antibiotics (including here AMX) are the oldest and important antimicrobial agent that are still widely used to treat human and animal diseases. Various analytical methods have been reported for the separation and determination of AMX based on spectrophotometric [2], [3] and [4], fluorimetric [5] capillary electrophoresis [6] and [7], high-performance liquid chromatography [8] and [9] and electrochemical methods [10-12].

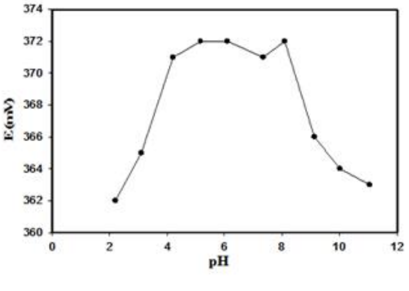
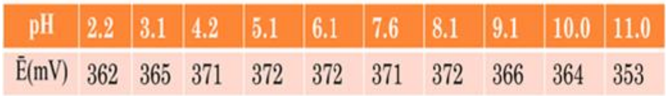


Fig.1. pH effect on the electrode response



pH	2.2	3.1	4.2	5.1	6.1	7.6	8.1	9.1	10.0	11.0
$\bar{E}$(mV)	362	365	371	372	372	371	372	366	364	353

Table.1. pH effect on the electrode response

Keywords: *potentiometry, zeolite modified electrode, amoxicillin*

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Voltammetric determination of acetaminophen in the presence of NADH using ionic liquid /ZnO nanoparticle carbon paste electrode

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Abstract

Acetaminophen (AC) with an acetylated aromatic amide is the most widely used antipyretic and analgesic drug in the world. It is commonly used for the treatment of fever, minor aches and pains. However, many studies have shown that hypersensitivity or overdose in few cases leads to the formation of some liver and nephrotoxic metabolites [1]. AC toxicity is highly dependent to the formation of the reactive metabolite, N-acetyl-p-benzoquinone imine (NABQI) [2,3]. On the other hand, studies show that Dihydronicotinamide adenine dinucleotide (NADH) efficiently reduces NAPQI to AC. By having enough NADH in the body, we can ensure that NAPQI levels will be kept low [4]. Thus, it is very important to create suitable conditions for the simultaneous analysis of AC and NADH in biological samples such as urine and blood. In the present study a carbon paste electrode modified with ZnO nanoparticle (ZnO/NPs) and room-temperature ionic liquid (RTIL), 1-methyl-3-butylimidazolium chloride was fabricated. The direct electro-oxidation behavior of acetaminophen (AC) was carefully studied by cyclic voltammetry (CV), chronoamperometry and electrochemical impedance spectroscopy (EIS). The results exhibited remarkable increase in the electron transfer rate and significant decrease in the overpotential for AC oxidation reaction in contrast to that on the bare carbon paste electrode (CPE). The oxidation peak current was linearly dependent on AC concentration in the range of 0.1 – 550 µM with the detection limit of 0.07 µM, using square wave voltammetry (SWV). Synergistic effects in the enhanced signal were observed when both ZnO nanoparticles and ionic liquid were employed. The proposed sensor has been successfully applied for the determination of AC in urine, serum and pharmaceutical samples, demonstrating the feasibility and reliability of the proposed method.

Keywords: *Acetaminophen, Electrochemical sensor, Ionic liquid, Zinc oxide, Nanoparticle*

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Preparation of carbon paste electrode with polypyrrole / titanium dioxide modified by Deferasirox and its application as nanosensor

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Abstract

In this study developed a simple and effective method for the preparation of carbon paste, Polypyrrole / titanium dioxide electrode modified by Deferasirox and its application as a nanosensor. This modified carbon paste electrode with the nanocomposite was used as an indicator electrode for determination of Fe^{3+}. The electrochemical behavior of Fe^{3+} on this electrode was studied by cyclic voltammetry and effective parameters such as composition of electrode, pH of solution, type of buffer and potential scan rate have been optimized. The prepared nanosensor showed enough stability and good response to Fe^{3+} in the concentration range of 50-300 µM with a detection limit of 25 µM in the phosphate buffer solution of pH= 7. The functional groups were examined by FTIR spectroscopy and the size of nanocomposite was determined by SEM analysis. This modified electrode could be applied to determine Fe^{3+} in real samples.

Keywords: *Carbon paste electrode, Polypyrrole / TiO_2, Deferasirox ¤Nanosensor*

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Synthesis of MWCNT-Fe_3O_4@PDA-Ag nanocomposite and application for simultaneous determination of DNA purine bases by characterization of a novel electrochemical sensor

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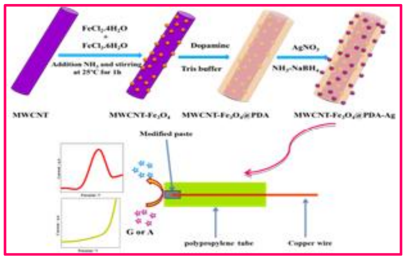
Abstract

Recently, using of self-polymerization of dopamine (DA) in various Nanocomposites has been prevalent as multifunctional coating material onto many surfaces [1]. CNTs also have been used widely as electrode modifier materials because they enhanced electronic properties and rapid electrode kinetics [2]. Herein, we report the preparation of multiwall carbon nanotube-Fe_3O_4 nanoparticles@polydopamine-Ag nanoparticle (MWCNT-Fe_3O_4@PDA-Ag) nanocomposite which was characterized with FT-IR, FE-SEM, EDS and TEM. The characterization results showed that AgNPs were well anchored onto the surface of the MWCNT-Fe_3O_4@PDA nanocomposite. Changes in the concentration of DNA bases affect the activities of catabolic and anabolic, and cause various diseases so the prepared nanocomposite, was used as a novel electrochemical sensor for simultaneous determination of guanine (G) and adenine (A). The modified electrode shows an excellent electrocatalytical function towards determination of G and A. The oxidation peak currents were linear with the concentration of G and A on the range of 8–130 and 10–120 µM, respectively. The lower detection limit of the sensor was estimated to be 1.47 µM for G and 5.66 µM for A. The MWCNT-Fe_3O_4@PDA-Ag nanocomposite based sensor was successfully applied to detect G and A in some real sample.We synthesized MWCNT-Fe_3O_4 [3], MWCNT-Fe_3O_4@PDA [4] and incorporated Ag-nanoparticles (AgNPs) into MWCNT-Fe_3O_4@PDA nanocomposite by simple stirring of MWCNT-Fe_3O_4@PDA and Ag^+ ion in a basic medium followed by $NaBH_4$ reduction. The procedures used for preparation of the MWCNT-Fe_3O_4@PDA-Ag nanocoposite are demonstrated pictorially in Scheme 1. The morphology of Fe_3O_4-MWCNTs and MWCNT-Fe_3O_4@PDA-Ag nanocomposite were investigated by SEM and TEM respectively (Fig. 1a&b). Fig. 2a presents the results obtained from EIS. As shown in Fig. 2b we investigate the electrochemical behavior of G or A at various pH (from 3.0 to 9.0, in 0.1 M ABS) on the surface of MWCNT-Fe_3O_4@PDA-Ag/CPE. We used DPV technique for individual and simul taneous determinations of the purine



Scheme 1. Schematic illustration of the preparation steps of MWCNT-Fe_3O_4@PDA-Ag nanocomposite

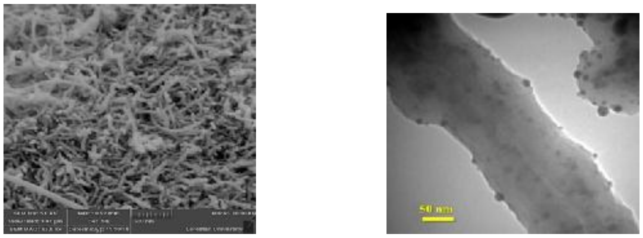


Fig.1. (a) SEM image of Fe_3O_4-MWCNTs and (b) TEM image of the MWCNT-Fe_3O_4@PDA-Ag nanocomposites.

bases. Fig. 3 illustrates the DPV plots for the simultaneous determination of G and A. As can be seen, the responses show two separated anodic peaks for G and A. The repeatability, selectivity, reproducibility and stability of the sensor were also investigated. These results demonstrate that The proposed system provides a simple, economical, robust and a rapid measuring tool for monitoring guanine and adenine in real sample.

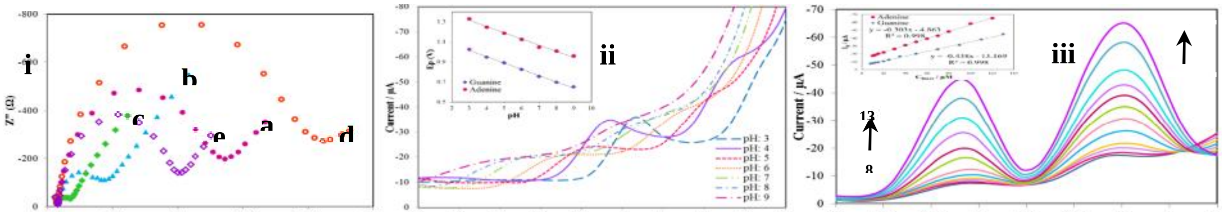


Fig. 2. (i) EIS of kind of electrodes in 0.1 M KCl and 5.0 mM $[Fe(CN)_6]^{3-/4-}$, (ii) LSV of MWCNT-Fe_3O_4@PDA-Ag/CPE in 0.1 M ABS at various pH, (iii) DPV of simultaneous determination of G (8–130 μM) and A (10–120 μM) at MWCNT-Fe_3O_4@PDA-Ag/CPE, in ABS (pH 4.0).

Keywords: *Adenine, Guanine, Nanocomposite, Polydopamine, Silver-nanoparticle*

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Ultra-trace electrochemical impedance determination of bovine serum albumin by a two dimensional silica network citrate-capped gold nanoparticles modified gold electrode

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Abstract

In this work, two dimension silica network/ citrate capped gold nanoparticles/poly (diallydimethylammonium chloride) modified gold electrode (TDSN-CGNP-PDDA-GE) was prepared for ultrasensitive determination of Bovine Serum Albumin (BSA). Analytical properties of TDSN-CGNP-PDDA-GE were studied by Electrochemical Impedance Spectroscopy (EIS). The detection limit for BSA was found to be 8.38×10^{-13} mol L^{-1} and the linear concentration range of the proposed sensor was 9.9×10^{-12}-1.6×10^{-10} mol L^{-1}. Also, TDSN-CGNP-PDDA-GE showed good stability and selectivity and was applied for determination of BSA in bovine serum sample with satisfactory result.

One of the major components of blood plasma is albumin. Albumin concentration level is considered as vital parameter for the diagnosis of significant problems in biological system [1-3]. In recent years Electrochemical Impedance Spectroscopy (EIS) sensors are widely used to the characterization and determination in bioanalytical field [4]. However, to the best of our knowledge, no research about direct BSA determination based on EIS had been published. Scheme 1 shows the fabrication steps and the interaction of BSA and synthesized electrode.

Scheme 1

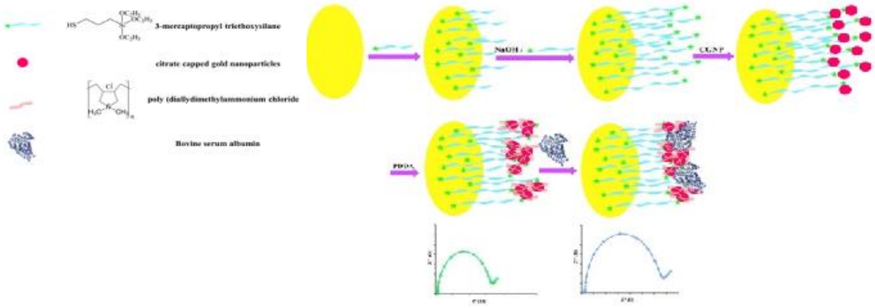
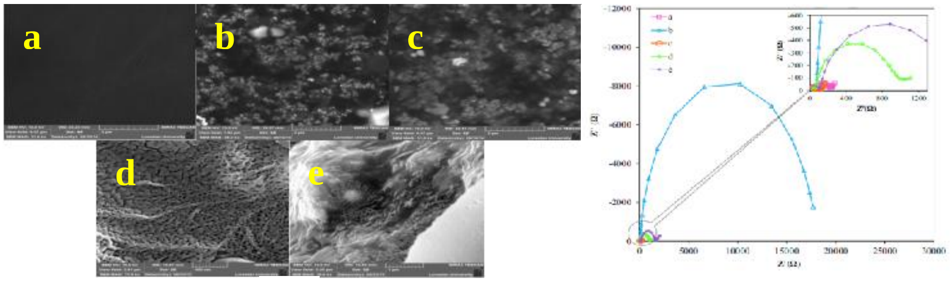


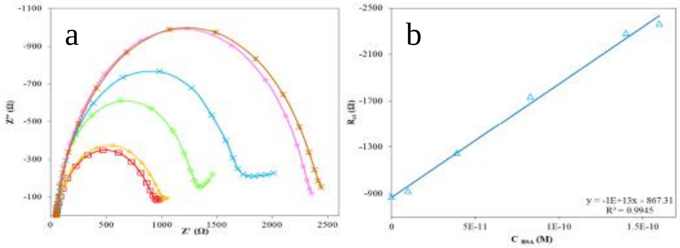
Figure 1 shows (A) the FESEM analysis and (B) EIS spectra for different steps of the electrode modification. (A. FE-SEM images of the GE surface (a), TDSN-CGNP-GE surface (b), TDSN-CGNP-PDDA-GE surface (c), TDSN-CGNP-PDDA-BSA-GE surface top (d) and side view (e).B. EIS spectra of (a) GE (b) TDSN -GE (c) TDSN-CGNP-

GE (d) TDSN-CGNP-PDDA-GE and (e) TDSN-CGNP-PDDA-BSA-GE. The inset shows the high frequency region in detail.)



A B

After optimization of experimental parameters pH=8 and incubation time 35 min was adopted for complete immobilization of BSA. Figure 2 a displayed the EIS spectra of TDSN-CGNP-PDDA-GE after incubated with different concentration of BSA in 0.1 mol L^{-1} PBS (pH=8.0). As can be seen in the Figure 6 b, the R_{ct} was proportional to the concentration of BSA in the range of 9.9×10^{-12}-1.6×10^{-10} mol L^{-1}.



We have prepared a novel type of sensor with good stability and high sensitivity for successfully determination of BSA in pure serum using electrochemical impedance spectroscopy. These great results attributed to the high electrode active surface of modified electrode, strong interaction of BSA and PDDA and intrinsic sensitivity of EIS sensors.

Keywords: *Bovine serum albumin (BSA), Electrochemical Impedance Spectroscopy (EIS), electrostatic interaction.*

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Comparison of PAMAM dendrimer and dendrimer functionalized reduced graphene oxide modified pencil graphite electrodes for electrochemical determination of anticancer drug

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Abstract

This study aims to comparison between the first generation poly (amidoamine) (PAMAM) dendrimer (G1) and dendrimer functionalized reduced graphene oxide (G1/rGO) to measure the anti-cancer drug using modified pencil graphite electrodes (PGEs). As new electrochemical sensors, modified PGEs were developed and used for monitoring rituximab (RTX) drug using differential pulse voltammetry (DPV), and cyclic voltammetry (CV). In so doing, for both sensors, a well resolved reversible diffusion controlled voltammetric peak was obtained in phosphate buffer solution (pH=7). However, compared to the G1/PGE, the G1/rGO/PGE functioned far better in the drug detection. To obtain linear relationship between peak current and concentration of rituximab, differential pulse voltammeter was applied and used for quantitative detection of rituximab drug in biological fluids. Linear response was obtained in the range of 0.0700 to 0.8340 μM with a detection limit of 0.0029 μM for G1/PGE and 0.0012 μM for G1/rGO/PGE.

Keywords: *Rituximab, Dendrimer, Graphene oxide, Differential pulse voltammetry.*

Methods

In this study, we fabricated two new sensitive electrochemical sensors based on PAMAM dendrimer and PAMAM functionalized reduced graphene oxide as the nanocarriers. Graphene oxide synthesized of graphite powder on the basis of the modified Hummers and Offeman method [1]. G1 and G1/rGO were synthesized in our lab in order to modify the PGE. Voltammetric measurements were performed using differential pulse voltammetry (DPV) and cyclic voltammetry (CV) techniques.

Results and discussion

Electrochemical behavior of RTX with G1/PGE and G1/rGO/PGE in phosphate buffer solution (pH=7.0) was studied by cyclic voltammetry (CV) and differential pulse voltammetry (DPV).For a solution of 0.100 µM RTX, in the CV technique, with scan rate of 0.5 Vs^{-1}, a well resolved reversible peak from -0.40 to +0.40 V and also DPV voltammograms, with the scan rate of 0.6 Vs^{-1}, and a pulse amplitude of 0.5 V from -0.10 to +0.30 V were obtained for both electrodes. The results of the investigate pH showed that the maximum value of peak current with the lowest background current was obtained for both electrodes at pH 7.0. Scan rate studies showed that there is a linear relationship between the root of scan rate of 50 to 470 mVs^{-1} and the peak current, and this confirms that the current is under the diffusion controlled [2]. Under optimal conditions, the response of current as a function of the RTX concentrations was monitored by DPV technique. A good linear relationship between peak current and concentration of rituximab was obtained in the range of concentrations from 0.0700 to 0.8340 µM for both electrodes. As well as results showed that the developed method is robust and can be used to analyze the rituximab anti-cancer drug with an acceptable repeatability and reproducibility.

Conclusions

We represent two novels, inexpensive, sensitive, precise and accurate sensors for rituximab anti-cancer drug using electrochemical methods. Designed sensors had high performance to determine rituximab with acceptable linear range, low detection limit and good repeatability and reproducibility. But G1/rGO/PGE compared to G1/PGE has shown lower limit of detection and more sensitivity. The developed procedure could successfully be applicative for serum samples, with good recoveries obtained at the levels tested. In addition, the sensors based on dendrimers can be used as biosensors to detect a wide range of biological agents.

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Pt nanoparticles /Fe/Al -Layered Double Hydroxide Modified Glassy Carbon for Sensitive Determination of Warfarin

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Abstract

Layered double hydroxides (LDHs) also called anionic clays have been recently attracted because of their potential in the field of catalysis, adsorption and nanocomposite [1]. The LDHs composition can be expressed as $[M_a(II)_{1-x} M_b(III)_x (OH)_2]^{x+} (A_{x/n})^{n-}.mH_2O$ formula, where M(II) and M(III) can be most divalent and trivalent metal ions and A^- is any type of anions [2]. Due to desirable properties of LDHs nanoparticles, they can serve as an effective support for metal nanoparticles. In recent years, noble metal nanoparticles (NPs) such as Pt, Au, Pd NPs have widely been considered due to their excellent properties such as stability, biocompatibility, low cytotoxicity and catalytic properties. Warfarin, 4-hydroxycoumarin, is widely used as anticoagulant drug to treat and prevent thromboembolism [3]. Warfarin has a narrow therapeutic index having a propensity for many drug–drug interactions which require conscientious monitoring of its concentrations to maintain it within therapeutic range [4]. Therefore, in clinical treatment, it is useful to develop a fast and sensitive method with simple sample preparation and determination steps for warfarin analysis. In this work, a sensitive warfarin sensor has been fabricated by electrodepositing of Pt nanoparticles on Fe Al-layered double hydroxide modified glassy carbon. Study of layer formation on the electrode surface followed by electrochemical impedance spectroscopy and cyclic voltammetry using redox couples $Fe(CN)_6^{3-/4-}$ species. The nanocomposite was characterized by field emission scanning electron microscopy, fourier transform infrared and energy dispersive X-Ray spectroscopy. The fabricated sensor exhibits excellent electrochemical catalytic activities toward the oxidation of warfarin. The oxidation peak current was proportional to the concentration of warfarin from 0.1 to 400.0 μmol L^{-1} with a detection limit of 0.03 μmol L^{-1} at signal to noise ratio of 3. The capability of the proposed sensor for determination of warfarin was examined by the standard addition method in real samples.

Keywords: Warfarin, Pt nanoparticles/ Fe/Al -Layered double hydroxide modified glassy carbon, Electrochemical sensor, Electrocatalytic determination.

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Design and construction of a new electrochemical nanobiosensor based on nanocomposite of polypyrrole and graphene for enantioselective detection of mandelic acid

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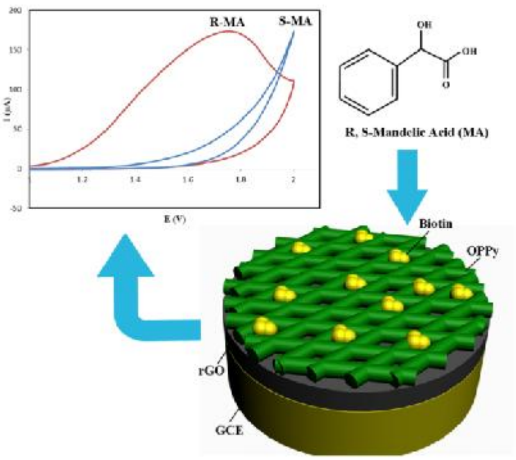
Abstract

Analysis of chiral mandelic acid (MA) is essential, owing to its important role in natural product synthesis and drug development [1]. Stereoselective electrochemical sensing based on chiral modified-electrodes has recently been reported to provide a promising entry to direct screening of chiral molecules, especially MA [2-8]. Enantioselective sensing based on electrochemical sensors offers a variety of advantages over chiral chromatographic and spectrophotometric techniques, such as simplicity, low cost, rapid detection and possibility of real time analysis [9]. A novel chiral biosensor for enantioselective detection of mandelic acid enantiomers was fabricated based on multilayered electrochemically deposition of D-(+)-biotin-loaded overoxidized polypyrrole (OPPy-biot) film on the nanosheets of reduced graphene oxide (rGO)-modified glassy carbon electrode (OPPy-biot/rGO/GCE). The nanocomposite film was characterized by scanning electron microscopy (SEM), differential pulse voltammetry (DPV), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The composite of D-(+)-biotin-loaded OPPy and reduced graphene oxide (rGO) was highly stereoselective toward the R-mandelic acid (R-MA) in the presence of high concentrations of S-mandelic acid (S-MA).



The sensing performance of the chiral-modified electrode was investigated by differential pulse voltammetry (DPV), revealing a linear range of 5–80 mM with a detection limit of 1.5 mM. Under the optimum conditions, the sensor exhibited good reproducibility and stability for R-MA determination. The designed sensor has been successfully applied for determination of R-MA and S-MA in a synthetic mixture and the satisfactory results were obtained.

Keywords: *Chiral electrochemical biosensor, D-(+)-Biotin, Mandelic acid, Enantioselective recognition*

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Simultaneous Determination of Epinephrine, Acetaminophen and Tryptophan Using Pt-nanoparticles/Poly 4-(2,4- dihydroxyphenyl) Azo-hydroxyl benzene Film Modified Glassy Carbon Electrode

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Abstract

In recent years, electrochemically conductive polymers have been widely used owing to their excellent unique physical and chemical properties [1-2]. These electrodes show broad potential windows and can catalyze some electrochemical reaction which have high over potential and poor selectivity [3]. Incorporation of nanoparticles with conductive polymers can be extensively enhancing the catalytic activity of electrode towards many biological molecules. Among nanoparticles, platinum nanoparticles is one of the most stable nanoparticles which receive considerable attention because owing excellent electronic properties and biocompatibility. Acetaminophen is a widely-used analgesic and antipyretic drug, which is considered safe at therapeutic levels for humans with normal drug use. Overdoses of acetaminophen produce toxic metabolite accumulation in liver, which may cause severe and sometimes fatal hepatoxicity and nephrotoxicity. The stimulatory effect of acetaminophen on cyclo-oxygenase activity in intact cells was abolished in the presence of electron-donating co-factor epinephrine [5]. Acetaminophen administration also is known to increase brain neurotransmitter serotonin levels because Acetaminophen alters tryptophane metabolism by inhibiting tryptophan 2,3-dioxygenase. Therefore, simultaneous determination of epinephrine, acetaminophen and tryptophane is important. In this study, Pt nanoparticles supported on glassy carbon electrode (GCE) by simple electrodeposition technique. In this study a novel platinum nanoparticles poly 4-(2,4-dihydroxyphenyl) azo-hydroxyl benzene (DAHB) film modified glassy carbon electrode was fabricated for the simultaneous determination of epinephrine, acetaminophen and tryptophane. The bare glassy carbon electrode (GCE) fails to separate the oxidation peak potentials of these molecules while poly-DAHB film modified GCE can resolve them. Electrochemical impedance spectroscopy (EIS) study indicates that charge transfer resistance of bare electrode increased as poly-DAHB was electropolymerized at the bare electrode. Furthermore, EIS exhibit enhancement of electron transfer kinetics between analytes and electrode after electrodeposition of Pt nanoparticles. Differential pulse voltammetry results show that the electrocatalytic current increase linearly in the ranges of 2-540 µmol L^{-1} for epinephrine, 5-820 µmol L^{-1} for acetaminophen and 1.0-560 µmol L^{-1} for tryptophan with detection limits (S/N =3) of 0.1 µmol L^{-1}, 0.04 µmol L^{-1} and 0.2 µmol L^{-1} for epinephrine, acetaminophen and tryptophan.

Keywords**:** *Simultaneous determination; Epinephrine; Acetaminophen; Tryptophan; Poly 4-(2,4-dihydroxyphenyl) azo-hydroxyl benzene modified GC electrode ; Pt nanoparticles.*

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Voltammetric determination of N-acetyl-L-cysteine at the surface of glassy carbon electrode modified with Prussian blue nanoparticles

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Abstract

N-Acetyl-L-cysteine (NAC) is an acetylated derivative of the L-cysteine, as an amino acid. NAC is commonly used as pharmaceutics. It has first been managed as a mucolytic agent reducing the viscosity of pulmonary secretions in chronic respiratory illness as well as an antidote for hepatotoxicity due to acetaminophen overdose. It has also been efficient in the treatment of Sjogren's syndrome, smoking cessation, influenza, hepatitis C, and myoclonus epilepsy [1]. Another less expanded chemical property of NAC concerns its antioxidant activity. As a matter of fact, NAC constitutes an excellent source of sulphydryl groups (SH), which is converted in organism into metabolites able to stimulate the synthesis of reduced glutathione (GSH). It also acts as a scavenger of free radicals and reactive oxy- gen species (ROS), consuming directly super oxide anion [2], or hypochlorous acid [3]. This work describes the electrocatalytic properties of a glassy carbon electrode (GCE) modified with poly(*o*-phenylenediamine) (PoPD)/Prussian blue (PB) nanoparticles (NPs) for the electrocatalytic oxidation of NAC. The stepwise fabrication process of PBNPs-modified PoPD/GCE was characterized by scanning electron microscopy (SEM) and electrochemical impedance spectroscopy. The mechanism and kinetics of the catalytic oxidation reaction of NAC were monitored by cyclic voltammetry and chronoamperometry. Some important advantages such as simple preparation, fast response, good stability and reproducibility of the sensor for the voltammetric determination of NAC were achieved.

Keywords: *N-Acetyl-L-cysteine, Prussian blue nanoparticles, Poly (o-phenylenediamine), Glassy carbon electrode*

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Glassy carbon electrode incorporating Prussian blue nanoparticles for voltammetric determination of *D*-penicillamine

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Abstract

Penicillamine (PA) (SH-C(CH$_3$)$_2$-CH(NH2)-COOH, 2-amino-3-mercapto-3-methylbutanoic acid, β,β- dimethylcysteine, 3-mercaptovaline) is derived from hydrolytic degradation of penicillin, which has many therapeutic applications. This compound is a strong chelating agent and can react with the majority of heavy metal ions. The outstanding metal-binding capability is reflected in the pharmaceutical importance of PA [1]. The typical therapeutic dose administered to humans is in the range of 0.5–2.0 g daily. Increasing the amount of penicillamine can cause rashes early in treatment. It can also cause loss of appetite, nausea, abdominal pain, and loss of the sense of taste. While the D-enantiomer of PA is therapeutic, the L-enantiomer is highly toxic; since it possesses the same configuration as L-amino acids (which are the constituents of proteins) and can interfere with amino acid metabolism [2]. This work describes the electrocatalytic properties of a glassy carbon electrode (GCE) modified with poly(*o*-phenylenediamine) (PoPD)/Prussian blue (PB) nanoparticles (NPs) for the electrocatalytic oxidation of D-Penicillamine (D-PA). The stepwise fabrication process of PBNPs-modified PoPD/GCE was characterized by scanning electron microscopy (SEM) and electrochemical impedance spectroscopy. The mechanism and kinetics of the catalytic oxidation reaction of D-PA were monitored by cyclic voltammetry and chronoamperometry. Some important advantages such as simple preparation, fast response, good stability and reproducibility of the sensor for the voltammetric determination of D-PA were achieved.

***Keywords**: D-penicillamine, Prussian blue nanoparticles, Poly(o-phenylenediamine), Glassy carbon electrode*

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Photocatalytic Degradation of Diclofenac Sodium in Aqueous Solution Using N, S, and C-doped ZnO

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Abstract

In this investigation photocatalytic degradation of diclofenac sodium as drug pollutants was studied. N, S, and C-doped ZnO (N,S,C-ZnO) particles were supported from thiourea and zinc sulfate via a precipitation method and characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS). The degradation was studied under different conditions such as the catalyst concentration, concentration of drug, initial pH value and presence of electron acceptor. The results showed that photocatalytic degradation of drug was strongly influenced by these parameters. The best conditions for the photocatalytic degradation of diclofenac sodium were obtained. The optimum concentrations of N,S,C-ZnO was found to be 0.44g/L. The photodegradation efficiency of diclofenac sodium decreased with an increase in the initial concentration of diclofenac sodium. In acidic solutions, photocatalytic degradation efficiency was higher than in alkaline solutions.The photodegradation efficiency of diclofenac sodium was accelerated by addition of a small amount of $K_2S_2O_8$ and H_2O_2.

Keywords: N, S, C-ZnO, *Photocatalytic Degradation*, *Precipitation method*, *Drug*, *Diclofenac Sodium*

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DPV Study on Platinum Core-Shell Nanoclusters

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Abstract

Nanoparticles whose properties depend on their size are, in purely scientific terms, fascinating. Large (>4 nm) metal ones have properties like those of bulk metals, whereas small ones exhibit molecule-like properties such as HOMO-LUMO gaps. In between, one finds quantized capacitors. Size dependent electrochemical behavior of nanoclusters has been investigated by voltammetry at nanoscale. Due to the high sensitivity of differential pulse voltammetry (DPV) to detect very small faradaic current, this technique is considered as a method of choice in this research. In this regime of nanoparticle voltammetry, the MPCs behave as quantum capacitors. It means that the MPCs behave as multivalent redox species during charge transfer at nanoscale as the injection of charge to the cores is quantized. Because the quantized charging currents of the clusters are diffusion controlled, their voltammetric behavior is proportional with their size. CV/DPV electrochemical characterization of fractionated nanoclusters approves observation of Quantized Double Layer (QDL) phenomena which is detected as a fingerprint on the size of as-prepared nanoclusters. Long-term stability of nanoclusters has been checked after even one year at room temperature. Chemically synthesized platinum nanocluster is fractionated in a dispersant and then the solid phase repeatedly separated. Voltammetry behaviour of finalized dispersion seriously can be attributed to the size of generated nanoclusters. Quantized capacitance charging of Pt nanoclusters so called Monolayer Protected Clusters (MPC) has been frequently observed which confirms the nanometric size of as-prepared nanoclusters. The equally spaced peaks in CV and DPV arise from successive, quantized (single-electron) capacitative charging of ensembles of individual cluster cores (i.e., electrochemical ensemble Coulomb staircase charging). The final application of this ultrafine grained nanostructured material is in catalysis, energy storage and conversion.

Keywords: *Monolayer Protected Clusters (MPC), Electrochemical Quantized Charging*

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The effect of the added conventional surfactant to the gemini surfactant solutions, a Monte Carlo simulation

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Introduction

Gemini surfactants (m-s-m) are made up of two hydrophobic chains and two hydrophilic heads connected through a spacer [1]. These surfactants have demonstrated many unique properties, such as lower critical micelle concentration (CMC), greater efficiency in lowering the surface tension of water and better solubilization capability compared to the conventional surfactants. They have been widely used in the fields of soil remediation, separation of biomaterials, enhanced oil recovery and drug entrapment and release [2-4]. In this paper, the properties of binary surfactant systems of gemini and conventional surfactants have been investigated by means of 3D lattice Monte Carlo simulation.

Simulation Method

The simulation model we used employs a three dimensional 100×100×100 cubic lattice. The coordination number of $z = 6$ (i.e., only considering interactions between nearest neighbors) has been used. Excluded volume and periodic boundary conditions has also been applied. The amphiphile chains occupy a chain of connected adjacent sites on a lattice. With representation of the tail groups by T (B), head groups by H (A), and spacer groups by S, the gemini surfactant chains with $T_3H_1S_2H_1T_3$ and conventional surfactant with A_4B_4 have been labeled. The only type of move used to modify the configuration is the reptation which is a snake-like movement. The Monte Carlo simulations applied here are based on the Metropolis algorithm.

Results and Discussion

Mixed micelle formation is a specific phenomenon for the surfactant–surfactant mixtures. The composition dependence of the mixed CMC (CMC_M) for the $T_3H_1S_2H_1T_3/A_4B_4$ at different ratios in aqueous solutions has been represented in Fig. 1. In the mixed gemini/conventional surfactants, the CMC_M values are the intermediate of the constituent CMCs at all volume fractions. The presence of the A_4B_4 surfactant in the mixture decreases the CMC value of the $T_3H_1S_2H_1T_3$ surfactant with α_1 (α_1 is the volume fraction of conventional surfactant A_4B_4 in the mixed aggregate surfactants) lower than 0.2 and then increases to reach the CMC value of the A4B4 surfactant. The steep increase in the CMC_M values is found at A_4B_4 volume fraction (α_1) above 0.5. The decrease in the CMC values is ascribed by the nature of A_4B_4 surfactant, which reduces the repulsion interaction near the micellar surface, hence lowering the entropic penalty of forming micelles. In order to obtain more information about such mixture of surfactant systems, we have measured the average numbers of gemini tail and conventional tail contacts in the mixed micelles provided by the simulation data. As shown in Fig. 2, the average numbers of tail–tail contacts (n_{TT}) reach a maximum in $\alpha_1 = 0.5$ and then decrease which is a proof of the above mentioned results.

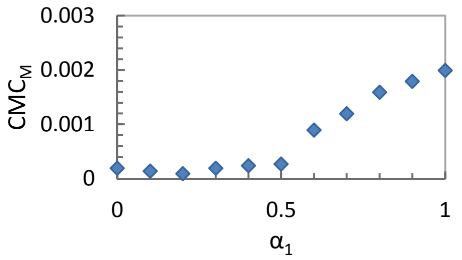

Fig. 1. Variation of the CMC_M with A_4B_4 fraction in the mixed micelle.

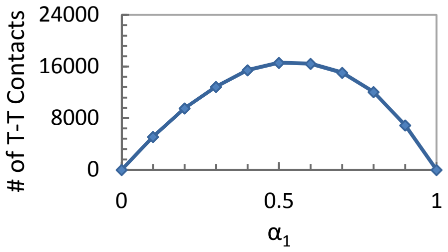

Fig.2. Simulated number of tail (gemin)–tail (conventional) contacts, n_{TT}, as a function of the concentration of A_4B_4.

Conclusion

Our simulations indicate that since the CMC of gemini surfactant is lower than the A_4B_4 surfactant, the mixed micelles must ideally contain more $T_3H_1S_2H_1T_3$ surfactants. The presence of the A_4B_4 surfactant in the mixture decreases the CMC value of the $T_3H_1S_2H_1T_3$ and then will increase the CMC of the A_4B_4 surfactant.

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Keywords: *Lattice Monte Carlo, Mixed micellization, Gemini surfactant, Conventional surfactant.*

Application of genetic algorithms for pixel selection in multivariate image analysis for a QSPR study of half-wave potentials for benzoxazines compounds

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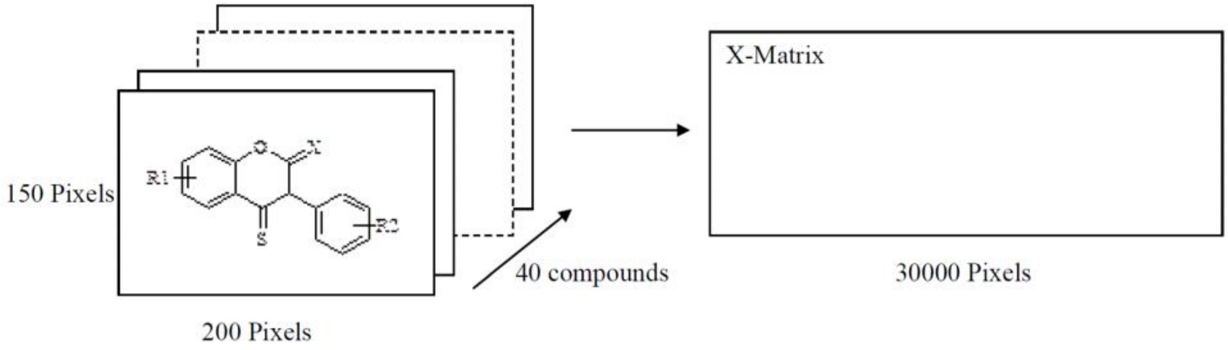
Abstract

The Half-wave potential ($E_{1/2}$), which is an important electrochemical property for a reversible oxidation-reduction system, can be useful for predicting other electrochemical properties and activities of organic compounds. In this study, a quantitative structure-property relationship (QSPR) analysis has been directed to a series of 40 benzoxazines compounds with half-wave potentials ($E_{1/2}$) (1) property that was performed by chemometrics methods. Bidimensional images were used to calculate some pixels (2). Multivariate image analysis was applied to QSPR modeling of the $E_{1/2}$ potential of benzoxazines derivatives by means of multivariate calibration such as principal component regression (PCR) and partial least squares (PLS) (3).



In this paper we investigate the effect of pixel selection by application of genetic algorithms (GAs) for PLS model (4). GAs is very useful in the variable selection in modeling and calibration because of the strong effect of the relationship between presence/absence of variables in a calibration model and the prediction ability of the model itself. The subset of pixels, which resulted in the low prediction error, was selected by genetic algorithm. The resulted model showed high prediction ability with RMSEP of 0.1428, 0.1105 and 0.0103 for PCR, PLS and

GA-PLS models, respectively. Furthermore, the proposed QSPR model with GA-PLS can contribute to the $E_{1/2}$, and can be useful in predicting the $E_{1/2}$ of the other compounds.

***Keywords**: Half-wave potential, QSPR, multivariate image analysis, PCR, PLS, genetic algorithms*

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Theoretical study on the functionalized graphene nanostructures with carbendazim

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Abstract

Since the discovery of graphene in 2004 [1], due to their unique electronic, mechanical, and thermal properties is strongly affected by the adsorption of molecules making this material very attractive for sensing application. Unfortunately, the poor solubility have hampered the future application of graphene in sensing of materials in aqueous solutions. By experimental treatment of graphene in an oxidizing environment, the oxygen-containing groups such as –COOH, −COO and −OH are introduced to the ends and surface of the sheets [2]. According to experimental treatment, our results may be useful for further studies in functionalization of graphene with a carboxyl group and construction of nanodevices and nanosensors for sensing electroactive materials. Carbendazim (CBZ, methyl 2-benzimidazole carbamate) is a benzimidazole fungicide widely used to control black spot (a fungal disease of citrus, cereals and bean) in many countries. The environmental protection agency (EPA) allowed limited use of CBZ in citrus fruit until 2009. Due to the high consumption of orange juice and cereals in the world and the high environmental impact that may result, the control of CBZ levels is extremely important [3, 4]. Within this work, we performed a DFT study on the interactions of a CBZ molecule, with the surface of a functionalized graphene with carboxyl group (Gr-COOH), consequently adsorption energy, HOMO/LUMO energy gap, charge transfer and electronic properties in the adsorption process were investigated.

The full geometry optimizations and property calculations were performed with the quantum-ESPRESSO suite of codes [5]. The widely used generalized gradient approximation (GGA) with the exchange-correlation functional parameterized by Perdew, Burke and Ernzerhof (PBE) was adopted, using spin-polarized calculations [6].The Brillouin zone was sampled with $4 \times 4 \times 2$ Monkhorst-Pack k-points mesh, to ensure convergence. All of the proposed complexes are calculated in the same periodic supercell, with the same k-point sampling grid, the same DFT approach and used solvation model with water solvent, ensuring consistency between calculations. To study CBZ adsorption, the CBZ molecule are positioned in three configurations at the surface. In model A, B and C interaction of imin, amin and ester functional group with -COOH on graphene sheet was investigated, respectively. The adsorption energy and more detailed information for considering configurations are listed in Table 1. According to the obtained information, adsorption energy of configuration A shows the strongest interaction between CBZ molecule and Gr-COOH sheet than other configurations.

Table 1 Calculated adsorption energy (E_{ads}),Fermi level energy(E_{FL}), HOMO-LUMO energy gap(E_g) and of models in eV.

Model	E_{ads}	Q_T(e)[a]	E_{FL}	E_g	ΔE_g[b](%)	Distance(Å)
CBZ	−	−	-3.43	3.851	−	-
Gr-COOH	−	−	-4.86	0.094	−	-
A	-0.750	0.500	-4.74	0.037	60.64%	1.07
B	-0.061	0.006	-4.87	0.094	0%	2.32
C	-0.342	0.045	-4.86	0.095	1.06%	1.58

[a] Q_T is defined as a average of total Mulliken charge on the adsorbed molecule.

[b] The change of HOMO-LUMO energy gap of Gr-COOH after CBZ adsorption.

To elucidate the effects of CBZ adsorption on the electronic structure of Gr-COOH, it's image, density of state (DOS) plot and band structure of configuration A are represented In Fig. 1.

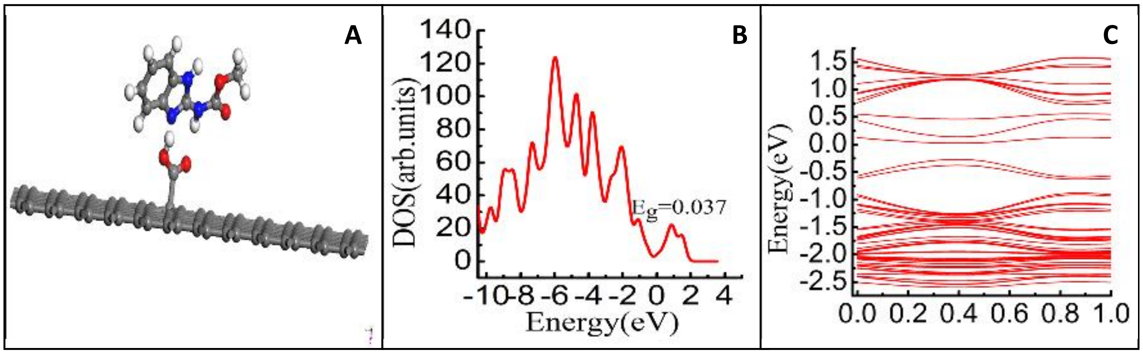

Figure 10The image of CBZ on surface (A), DOS plot (B) and Bandstructure (C)

In conclusion, in this work adsorption process of CBZ on Gr-COOH sheet and electronic properties of systems were investigated. We suggest that the functionalized graphene may be potential sensor for CBZ fungicide detection in environmental and agricultural studies.

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Application of multielectrode systems

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Abstract

Multielectrode systems in two types of coupled and uncoupled systems are employed as a high throughput devices to measure the stochastic behavior of pitting corrosion. Since the coupled multielectrode arrays as a sensor (CMAS) can be arranged in any given pattern and each electrode is addressable, these systems are widely used by researchers in the study of online and real-time corrosion monitoring and can provide not only temporal, but also spatial information on corrosion, especially localized corrosion in two dimensions.

Keywords: *Multielectrode, array, corrosion, monitoring*

Introduction

The use of multielectrode systems in electrochemical and corrosion studies has started three decades ago. Coupled multielectrode systems, in which several electrodes are connected to each other through an external circuit and all are at the same potential, was employed as a high throughput devices to measure the stochastic behavior of pitting corrosion for the first time in 1977 [1]. Similar studies were conducted in the field of corrosion detection in concrete in 1991 and to measure the crevice corrosion in 1993 [2]. Multielectrode arrays, in which multiple electrodes are arranged in a given pattern and each electrode is addressable, have been used since 1984. It seems that early work in multielectrode arrays have been for development of electronic devices. Using uncoupled multielectrode arrays were reported for the first time in 1991 for corrosion studies. The first coupled multielectrode array to simulate a one-piece of metal and study the spatiotemporal electrochemical behavior and corrosion processes of iron in sulfuric acid solution was published in 1996 [3]. The coupled multielectrode arrays are used as a sensor (CMAS) for online and real-time corrosion monitoring in laboratories and industrial plants lately. Because these sensors do not need the bulk electrolyte, CMAS probes are used for quantitative measurement of localized corrosion of metals not only in aqueous solutions, but also in wet gases, oil / water mixtures, soil, salt deposits, biodeposits, concrete and undercoating. CMAS probes are also used for cathodic protection monitoring systems. In addition, in quantitative measurement of localized corrosion such as pitting corrosion and crevice, CMAS probes are used to measure the average rate of corrosion [4].

Principles

It seems that the first use of a multielectrode system, has been reported by Shibata and Takyama to assess the stochastic behavior of pitting corrosion (Fig.1). The potential of the samples was increased in the anodic direction at a given constant rate and a timer was used for each sample to trigger the opening of the relay when the current exceeded a given value from that sample, which indicated the commencement of pitting corrosion for that sample. In this way, they were able to determine the pitting potential of 12 samples in an experiment that greatly increases the efficiency of pitting potential measurement, and enable them to study the stochastic behavior of the pitting corrosion of stainless steel [5]. In the first coupled multielectrode array to simulate a one-piece of metal and study the spatiotemporal electrochemical behavior and corrosion processes of iron in sulfuric acid solution (Fig.2), by comparing the total current of the electrode array with the current of one-piece electrode, the authors concluded that array of electrodes acts as a one-pies electrode that has the same shape and total area. Therefore, the electrochemical spatial patterns observed from the electrode array are representative of a one-piece electrode patterns. By means of the coupled multielectrode array, we are able to determine the spatial pattern of the active passive electrochemical oscillations directly and how the oscillation wave front travels on a large iron electrode [6].

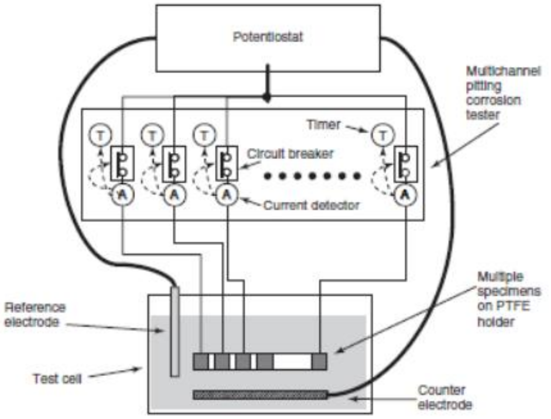

Figure 11: A multielectrode system for pitting potential measurements [5].

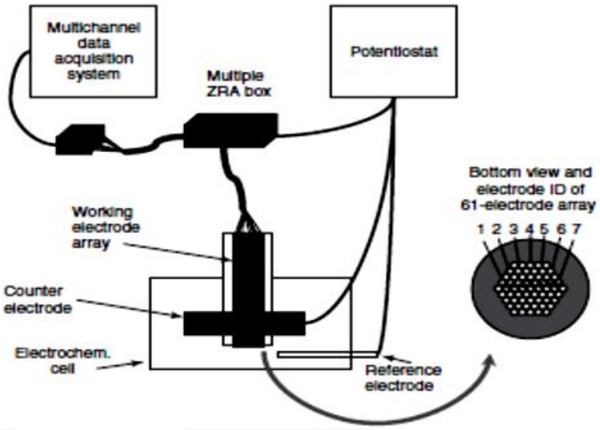

Figure 12: A coupled multielectrode array system used to study the spatiotemporal pattern of the nonuniform corrosion of iron in sulfuric acid solution [6].

Conclusion

The coupled multielectrode systems are used for the quantitative evaluation of corrosion in concrete for nearly three decades and more than 30 years, is used to detection of crevice corrosion. The coupled multielectrode arrays that can be arranged in any given patterns have been used by many researchers for studying the spatial patterns and the electrochemical behaviors of the corrosion processes, especially the localized corrosion processes of metals. With the advancement of the coupled multielectrode arrays and multichannel instrumentation, real-time CMAS probes have been developed. These probes provide simple parameters, such as maximum localized corrosion rate, maximum localized corrosion penetration depth, and estimation for average corrosion rate.

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MoS_2(001) Supported Pt Nanoparticles as an high performance electrocatalyst:Density Functional Theory Study

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Abstract

The deposition of Pt metallic nanoparticles on different supports is of high importance for designing more efficient and expensive durable[1]. In order to recognize the nucleation of Pt nanoparticles on MoS_2 monolayers, we have systematically studied, by first-principles density functional calculations, the evolution structure and morphology of supported (Pt)n nanoparticles (NPs) on MoS2(001) for $n \leq 12$. The result show that the cluster with the size of n==5 where the growth of the NPs converts from two- to three-dimensional (2D to 3D)[2]. Owing to the structure of MoS_2(001), the 2D NPs mostly attach to the support via direct bonding with Mo atoms that sit in the troughs of the surface, while the 3D NPs are bonded to the sulfur atoms that are more stretched in the vacuum region. Moreover, we realized that Pt is sufficiently mobile on the surface where the number of hopping events per second is ≈103s along [101] and ≈10 s^{-1} along [110] at room temperature. The somewhat large mobility suggests that monomer diffusion is not likely to be the rate-limiting step for Oswald ripening and that Pt sputtering on MoS_2(001) will result in relatively large particles rather than a fine dispersion. The existence of a fast diffusion channel along [101] suggests that the morphology of the NPs is anisotropic Overall, the high mobility of Pt atoms proposes that Pt sputtering on MoS_2 will leads to relatively large islands rather than a fine dispersion.

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Polymeric membrane electrode for citrate ion selective by potentiometry and Impedance technique

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Abstract:

A Citrate Ion-Selective polyvinyl chloride (PVC) membrane electrode based copper(II) complexes bearing salicylaldehydesemicarbazone tridentate Schiff bases ligand as a carrier for the Citrate anion is reported. In this work, a new strategy for optimizing membrane components by electrochemical impedance spectroscopy (EIS) is presented. The performance of this electrode was investigated using potentiometric and EIS techniques. The potentiometric results indicated that the prepared electrode had a Nernstian slope of −19.7 ± 0.3 mV in a linear concentrations range of 1.0×10^{-7}-1.0×10^{-1}M, a detection limit of 6.3×10^{-6} M, an applied pH range of 5.03-11, and a response time of less than 15 s; while using the EIS technique, the linear concentrations range was $1.0 \times 10{-}^{8}$ to $1.0 \times 10{-}^{1}$ M and the pH range increased to 4.40-10.60

Introduction

Potentiometry with ISEs is one of the most successful methods for direct detecting of ionic species[1]. and for indirect detecting of non-ionic species [2]. Electrochemical impedance spectroscopy (EIS) is anothertechnique used for evaluating interactions within the membrane [3]. Citrate is the key metabolite in the Krebs cycle (citric acid cycle) of virtually every aerobic cell. Determination of citrate levels is important in clinical conditions and in normal cell metabolism. Diminished citrate level in urine has been linked to various aspects of kidney dysfunction, for example in the pathogenesis of nephrolithiasis and nephrocalcinosis[4].

Experimental

A mixture of poly(vinyl chloride); PVC, plasticizer i.e. di butyl phthalate; DOP, and ion exchanger i.e. trioctylmethyl ammonium chloride; TOMAC, were dissolved in a minimal amount of THF and DMF and solution was mixed well. The resulting mixturewas transferred into a small flat bottom glassy dish. The solvent was evaporated slowly untilan oily concentrated mixture was obtained. An opening of a PVC tube was dipped into the mixture , so that a transparent membrane was formed. After removing the tube from the mixture, it was kept at room temperature for about 24 h. The tube was then filled with an internal filling solution(1.0×10^{-2} M sodium citrate sal). The electrode was finally conditioned for 2 h by soaking in 1.0×10^{-2} M sodium citrate sal solution. an Ag/AgCl electrode was used as an internal reference electrode.

Potentiometric Measurements. Potentials were measured with a digital pH-ion meter and an electrochemical cell consisting of two electrodes; a SCE as the reference electrode and a Ag/AgCl electrode embedded in a citrate-selective membrane as the working electrode.The performance of the electrode was investigated by measuring its potential in prepared solutions in a concentration range from 1.0×10^{-9}-1.0×10^{-1}M. During these measurements, the sample solution was stirred using a magnetic stirrer. Additionally, the pH changes were measured using a pH meter

Electrochemical Impedance Measurements: EIS measurements were carried out using a potentiostat/galvanostat Instrument. controlled by Frequency Response Analyser (FRA) software and an electrochemical cell consisting of three electrodes: a SCE as reference electrode, a Ag/AgCl electrode embedded in the citrate -selective membrane as the working electrode, and a platinum electrode as the counter electrode. During this analysis, frequency range of 50 000−130 Hzwith 40 frequency points, the sample solution was fully static.

Results and Conclusion: The best performing citrate - selective membrane was composed of PVC (0.03g), ionophore (0.004g), additive (0.0037g), plasticizer (0.060g).

Evaluation of Potentiometric Studies: This electrode These studies were carried out under the same experimental conditions using a 1.0×10^{-2} M solution of the corresponding anions as the internal and external solutions of the electrode, that between all the salts, $C_6H_5Na_3O_7.2H_2O$ solutions have the best Nernstian slope. The proposed membrane electrode was also examined with different concentrations of the inner reference solution from 1×10^{-2} M to 1×10^{-6} M, so the best inner solution was choosed 10^{-2} M.

Evaluation of EIS Studies of the Membrane with and without Ionophore: In this study, impedance measurements were carried out on the membrane with and without ionophore, and 1.0 × 10^{-3} and 1.0 × 10^{-4} M solutions of sodium citrate as the internal and external solutions of the electrode were used, respectively.the charge transfer resistance of the membrane without ionophore (8.4247 Mohm) is more than that of the membrane with ionophore (3.2276 Mohm).

Keywords: *Ion selective electrode*, *Potentiometric*, *Citrate*, *Membrane*, *Plasticizer*, *Additive*. *Impedance*

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Exploring the effect of structural defect on the performance of P-doped (6, 6) CNT-based supercapacitors

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Abstract

Supercapacitors due to high power density, enabling fast charging and discharging, are used to store electrical energy. However, their lower energy density in comparison with conventional batteries, limits the use of this energy storage device. In this regard, extensive researches in the field of supercapacitors are performed to increase the capacity of supercapacitors [1]. Carbon nanotube (CNTs)-based material are promising materials for use in supercapacitor electrodes [2]. Despite of advantage of CNTs-based electrode, major limitation of low quantity of specific capacity due to their low quantum capacitance remain [3]. All density functional theory (DFT) calculations were completed using QUANTUM ESPRESSO code and predew-Wang91 (GGA-PW91) exchange-correlation functional. Our results indicate that quantum capacitance significantly is improved by changing in the electronic structure through dopants and defects. The obtained results from density of state (DOS) of P-doped (6, 6) CNTs indicates that impurity states are created around the Fermi level (see figure 1a). Quantum capacitance of P-doped (6, 6) CNTs in the water stability range (for V= -0.4-0.83) are increased compared with quantum capacitance of pure (6, 6) CNTs. In these cases the quantum capacitance is almost symmetric around zero voltage and increased both the negative and the positive bias (see figure 1b).

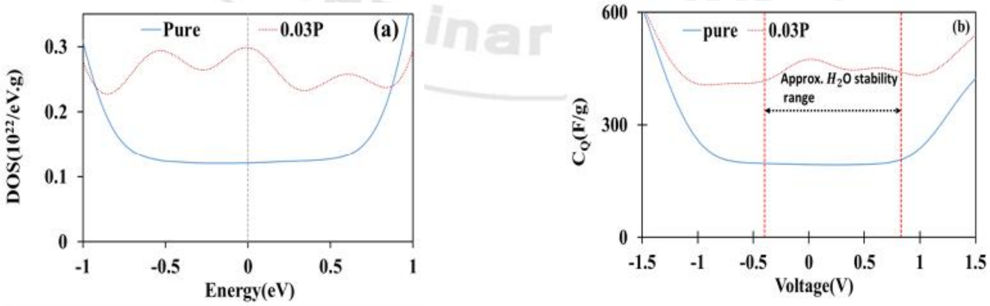

Figure 1. (a) The plots of DOS for P-doped (6, 6) CNTs and (b) The integrated quantum capacitance of P-doped (6, 6) CNTs. Fermi level is labelled by dashed line

In another part of this paper, the effect of structural defects in P-doped (6, 6) CNTs on the quantum capacitance were studied. Results show that DOS of this structure is increased compared to DOS of pure CNTs at negative bias and Fermi Level (see figure 1a). Their calculated quantum capacitance indicate that significantly enhancement has been appeared as compared to their pure form especially at positive bias. It could be seen that the quantum capacitance is asymmetric around zero voltage (see figure 2b). As a result, these materials are proposed to operation as a positive electrode .

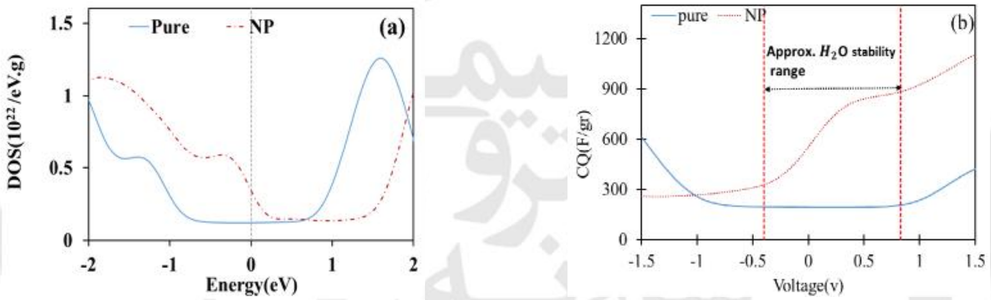

Figure 2. (a) The plots of DOS for structural defects in P-doped (6, 6) CNTs and (b) The plots of integrated quantum capacitance of structural defects in P-doped (6, 6). Fermi level is labelled by dashed line.

In short, in this paper, Using DFT calculation, we investigated the effects of dopants and structural defects in carbon nanotubes electrode on the quantum capacitance. We observed that quantum capacitance has increased due to dopant and structural defects.

Keywords: *Supercapacitors, P-doped-CNTs, DFT, Quantum Capacitance*

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Determination of Nitrate by Electrochemical impedance spectroscopy and potentiometric Techniques

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Abstract

Ionophore derivative anion receptor has been tested as electroactive material for the development of anion selective electrodes. The receptor was incorporated in plasticized poly (vinyl chloride) membranes of different compositions. The membrane that provided the best response and selectivity towards nitrate was selected to develop a new nitrate-selective electrode. In this work a new strategy for optimizing membrane components by electrochemical impedance spectroscopy (EIS) is used. The performance of this electrode was investigated using potentiometric and EIS techniques. The electrode exhibited a Nernstian response over the nitrate concentration range of 1.0×10^{-7} to 1.0×10^{-1} M with a slope of 59.5 mV/decade by potentiometric technique. It showed good selectivity to nitrate relative to many common anions. While using the EIS technique, the linear concentration range was 1.0×10^{-8} to 1.0×10^{-1} M and the pH range increased to 4.0-10.0. The proposed electrode was applied to the determination of nitrate in wastewaters.

Introduction

Potentiometric measurements using ion-selective electrodes (ISE) for determination of the respective metal ions is advantageous due to speed, wide dynamic ranges, and no requirement for the sample pretreatment [1]. Electrochemical impedance spectroscopy (EIS) is a powerful technique for studying the structure of the electrical double layer formed at the semiconductor electrode/electrolyte interface, the charge transfer processes in the semiconductor and electrolyte, as well as the parameters defining the limiting steps of the electrode processes [2]. Nitrates are widely used in explosives, fertilizers, drugs and many industrial products and hence their effluents may contain appreciable concentrations of nitrates and related ions [3]. Nitrate (NO_3^-) is an important and commonly occurring nitrogen species in the environment. It is applied in both urban and rural areas as a component of fertilizer and is a major component of concern in the effluent of waste water treatment plants [3].

Experimentals

A mixture of dioctyl phthalate (DOP), Methyl trioctyl ammonium chloride (MTOAC), and the ionophore was dissolved in THF. PVC was dissolved in THF separately and was added to the mixture. The total mass of these compounds should be 0.1 g. An opening PVC tube with 3 mm in diameter and 2 cm in length was dipped into the mixture for about 10 s to form a 0.3 mm thick transparent membrane and was kept at room temperature for about 24 h. Then, the tube was filled with the nitrate ion solution and conditioned by 1.0×10^{-2} M KNO_3 solution for 2 h. Finally, the nitrate-selective electrode was prepared by incorporating the tube to a saturated calomel electrode (SCE).

Potentiometric Measurements: Potentials were measured with a digital pH-ion and an electrochemical cell consisting of two electrodes; a SCE as the reference electrode and a Ag/AgCl electrode embedded in a nitrate anion-selective membrane as the working electrode.

The performance of the electrode was investigated by measuring its potential in prepared solutions in a concentration range from 1.0×10^{-8} to 1.0 M. During these measurements, the sample solution was stirred using a magnetic stirrer. Additionally, the pH changes were measured using a pH meter and a pH electrode.

Electrochemical Impedance Measurements: EIS measurements were carried out using a potentiostat/galvanostat Autolab instrument controlled by Frequency Response Analyser (FRA) software and an electrochemical cell consisting of three electrodes: a SCE as reference electrode, a Ag/AgCl electrode embedded in the nitrate-selective membrane as the working electrode, and a platinum electrode as the counter electrode. During this analysis, a frequency range of 50000−60 Hz with 40 frequency points, the sample solution was fully static and the system was held at the open circuit potential (OCP).

Results and Conclusions: The best performing nitrate- selective membrane was composed of PVC (0.0327g), ionophore (0.0043g), additive (0.0006g), plasticizer (0.0635g).

These studies were carried out under the same experimental conditions using a 1.0×10^{-2} M solution of the corresponding anions as the internal and external solutions of the electrode, that between all the salts, KNO_3 solutions have the best Nernstian slope. The proposed membrane electrode was also examined with different concentrations of the inner reference solution from 1.0×10^{-1} M to 1.0×10^{-5} M, so the best inner solution was choosed 1.0×10^{-2} M. Selectivity coefficients for the phosphate ion were determined by fixed primary ion method (MPM).

Evaluation of EIS Studies of the Membrane with and without Ionophore: In this study, impedance measurements were carried out on the membrane with and without ionophore, and1.0×10^{-3} M solutions of potasiom nitrate as the internal and external solutions of the electrode were used, respectively. The charge transfer resistance of the membrane without ionophore (34.585 Mohm) is more than that of the membrane with ionophore (4.336 Mohm).

Keywords: *Ion selective electrode, Potentiometric, nitrate, Membrane, Plasticizer, Additive*.

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Theoretical analysis of the electrochemical oxidation of some *p*-benzoqoinone derivatives in aqueous solution

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Abstract

Electrochemical methods are widely applied to study of the reactions of electroactive compounds. They can be used to obtain both thermodynamic and kinetic information (1,2). Among electrochemical techniques, cyclic voltammetry has been used as a powerful independent route for qualitative and quantitative characterization of complex electrode processes. In this work electrochemical oxidation of some *p*-benzoqoinone derivatives (**1-5**) in aqueous solution has been investigated theoretically to bring hints into the connection of thermodynamic and oxidation potential. The effect of ΔG_{tot} of the electrochemical oxidation was investigated with considering a general thermodynamic cycle (Born- Haber cycle). ΔG_{tot} of the oxidation of *p*-benzoqoinone derivatives were calculated at DFT (B3LYP, BP86) levels of theory using 6-311+G (p,d) and 6-311G (p,d) basis sets. $E_{1/2}$ of studied species in pH=6.0, obtained using cyclic voltammetry (3), were used as experimental data, and ΔG_{tot} of the electrochemical oxidation of studied species (**1-5**) have been calculated from computational method. The results show a good correlation between ΔG_{tot} of electrochemical oxidation and $E_{1/2}$. These data illustrate that thermodynamic indicates precedence of electrochemical oxidation of studied species. In other word it can be concluded that species with more positive oxidation potential have larger ΔG_{tot} values.

Keywords: *p*-benzoqoinone derivatives, electrochemical oxidation, Gibbs free energy, Cyclic voltammetry.

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Structural and Dynamic Investigation of $[EMIM]^+[PF_6]^-$ Electrolyte: An Atomistic Simulation

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Introduction

Ionic Liquids (ILs) have received a great deal of attention in recent years due to their potential in gas storage, electrodeposition, biocatalysis, lubricant, and as electrolyte. Wide electrochemical window, excellent thermal stability, low vapor pressure, [1, 2] and their other unique features cause these materials find remarkable applications in electrochemistry. [2, 3]

The present research involves the structural and dynamic properties of IL consist of 1-ethyl, 3-methyl imidazolium cation and hexaflourophosphate anion ($[EMIM]^+[PF_6]^-$) performed by molecular dynamics simulation.

Simulation Details

300 ion pairs of $[EMIM]^+[PF_6]^-$ were located and simulated in a periodic box. A 2 ns NPT production run was performed at 373 K and 1 atm, with 1 fs time step and 12 Å cutoff distance. Hoover thermostat and barostate were applied to the system. The force field parameters were taken from Lopes et al. [4].

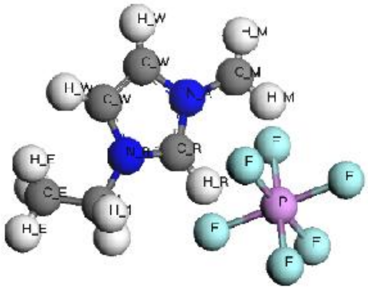

Figure 13: The structure of $[EMIM]^+[PF_6]^-$

Results and Discussion

Mean square displacement (MSD) is related to the self-diffusion coefficient of ions by the well-known Einstein equation. Calculated diffusion values are 5.19×10^{-11}, 2.4×10^{-11}, and 3.79×10^{-11} m^2/s for cation, anion, and IL, respectively. Cation has higher diffusion value due to its lower charge density.

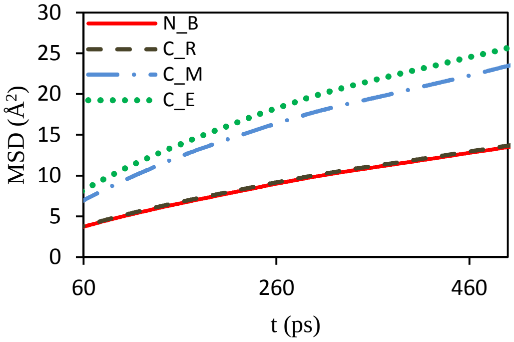

Figure 14: MSD of cation atoms at last 500 ps of simulation.

Analyzing atomistic MSD of cation showed that alkyl chain atoms possess higher MSD values than ring atoms (Fig. 3), because of their high mobility and low spatial hindrance.

Anion has stronger attraction with C_R and C_M (shown in Fig. 1) in comparison with tail and other atoms of cation. Thus, it is reasonable to consider the anion was placed in the region between methyl tail and C_R head of the ring. As it can be obvious in Fig. 1.

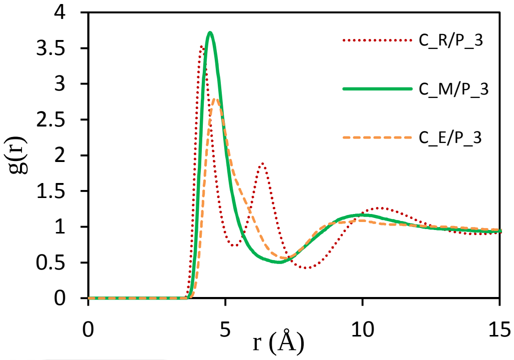

Figure 15: Cation-Anion correlation

Cation-anion RDF has been applied to characterize the ability of hydrogen bonding. Figure 4 shows a clear strong interaction between H_R and F, which can be considered as a hydrogen bond. This correlation causes strong intermolecular attraction reducing the ions diffusion.

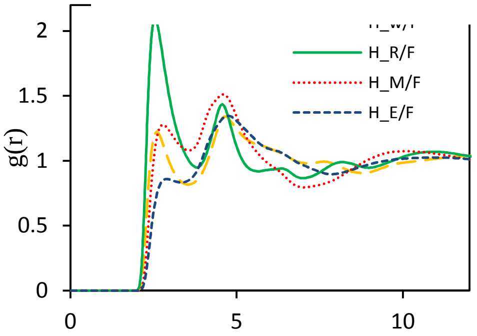

Figure 16: correlation of all hydrogen atoms with fluoride

Conclusion

A molecular level description of $[EMIM]^+[PF_6]^-$ was provided which considered structural and dynamic properties of IL. $[EMIM]^+$ cation has higher diffusion values than anion, due to its lower charge density. The RDF plots showed anion placed near the ring of cation. Moreover, the results of hydrogen correlation showed the hydrogen bond between H_R of cation and F of anion.

Keywords: *Molecular dynamics, IL, Self-diffusion coefficient, Hydrogen bond*

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The Investigation of Surfactants Morphology Changes with the Graphene Sheet Using Molecular Dynamic Simulation

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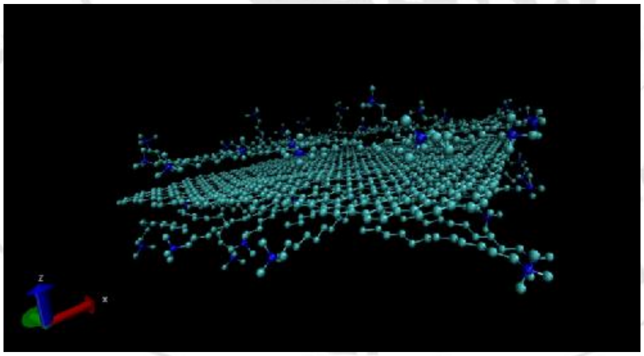
Abstract

Physical adsorption of surfactants on graphene sheet is the applicable method for dispersing the graphite. Understanding the surfactants self-assembly have a deep effect on dispersing process. For this purpose, we conducted a large-scale all-atomistic molecular dynamics (MD) simulation to investigate the self-assembly of surfactants on graphene sheet. The effect of concentration and tail length of $C_{12}TAB$ and $C_{16}TAB$ has been studied on the pristine graphene sheet. Our results showed that the morphology of surfactants upon the graphene change depending on the surface coverage for both molecules. So that, the diagonally oriented has been observed by increasing the concentration of surfactants. Furthermore, the observation showed that the tail length of surfactants play the key role in morphology.



Keywords: *Graphene, Surfactants, Molecular Dynamic, Simulation*

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A DFT exploration of the adsorption of benzene and phenol on the industrial nanostructruredcatayst (ZSM-5)

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Abstract

Adsorption of benzene and phenol on the 8T cluster model of ZSM-5 and Al-ZSM-5 catalysts, defined as $((H)_3SiO)_3$-Si-O-Si-$(OSi(H)_3)_3$ and $((H)_3SiO)_3$-Si-O(H)-Al-$(OSi(H)_3)_3$ structures, respectively,has been investigated comparatively using B3LYP, M06-2X, and *w*B97XD functionals employing 6-311++G** standard basis set. Geometric parameters predict oneand two types of hydrogen bondings in the guest-ZSM-5 and guest-Al-ZSM-5 complexes, respectively. Variations of adsorption energy have been well correlated with the strength of hydrogen bonds.ΔE_{ads}, of benzene and phenol on the zeolites was considered as the energy difference between the absorbed complex system and the total energy of separated fragments as follows:

$$\Delta E_{ads} = E_{complex} - (E_{benzene/phenol} + E_{zeolite})$$

Where $E_{complex}$ represents the single-point energy of the optimized adsorption complex while $E_{zeolite}$ and $E_{benzene/phenol}$ are the single-point energies of the optimized bare zeolite, separate benzene or phenol, respectively. According to obtained data, the deformation energy is more prominent for Al-ZSM-5...Phenol adsorption complex compared to other adsorption complexes that can be due to the stronger hydrogen bonding in Al-ZSM-5...Phenol. Atom in Molecules (AIM) and Natural Bonding Orbital (NBO) calculationsshowed a covalent nature for hydrogen bonds in the phenol…Al-ZSM-5 adsorption complex.It is worth mentioning that the energy calculation with different analysis obey the similar trend from hydrogen bonding strength standpoint.The differences in the adsorption behaviorbetween benzene and phenol on the ZSM-5 and Al-ZSM-5 are attributed to the differences in the strength of hydrogen bonding interactions.

Keywords: *ZSM-5, adsorption energy, DFT*

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Electrochemical synthesis

Electrochemical oxidation investigation of acetaminophen drug in the presence of diethylamine by electrochemical methods

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Abstract

The investigation of electro-oxidation of acetaminophen shows that the formed quinonimine is quite reactive and can be attached as a Michael acceptor by nucleophile , producing various compounds through the 1,4 - Michael addition reaction . On this direction , the electro-oxidation of acetaminophen has been studied in absence and presence of Diethylamine as a nucleophile by using cyclic voltammetry and controlled-potential coulometry in phosphate buffer (pH=8) as a supporting electrolyte . The results indicate that the quinonimine formed from the oxidation of acetaminophen with arriving in a 1,4 - Michael addition with Diethylamine convert to a new derivative . According to obtained results the reaction mechanism of electrooxidation of acetaminophen in the presence of Diethylamine is a successive ECE mechanism. The homogeneous rate constant were estimated by comparing the experimental cyclic voltammetric responses with the digital simulated results.

Keywords**:** *Acetaminophen*, Diethylamine, *ECE mechanism*, Cyclic voltammatry

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Preparation Of CdTe Based Photoelectroatalysts By Electrochemical Method And Study Of its photoelectrocatalytic Activity

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Abstract

The increasingly serious energy crisis and the environmental contamination have led to an aggressive search for renewable and environmental-friendly alternative energy resources using photocatalysts. (1)

Metal - chalcogenide nanomaterials, as compared to their wide bandgap counterparts, are particularly attractive photocatalytic materials for the conversion of solar energy into chemical energy under visible-light irradiation. (2)

Cadmium telluride (CdTe) is a widely used semiconductor in thin film solar cell modules. Since cadmium telluride is a direct gap semiconductor with a room temperature energy gap of 1.44 eV , it is considered to be a promising material for low cost thin film photovoltaic and photoelectrochemical cells. (3)

A variety of methods have been employed to prepare CdTe thin films on foreign substrates. CdTe can also be deposited electrochemically. Electrodeposition has advantages such as low temperature deposition, low cost of production and high deposit quality. (4)

Photocatalytic hydrogen production from water splitting using semiconductor photocatalysts has drawn considerable attention as a promising way of resolving global energy and environmental problems. CdTe demonstrate extremely low photocatalytic activity for hydrogen production under visible light. To solve this problem, many approaches have been proposed to enhance the photocatalytic activity of CdTe particles, including the preparation of quantum-sized CdTe and deposition of noble metals. (5)

In the present work, we report on the fabrication and characterization of CdTe thin films on gold substrate by electrochemical atomic layer deposition (EC-ALD) method using separate solutions of tellurium dioxide and cadmium sulfate as precursors at room temperature. The amperometric I–t technique is used to fabricate the CdTe film. Therefore, The CdTe- modified indium-tin-oxide

(ITO) substrates are prepared by electrochemical - atomic layer deposition (EC-ALD) method at the optimized deposition potential and time. The structural, compositional, morphological properties and photocatalytic activity of thin film photocatalysts were investigated using scanning electron microscopy (SEM), energy dispersive analysis by X-rays (EDAX) and electrochemical techniques.

The SEM images of CdTe optimized thin film reveal the homogeneity of the deposited samples on ITO. The thin films display photocatalytic activity in sodium sulfide solution. We have shown that the performance of the photocatalysts for hydrogen evolution strongly improved by deposition of noble metal on the CdTe thin films. This study demonstrates that the amount of the deposited noble metal can be adjusted to obtain a level of activity that is appropriate for the desired photoelectrocatalytic reaction.

Keywords**:** *renewable enregy, CdTe, Electrochemical atomic layer deposition (EC-ALD), Photoelectrocatalyst, Hydrogen evolution*

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Electrochemical investigation of Ti/ IrO_2–Ta_2O_5 DSA electrodes for the oxygen evolution reaction

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1. Introduction

Ti based dimensionally stable anodes (DSA) have been widely employed for oxygen evolution reaction (OER) in the electrochemical industry. DSAs made of IrO_2 and Ta_2O_5 as an electrocatalytically active layer coated on a titanium substrate was prepared by the several methods and successfully used for OER in the mineral extraction, cathodic protection, electroplating, etc. In the present work, the IrO_2-Ta_2O_5 coated titanium anode was synthesized and characterized, and OER on IrO_2–Ta_2O_5 mixed oxide electrodes in H_2SO_4 solution was studied by performing current-potential and EIS measurements.

2. Methods

Titanium substrates were prepared from 2 mm thick titanium mesh. Prior to the coating, the titanium sheets were treated by sandblasting, and then etched in the boiling oxalic acid (10 %). Synthesis of coatings made of the IrO_2-Ta_2O_5 with several IrO_2 concentration on a titanium mesh were performed using the sol–gel technique as follows: an aqueous solution was prepared by mixing (in a different mole ratio) appropriate analytically pure precursors of $IrCl_3$.3H2O (dissolved in HCl) and $TaCl_5$ (dissolved in n-butanol). Then the Ti substrates were painted with the coating solution by brushes and then samples were heated at 500 °C for 30 minutes in air furnace. The entire procedure was repeated for 15 times. The surface structures of the products were characterized by field emission scanning electron microscopy. CV, EIS, polarization curves, and galvanostatic stability testing of electrodes were performed in order to investigate the performance and stability of these electrocatalysts. All the electrochemical measurements were conducted in 0.5 mol.dm^{-3} H_2SO_4 solution, and were operated using three-compartment all-glass cell. A platinum plate (~ 2 cm ^{2}) was used as the counter electrode, and SCE as the reference.

3. Results and Discussion

Figure 1 shows the SEM image of Ti/ IrO_2–Ta_2O_5. From Figure 1, one can observe that the appropriate surface structure is formed, consisting of flat areas. From the micrographs, it can be seen that there are lots of surface and interface such as holes and moreover the size of most particles are less than 100 nm that is a key parameter in performance of these electrodes.

Figure 2 shows CV obtained on Ti/ IrO_2–Ta_2O_5 (in a different mole ratio) in 0.5 mol H_2SO_4 solution. As shown, both the initial potential of OER and the shape of voltammograms changed with the mole fraction of IrO_2. It is obviously that voltaic charge for IrO_2–Ta_2O_5 (50%-50%) is more than others, and it indicated that this composition have high current density.

Impedance of Ti/IrO_2–Ta_2O_5 anodes in H_2SO_4 solution at different anodic potentials is measured, and some representative results are shown in Fig. 3. R_f is the resistance of oxide layer and C_f the capacitance. The values of R_s, R_f, C_f and C_{dl} used for completing the circuit are obtained from the ZView program.

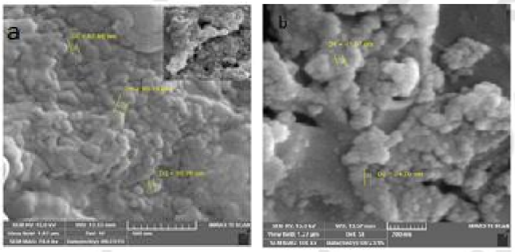

Figure 1. SEM images of Ti/ IrO_2–Ta_2O_5.

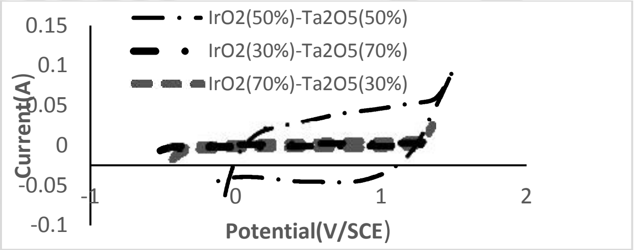

Figure 2. CV of Ti/ IrO_2–Ta_2O_5 in a different mole ratio in 0.5 mol H_2SO_4.

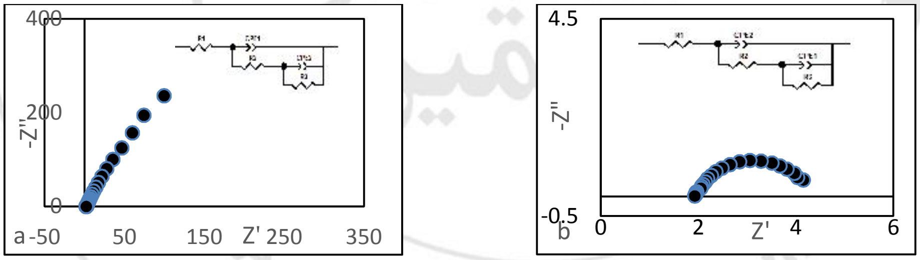

Figure 3. EIS patterns for Ti/IrO_2–Ta_2O_5 electrodes in H_2SO_4 solution at different potentials: (a) at OCP, (b) 1.2 V vs. SCE.

4. Conclusion

Ti/ IrO_2–Ta_2O_5 electrodes were developed via simple sol-gel method and the electrocatalytic activity of IrO_2 was revealed. The electrochemical properties and stability of Ti/ IrO_2–Ta_2O_5 electrocatalysts were studied by CV, polarization curves and stability test. IrO_2 exhibited a markedly higher stability in EIS measurement and the single cell stability test. Ta_2O_5 enhanced electrocatalytic activity of the IrO_2 based electrodes. The electrodes showed good activity and stability by shifting potential of OER to more negative values.

***Keywords**: Ti/ IrO_2–Ta_2O_5, DSA Electrode, OER, Electrocatalyst, EIS*

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Vertically-aligned Mn_3O_4 Nanorods: Electrochemical Preparation and Characterization

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Abstract

Since manganese oxides have unique electrical and chemical properties, it can be used as an electrode material for capacitors, electrochromic devices, ion-exchangers, and selective adsorption material of radio nuclides. Electrochemical supercapacitors are becoming attractive energy storage devices for applications involving high power requirements. There is an increasing interest in the development of advanced electrode materials based on manganese oxides. Nanostructured manganese oxides have been reported to show a promising as electrodes for lithium secondary batteries and supercapacitors, as well as redox catalysts. The preparation of nanowires and nanorods of metal oxides is of considerable interest. Herein, we report electrochemical synthesis of Mn_3O_4 nanorods and their supercapacitive performance. Deposition experiments were performed in manganese chloride bath and direct current mode with applying 2 mA/cm^2. XRD analysis (Fig. 1a) showed that the product is crystalline Mn_3O_4 phase (JCPDS no. 42-1124). SEM observation showed a rod texture with regular arrangement, i.e. vertically-align arrangement.

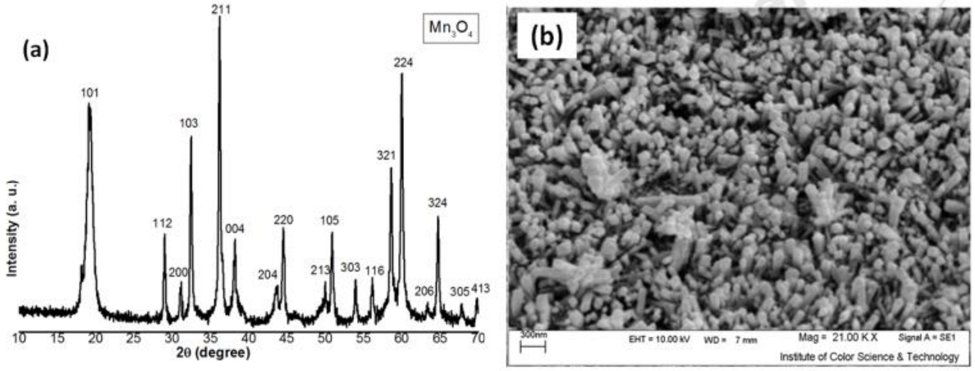

Fig. 1. (a) XRD pattern and (b) SEM image of nanoplates.

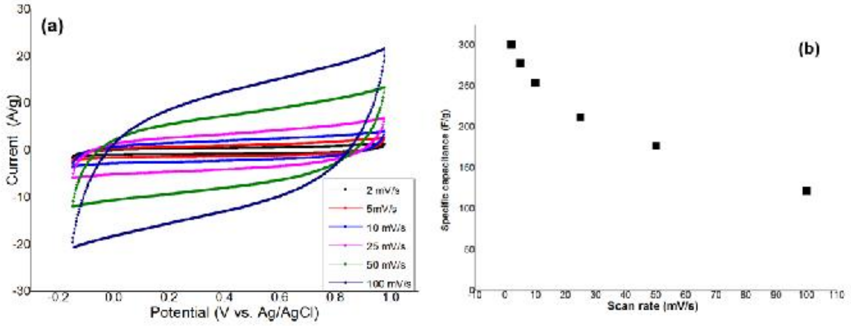

Fig. 2. (a) CVs of Mn_3O_4 nanorods and (b) SC vs. scan rate.

Fig. 2 shows the supercapacitive performance of the prepared Mn_3O_4. The specific capacitances of Mn_3O_4 nanorods were calculated to be 302.1, 285.8, 237.5, 202.1, 168.5 and 118 F g^{-1} at the scan rates of 2, 5, 10, 25, 50 and 100 mV s^{-1}, respectively (Fig. 2b). These values showed excellent supercapacitive performance of the prepared Mn_3O_4 nanorods.

***Keywords*:** *Mn_3O_4, Electrosynthesis, Nanorods, Supercapacitors*

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The factor affective quality and quantity of copper electrowinning process

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Abstract

Electrometallurgy is the last and the most important process for the recovery and therefore produces copper from the mining industry [1]. Copper is frequently present in the earth's crust as copper- iron- sulfide and copper sulfide minerals. The concentration of these minerals in an ore body is low. Copper also occurs to a lesser degree in oxidized minerals (carbonates, oxides, hydroxy-silicates and sulfates). Copper metal is usually produced from these minerals by leaching, solvent extraction and electrowinning [2]. This study investigates some factors that are effective in electrowinning i.e., time of reaction, concentration of copper, purity of cathode, the amount of copper extracted, surface morphology and other metals with copper in mineral. Other metals in ores of copper are: iron, lead, zinc, manganese, nickel and cobalt [3]. The concentration of copper and time of reaction are set to get the best copper quantity and quality extracted. To get bright and non-porous surface various factors were investigated. Although different conditions may lead to dendrite growth with voids between the crystals or resulted in powdery surface. An important factor in the quality and brightness of surface is the presence of organic matter (polyacrylamide) to produce smooth, bright and compact copper electrodeposits [1,4,5]. Different metals have shown different effect on the electrowinning. It has also shown that manganese ions impurity from 2-10 percent of the copper have an effect on increasing the rate of corrosion of the anodes and thereby the incorporation of lead on the cathodes [6,7]. Although the presence of iron is detrimental in relation to cathode current efficiency, about 10.0 g L^{-1} of iron in the electrolyte has been shown beneficial effects in lowering the solution potential and smoothing the cathode surface. Cobalt sulphate is normally added to provide about 100-200 mg L^{-1} Co^{2+} in the electrolyte to reduce both the corrosion rate and oxygen overpotential of the Pb anodes. The addition of cobalt(II) ion also reduces the rate of electrolytic production of manganese dioxide [8]. The data were obtained to provide more information for industrial processing of copper. The copper were quantitatively measured by flame atomic absorption.

Keywords**:** *Copper; Electrowinning; Morphology; Bright; Corrosion*

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Synthesis of functionalized graphene d and its application for oxygen reduction catalyst

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Abstract

In this work for the first time, used of the cholrosulfonic acid for efficiently exfoliate the pristine graphite directly into edge-selectively sulfonated graphene (SG). The procedure demonstrated in the present study is simple, low-cost, and facile one-pot approach to produce SG with any irreversible lattice damage to the hexagonal carbon plane. SG displayed a good electrical conductivity and charge transfer rate in comparison to GC. The sulfuric acid at the edge of graphene exhibits excellent electrocatalytic activity with a better fuel selectivity with a longer-term stability than those of the pristine graphite and commercial Pt/C electrocatalysts. Therefore, the SG developed in this study shows broad applications related to ORR such as alkaline fuel cells and metal air batteries.

Keywords: *Sulfonated graphene; Oxygen reduction reaction; Metal-free electrocatalysts; Fuel cell.*

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Electrochemical Preparation and Characterization of α/γ-Fe_2O_3 Nanoparticles

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Abstract

α-Fe_2O_3 (hematite), an environmental friendly n-type semiconductor (E_g=2.1 eV), is the most stable iron oxide under ambient atmosphere. Because of its low cost, high resistance to corrosion, and environmentally friendly properties, this transition metal oxide has been traditionally used as catalysts, pigments, gas sensors, electrode redox reaction at the electrode materials, and as the raw material for the preparation of magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3), which are of great importance as a ferrofluid and in magnetic recording materials [1]. Many efforts have been directed to the controlled preparation of nano or micro structural α-Fe_2O_3 to improve their properties and performance in application [2,3].

In this work, α,γ-Fe_2O_3 nanoparticles were synthesized *via* electrochemical deposition followed by heat-treatment method. The prepared products were characterized by XRD and SEM techniques (Fig. 1). XRD analysis revealed that the prepared sample has both α and γ phases of Fe_2O_3 (Fig. 1a), and SEM observation showed that the sample has particle morphology at nanoscale (Fig. 1b).

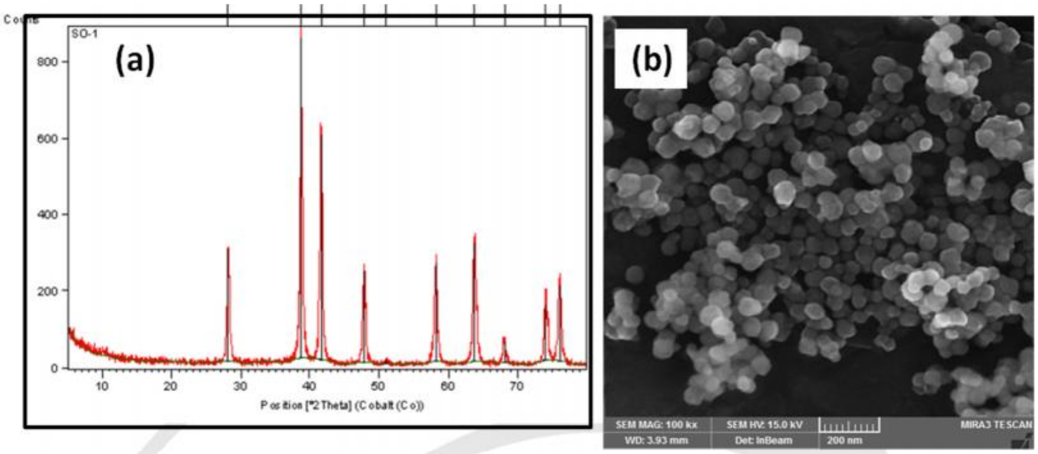

Fig. 1. (a) XRD pattern and (b) SEM image of α/γ-Fe_2O_3 nanoparticles.

***Keywords*:** *Fe_2O_3, Electrodeposition, Nanoparticles, Heat-treatment*

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Electrocatalytic Activities of Ni-P-La electrode for hydrogen evolution reaction in alkaline solution by electrochemical impedance spectroscopy

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Abstract

Ni–P–La electrodes were obtained by electrodeposition. the new electrode have been characterized by means of microstructural and electrochemical techniques in view of their possible applications as electrocatalytic materials for hydrogen evolution reaction. The morphology and microstructure were characterized by scanning electron microscopy (SEM) and energy dispersive analysis of X-ray (EDAX) and the electrochemical efficiency of the new electrodes has been studied on the basis of electrochemical data obtained from steady-state polarization curves, Tafel and electrochemical impedance spectroscopy (EIS) in 1 M NaOH solution at 298 K. The results were compared with Ni commercial electrode.

Based on these investigations, the embedded La(oxide) particles increase the electro-catalytic activity in hydrogen evolution reaction with respect to the Ni-P electrode. Results are presented to show the Ni–P–La electrodes were active for HER.

Keywords: *Ni–P–La composite coatings, Electrochemical impedance spectroscopy, Hydrogen evolution, Electrodeposited coatings*

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Electrochemical impedance studies of ethanol oxidation on synthesized poly methylene blue - poly pyrole films doped with nickel nano-particles

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Abstract

In this research, poly methylene blue and poly pyrole films were synthesized on the surface of platinum electrode by electrochemical method of cyclic voltammetry and their optimum conditions of synthesis are obtained. For investigation of the stability of poly methylene blue-poly pyrole composite, each freshly synthesized polymer separately undergoes 70 cycles in cyclic voltammetry. According to low decrease in anodic current peak, it was obvious that resultant polymers are stable. Poly methylene blue and poly pyrole films do not have electrocatalytic property for ethanol oxidation. So, poly methylene blue-poly pyrole- nickel nanocamposite was synthesized and optimum conditions were established for nickel particles dispersion in polymer matrix by changing time and current parameters (current of -10 mA, during 50 s) in chrono-potentiometry method. Scanning electron micrograph image of poly methylene blue-poly pyrole-nickel nano-composite showed that spherical nickel particles of 97-135 nm was dispersed on micro size poly pyrole. Electrocatalytic properties of nano-composite for ethanol oxidation were investigated in alkaline solution by electrochemical methods of cyclic voltammetry and impedance. It was found that poly methylene blue-poly pyrole- nickel nano-composite has higher electrocatalytic property than poly methylene blue and poly pyrole individually and also each homo-polymers contained nickel particles. The charge transfer resistance of ethanol electro-oxidation was reduced by increasing its concentration.

Keywords: *Ethanol electro-oxidation, Poly methylene blue, Poly pyrole, Nickel nano-particles.*

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Synthesis of Carbon-supported Pt-Ni nanoparticles as anode catalyst for high performance of direct borohydride-hydrogen peroxide fuel cell

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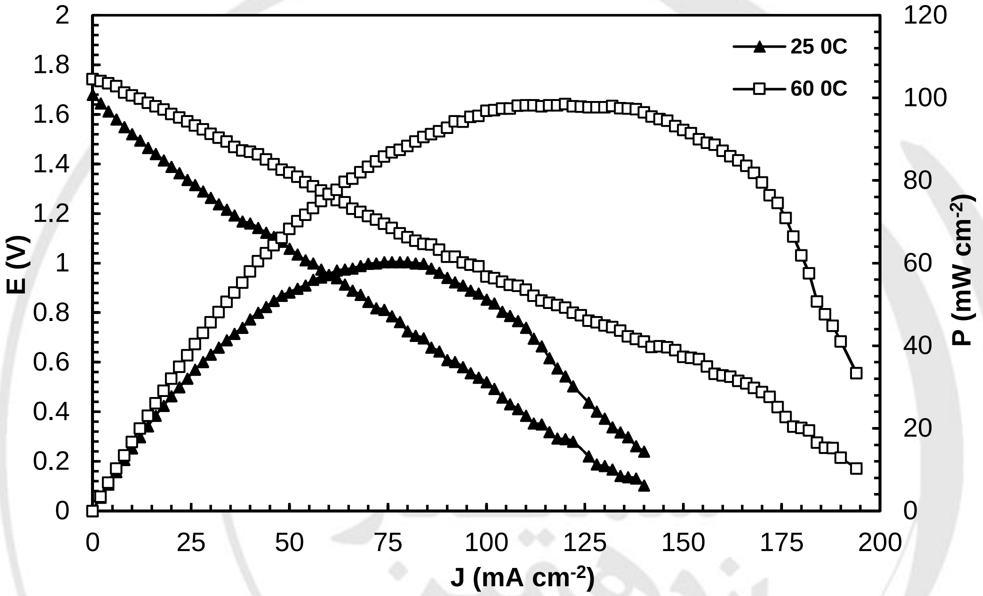
Abstract

Fuel cells have been extensively studied over the last fivedecades and increasing resources have been used to bring themto a commercial stage and to develop alternative fuels to hydrogen.As promising power sources for space and underwater applications, direct borohydride–hydrogen peroxide fuel cells (DBHPFCs),comprised of BH_4^-oxidation at the anode and H_2O_2reduction at the cathode, have attracted increasing attentions recently [1–6].In this study, Pt/C (20 wt.%)cathode andPt-Ni(1:1)/C anode (20 wt.%)were prepared by the borohydride reduction method.Briefly: Carbon black powder (Vulcan XC-72, Cabot Inc.) was used as a support for the catalyst,$H_2PtCl_6 \cdot 6H_2O$ (Merck, 99.99%) and $NiCl_2$ (Merck, 99.99%)were used as precursors. The carbon black was ultrasonically dispersed in a solution of ultrapure water and isopropyl alcohol for 2 h. The precursors were added to the ink and then mixed thoroughly for another 2 h. The pH value of the ink was adjusted by a NaOH solution to 9 and then raised the temperature to 80 ˚C. A solution of 0.1 mol $L^{-1}$$NaBH_4$ was added dropwise into the mixtures, and the bath was stirred for 3 h. The catalyst powderswere dried in a vacuum oven for 3 h at 80 ˚C and stored in a vacuum vessel.To obtain a uniform high purity film, Nafion® 117 were cleaned with a standard treatment procedure was addresed in ref [7].Prepared Ni-Pt/C and Ni/C powder were mixed with 5% nafionsoloution, water and isopropyl alcoholseparately to form catalyst ink.This ink brushed on carbon cloth with Gas diffusion layer(GDL). The loading of GDL on carbon cloth was 2 $mg.cm^{-2}$ and the loading of cathode (Ni/C) catalyst ink was 0.5 $mg.cm^{-2}$ but the loading of anode catalyst ink (Pt-Ni/C) was 1 $mg.cm^{-2}$. Finally anode, cathode and pre-treated Nafion ® 117 membrane were sandwiched together and hot pressed.The effective geometrical area of the anode and cathode was 5 cm^2.In this study, the influences of different operational conditions such as cell temperature, sodiumborohydride concentration, oxidantconcentration on the performance of direct borohydride fuel cellwere investigated. The experimental results showed that by increasing

the temperature from 25°C to 60°C ,power density was increased from 59.36 to 98.52 mW.cm^{-2} when we use $NaBH_4$ 2M + H_2O_2 2M and by increasing thesodiumborohydride concentration from 1M to 2M at 60°C power density was deacreased from 106.628 to 98.52 mW.cm^{-2}and by increasing the hydrogenperoxide concentration from 1M to 2M at 60 °C power density was increased from 97.208 to 98.52 mW.cm^{-2}. The maximum powerdensity which was achieved by Liu. X. et. al with Pt/graphene was 42 mW.cm^{-2}[8].



Keywords**:** *Borohydride oxidation, hydrogen peroxide, Pt-Ni/C, Fuel cell performance.*

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Electrodeposition of band gap reduced p-type ZnO nanorods on FTO; effect of Cu ion doping on its structural and electronic properties

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Introduction

Zinc oxide (ZnO) as a n-type semiconductor (3.37 eV) considered a promising alternative to TiO_2 for photocatalytic and photovoltaic applications. However, similar to TiO_2, its major drawback is the large band gap that allows it to absorb only uv light. P-type doping of ZnO has attracted great attentions, because of its potential application for next-generation short-wavelength optoelectronic devices. Like many other transparent metal oxides, p-type doping of ZnO is difficult. Among group IB elements those known as ideal candidate for p-type ZnO doping, Cu is the best choice to convert n-type to p-type ZnO, because substitutional Cu behave as an acceptor. Among several methods, electrochemical deposition (ECD) has been reported an appropriate technique for Cu-doped ZnO preparation, owing to its low cost, simplicity, low temperature process, controlling size and shape and p-type doping[1].

In this study, we have electrodeposited Cu-doped ZnO nanorods (NRs) on FTO. The effect of Cu doping on structure, optical and electrical properties of ZnO investigated.

Experimental

ZnO NRs were electrodeposited potentiostatically at -1 V vs. Ag/AgCl in three-electrode system, for 60 min at 80 ºC. After electrodeposition, prepared samples were annealed at 300 ºC for 30 min in the air atmosphere. The undoped and Cu doped ZnO NRs were electrodosited from aqueous solution containing 1 mM $Zn(NO_3)_2.6H_2O$, 1 mM hexamethylenetetramine, 0.1 M $NaNO_3$ and 0-1.5 µM $CuSO_4$.

Results and discussion

Fig. 1 shows XRD patterns of pure and Cu-doped ZnO prepared at different Cu doping concentration (0.5, 1 and 1.5 %). The observed patterns reveal a hexagonal wurtzite phase in agreement with JCPDS card no. 36-1451. All of the samples shows the strong (002) peaks, indicating preferential growth along c-axis. In addition to decrease in intensity, the position of the (002) peak shifted slightly to higher angles as Cu contents in ZnO:Cu increased, which is attributed to the substitution of Zn^{2+} ions by the smaller Cu^{2+} ions and changes in the atomic environment due to the extrinsic doping of ZnO.

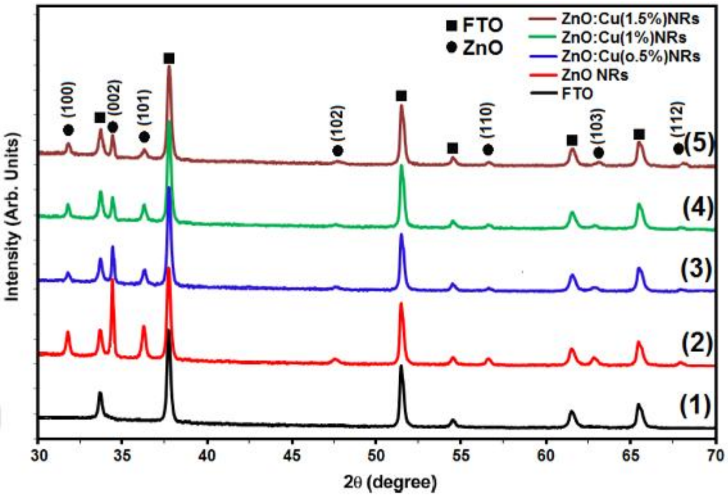

Fig. 1. XRD patterns of ZnO:Cu NRs for different Cu concentration: 0, 0.5, 1, and 1.5 %

Uv-vis absorption spectroscopy shows the optical band gap of un-doped ZnO NRs is 3.41 eV, while this value decreased to 3.21 eV, 3.10 eV and 3.04 eV when dopant concentration was 0.5 %, 1 % and 1.5 %, respectively.

Mott-Schottky analysis indicates the undoped ZnO NRs conductivity is n-type, however by doping with Cu ions, conductivity convert to p-type.

Conclusion

In summary, the influence of Cu doping in ZnO NRs was investigated. XRD patterns showed the substitution of Cu^{2+} in ZnO NRs. Uv-vis spectra revealed the optical band gap decreased by Cu doping. Also Mott-Schottky analysis indicate the conversion of n-type to p-type semiconductor by Cu doping.

Key words**:** *ZnO nanorods, Cu doping, Mott-Schottky analysis, Optical band gap*

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Electrochemical Synthesis of Poly (o-phenetidine) coating on 304 Stainless Steel and Investigation of Their Corrosion Inhibition Properties in HCl Medium

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Abstract

Corrosion control of metals is an important issue of technical, economical, environmental and aesthetical importance. A number of methods for the protection of metals against corrosion are known, but looking for new method of corrosion control continues to be subject of intensive research [1]. Among them, using of organic coating is a great way to protect metal from corrosion, especially if the coating also has good mechanical properties. Electrodeposit of conductive polymer on the surface of an electrode is a very wide research in electrochemistry during the last decades [2].

In this research, homogeneous and adherent poly(o-phenetidine) coatings were electrosynthesized on 304 stainless steel by using the chronopotentiometery under galvanostatic conditions method. These coatings in current densities viz. 0.5, 1.5, 2 and 2.5 mA.cm^{-2} for duration of time of 100 s were tested. The deposition times viz. 50, 70, 100 and 150 s were applied for the current density of 1.5 mA.cm^{-2} and the corresponding potential transients were recorded. The synthesized coatings were characterized by Fourier transform infrared spectroscopy (FT-IR), UV-Vis spectroscopy and SEM.

The corrosion inhibitions of coatings were investigated in 0.1M HCl solution by the polarization technique and electrochemical impedance spectroscopy (EIS). The obtained results show that the corrosion current decreases significantly from 3.7759 µA.cm^{-2} for blank electrode to 0.4101 µA.cm^{-2} for poly(o-phenetidine)-coated 304 stainless steel, under optimal conditions.

Keywords: *Electropolymerization, EIS, 304 Stainless Steel, Poly(o-phenetidine), Corrosion*

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One-Step Electrochemical Synthesis of Polypyrrole-Graphene Nanocomposite Film on the Copper and Its Corrosion Protection Performance

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Abstract

Electropolymerized polymer coatings on copper can replace for the carcinogenic chromate coating [1]. In this work, the corrosion protection ability of electropolymerized polypyrrole-graphene (Ppy-G) nanocomposite coating on has investigated by using the cyclic voltammetry method [2]. The synthesized coatings were characterized by Fourier Transform Infrared Spectroscopy (FT-IR), UV-visible absorption spectrometry and Scanning Electron Microscopy (SEM). The anticorrosion performances of nanocomposite coatings were investigated in 5000 ppm NaCl solution by the potentiodynamic polarization technique and electrochemical impedance spectroscopy (EIS). Corrosion protection is often afforded by isolating the metal from the corrosive environment by using polymer coatings. The current corrosion decreases significantly from 3.3 μAcm^{-2} for uncoated copper to 0.095 μAcm^{-2} for Ppy-G nanocomposite coated copper. The corrosion rate of the nanocomposite coated copper is found to be 7.08×10^{-4} $mmyear^{-1}$, which is ~50 times lower than that observed for bare copper. The potential corrosion increases from -0.84 V versus Ag/AgCl for uncoated copper to -0.78V versus Ag/AgCl for nanocomposite coated copper electrode. The positive shift (anodic protection) of ~0.06V in potential corrosion indicates the protection of the copper surface by the Ppy-G nanocomposite coatings. The EIS results are in good agreement with the potentiodynamic polarization measurements. This study demonstrates that Ppy-G nanocomposite has excellent corrosion protection properties and can be consider a potential coating material for the corrosion protection of copper in aqueous 5000 ppm NaCl.

Keywords: Copper, Polypyrrole-graphene, Electrochemical Synthesis, Corrosion

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Sn/Co electrodeposition on Ni substrate as anode and its application in Lithium ion batteries

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Abstract

Sn/Co nano - particles were synthesized in an electrochemical bath containing $Na_4P_2O_7$ and glycine as complexing agents in order to control the rate of Sn/Co electrodeposition on Ni collector electrode. The electrochemical bath containing $Na_4P_2O_7$ and glycine concentration of about 500 and 250 $mmol.lit^{-1}$ has the best condition resulting in the best discharge capacity and cycleability as two main criteria in lithium ion batteries[1]. Also, the pulsed current characteristics such as frequency and density were investigated and 100 Hz and 150 $mA.cm^{-2}$ respectively, were obtained as the optimum parameters. Discharge capacity of synthesized Sn/Co nano particles was obtained about 720 $mA.h.g^{-1}$ indicating about 35% increase compared to the synthesized Sn/Co particles with constant current electrodeposition method. Also, the obtained discharge capacity of was 550 $mA.h.g^{-1}$ in 20th cycle which showed an appropriate cycleability compared to the Sn/Co film electrode prepared by a constant current electrodeposition. The particles size of coated Sn/Co on collector electrode is resulted from an interplay between the rate of nucleation and growing rate of particles[2].

Keywords*: *pulsed current electrodeposition, cycleability, Sn/Co nano particles, complexing agent, discharge capacity

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Investigation of Electrochemical Behavior of Alizarin yellow GG on glassy carbon electrode

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Abstract

In the present work, the electrochemical behavior of Alizarin Yellow GG was investigated on glassy carbon electrode. Cyclic voltammetry studies showed that the reduction mechanism of azo group (N=N) in Alizarin Yellow GG in acidic media is different from alkaline media. In an Acidic media, the azo group is reduced in a $2e^{-}/2H+$ process through hydrazo intermediate with an ECE mechanism. In an alkaline media as the acidic media, the azo group was reduced by a $2e^{-}/2H+$ process and the hydroazo intermediate is produced. However, the hydroazo intermediate was not protonated in alkaline medium; this means that it is stable and azo bond was not broken and in the reverse sweep, it was oxidized and again produces Alizarin Yellow GG (E mechanism).

Keywords: *Alizarin yellow GG, Electrochemical behavior determination, Cyclic voltammetry, Glassy carbon electrode*

Introduction

Alizarin yellow GG (AYGG), [5-(3 – nitrophenylazo)- 2 – hydroxybenzoic acid sodium salt] is an Azo dye and an acid-base indicator. Azo dyes are characterized by chromophoric azo group. The azo aromatic compounds are important in industrial processes such as textile processing, paper, food, cosmetics medicine, leather, plastics, varnish, and automobile. Generally, the azo dyes are electrochemically active, both in the reduction and in oxidation potential region [1]. Many azo dyes were studied by polarography and by cyclic voltammetry [2], but no report is available for the electrochemical study of AYGG. As a part of our continuing effort to understand the mechanism of electro reduction/oxidation of various molecules [3], the results of the electrochemical investigation on the AYGG is being presented here.

Experimental

Electrochemical experiments were performed using AUTOLAB PGSTAT 30 electrochemical analysis system. A three-electrode system was used that consists of GCE, a saturated calomel electrode as reference electrode and platinum wire as auxiliary electrode. CV studies were done in 0.1 M phosphate buffer solution with different pH values and 0.2 M sodium perchlorate as a supporting electrolyte in the potential range of 0.8 to -0.8 V.

Results and discussion

CVs for two sequential scans for 5 mM solution of AYGG have been presented in Fig. 1A. As it was seen for first scan, two peaks were observed (E_{P1} = -0.527, E_{P2} = 0.251 V) while in the second scan a new peak was produced (E_{P3} = 0.266 V) and the height of P_1 was reduced while the P_2 was remained unchanged. These observations show that P_1 is related to an irreversible process while P_2 and P_3 are related to a reversible process. Further investigations with limiting the operating potential window to 0 to 0.8 and 0 to -0.8 and 0.7 to -0.8 confirmed that P_2 and P_3 related to each other and they are resulted from reduction products of P_1. In acidic media, the P_1 was attributed to the reduction of –N=N- bon to –NH-NH-. Because of reduction, AYGG was converted to hydrazo intermediate, and then it was protonated and converted to 5-amino salicylic acid (5-ASA) and meta-nitro aniline. The P_2 and P_3 peaks were attributed to reversible oxidation/reduction of 5-ASA. For confirmation of this, the redox behavior of 5-ASA was investigated in the presence of AYGG. As it was shown in Fig. 1B, by adding of 5-ASA (5 mM) to electrochemical cell containing 5 mM AYGG, the heights of peaks P_2 and P_3 were increased that shows they are related to redox behavior of 5-ASA and resulted from electro reduction of azo group.

Investigation of the effect of scan rate on CVs of AYGG, showed that at low scan rates, the P_3 peak was not observed which shows the product of oxidation of P_2 incorporate in chemical reaction. These observations are in good agreement with previous reports in which 5-ASA is converting to Quinone-Imine (QI) with $2e^-/2H^+$ mechanism following by hydrolyzing of QI and its conversion to non-electroactive Quinone. Thus, the electro oxidation of AYGG in acidic media is described by a $2e^-/2H^+$ EC mechanism.

The investigation of the effect of pH on electrochemical behavior of AYGG showed that with increasing of pH from 4.5 to 7, the heights of P_2 and P_3 were reduced and at higher pH values than 7 (Fig. 2), the P_2 and P_3 were diminished and a new peak, P_5 was observed at more negative potential. With increasing of pH the height of P_5 was increased which shows in alkaline media, the hydrazo intermediate is stable and was oxidized to AYGG.

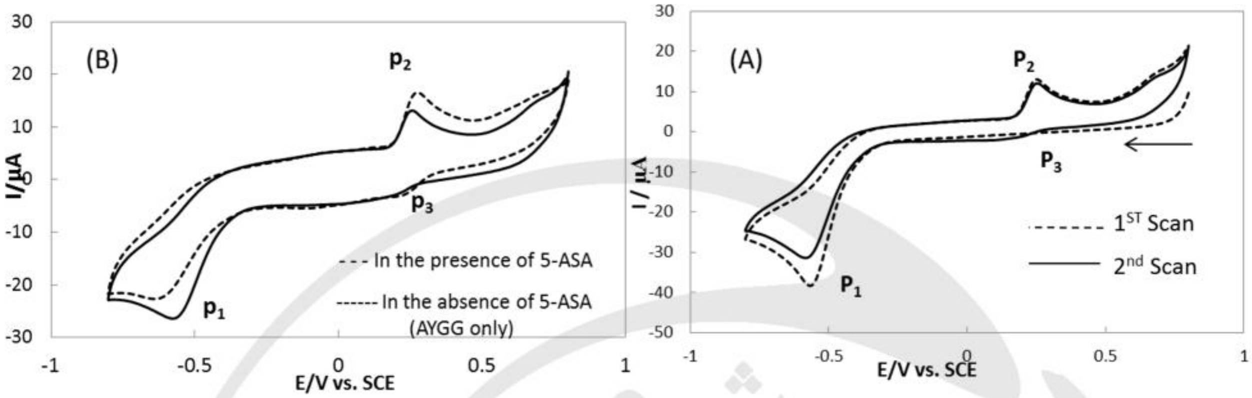

Fig. 1 CVs for (A) sequential scan rates for 5 mM of AYGG and (B) effect of addition of 5-ASA on CV of AYGG.

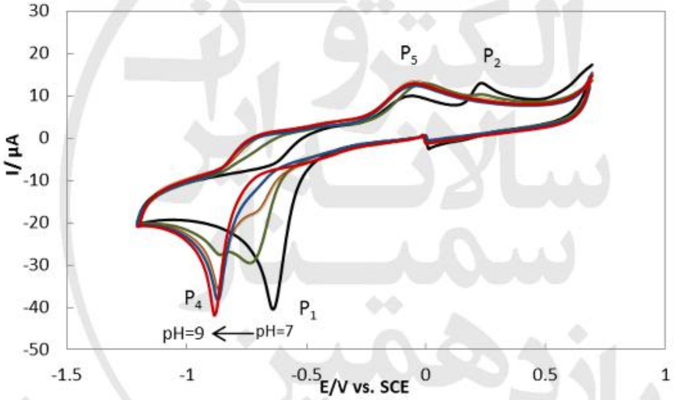

Fig. 2 CVs for 5 mM of AYGG for pH values of 7 to 9.

Conclusion

Electrochemical behavior of AYGG, AS a azo dye was investigated using CV technique and a mechanism was introduced.

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Electrochemical oxidation of some dihydroxybenzoic acid derivatives in the presence of various nucleophiles: Experimental and theoretical analysis

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Abstract

In this work, mechanistic study of the electrochemical oxidation of 2,5-dihydroxybenzoic acid (2,5-DHBA) and 2,3-dihydroxybenzoic acid (2,3-DHBA) in the presence of various nucleophiles have been investigated both experimentally and theoretically. The study was done by the use of cyclic voltammetry, controlled-potential coulometry and Density Functional Theory (DFT) from the perspective of thermodynamic. The theoretical results were calculated at DFT (B3LYP and BP86) levels of theory and 6-311+G (p,d) basis set. Results showed that two-electron oxidation of studied species is followed by a Michael addition reaction of nucleophiles and new dihydroxybenzoic acids are produced (1,2). Considering several mechanisms indicates that electrochemical oxidation potentials (E_p) of studied species are directly dependent on the ΔG_tot of electrochemical oxidation. It was found that the products which are produced on the surface of electrode, depending on their ΔG_tot of the electrochemical oxidation, will participate in the electrochemical or chemical following reactions (3).

Keywords: *Cyclic voltammetry, Controlled potential coulometry, Density Functional Theory (DFT), Total Change of Gibbs free energy (ΔG_{tot}).*

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Electrochemical study of micellization of Ester-Containing Gemini Surfactants in Water-Ethylene glycol system

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Abstract

Cyclic voltammetry has been used efficiently to investigate the phase transition observed at the studied concentration range. CV measurements were done to determine the diffusion coefficients of aggregates and the interparticle interaction parameters. The mean diameters of aggregates obtained by CV can be obtained by alternative methods such as DLS and TEM as well. The mean diameter of gemini surfactant aggregates obtained from DLS indicated that large aggregates changed to small micelles as indicated by CV measurement as a dramatic decrease in self diffusion coefficient. The interparticle interactions were assessed in terms of Water-Ethylene glycol as solvent effects on the micellar surface charge density, the morphology changes, and the phase transition[1] . Since the EG additive affects both micellar properties and dielectric constant, the overall effect is obtained from the resultant effect of these effects. As indicated by CV study, the dielectric constant is negligible while the effect of EG on micellar properties is significant since it results in a phase transition, from giant vesicular particles to partly smaller aggregates, and increase the diffusion coefficient consequently[1, 2].

Keywords: *cyclic voltammetry, diffusion coefficient, interparticle interaction parameter, Gemini surfactants, aggregates*

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Efficient Factors on the Hydrolysis Reaction Rate of Some P*ara*-diamines Derivatives: Experimental and Theoretical Studies

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Abstract

Electrochemical oxidation of some *para*-diamines derivatives (*N*,*N*-diethyl-*p*-phenylenediamine (**1**), 4-morpholinoaniline (**2**) and 2,5-diethoxy 4-morpholinoaniline (**3**)) in acidic solution has been investigated both experimentally and theoretically to provide insight into the influence of some factors on the hydrolysis reaction rate. Despite structural similarity of studied species there is a significant difference in the rate of hydrolysis. The result of this work shows that the electrogenerated *p*-quinonediimines (**1Hox^{2+}**, **2Hox^{2+}** and **3Hox^{2+}**) participate in the hydrolysis reaction and are converted to their *p*-benzoquinones (**2d** and **3c**). The hydrolysis reaction rate strongly depends on the structure of the *p*-quinonedimines. The effect of charge of reaction site (C_1 and C_4) and $N{=}C$ bond orders (Wiberg Bond Indices, WBIs) on the hydrolysis rate were studied. All calculations were performed using Density Functional Theory (DFT) B3LYP level of theory and 6-311+G (p,d) basis set.

Keywords**:** Cyclic voltammetry; *Para*-quinonediimines; Hydrolysis; *Para*-benzoquinone; Density Functional Theory (DFT).

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Electrochemical oxidation of Naphthalene-2,3-diol at various condition: Experimental and theoretical investigation

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Abstract

Electrochemical oxidation of Naphthalene-2,3-diol (**1**) has been studied in aqueous and nonaqueous solution by the use of cyclic voltammetry, differential pulse voltammetry and chronoamprometry. Recorded cyclic voltammograms (CVs) at various pHs (pH=1-8) show that **1** oxidized to its corresponding *o*-benzoquinone derivative (**1ox**) and the electrode reaction is a two-electron, two-proton process (1,2). Irreversible CVs indicates that produced *o*-benzoquinone (**1ox**) is unstable and participates to a following chemical reaction. The effect of different parameters such as pH, Naphthalene-2,3-diol (**1**) concentration and time window of chosen electrochemical method on the following chemical reaction has been discussed. In order to prove of two-electron, two-proton both electrochemical and computational study were performed (3). Also the value of diffusion coefficient of **1** was determined by the use of Cottrell plots by chronoamperometry.

Keywords*: *Cyclic voltammetry; Chronoamprometry; ortho-benzoquinone; Density Functional Theory (DFT).

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Electrochemical deposition of Cu_2ZnSnS_4 as a thin film solar cells absorption layer

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Introduction

According to the special place of thin film solar cells among the second generation solar cells, many studies have done on thin film solar cells. In this study, our intention is to provide the CZTS solar cells. The CZTS has low band gap, very low cost compared to the other thin film solar cells, direct band gap semiconductor material with a high absorption coefficient and a multilayer structure. The vacuum coatings[1] have been successfully employed in the CZTS thin film solar cells. Since the synthesis of CZTS thin films by vacuum coatings methods is hard because of its compound, we follow those by electrodepositions method[2].

Methods

We synthesis of CZTS thin films by electrochemical deposition because of its controllability and repeatability. In the first step, CZTS thin film was prepared from aqueous electrolytic containing $CuCl_2$ 0.1 M, $ZnCl_2$ 0.1 M, $SnCl_4$ 0.1 M. and $SeCl_2$ 0.1 M, in a conventional three-electrode electrochemical cell assembly under different temperatures and pH. The electrochemical cell contains a saturated solution of Ag/AgCl as a reference electrode, a graphite electrode as an inert counter electrode and stainless steel substrate (1×1 cm^2) was used as the working electrode.

Result and discussion

The effect of pH and temperature treatment on the structural, morphological and compositional of the CZTS thin films was investigated. The cyclic voltammetry (CV) and chronoamperometry curves show the best uniform film has been reached by pH=1.5 because of complexing agents (Fig. 1.a and d). In the next level, it was investigated the effect of temperature treatment in pH=1.5. The cyclic voltammetry and chronoamperometry curves show that co-electrodeposition was improved in high temperature. In low temperature, the higher current density was applied because of low conductivity of solution. On the other hand, when the temperature is increasing, it does not require high current (Fig. 1. c and b).

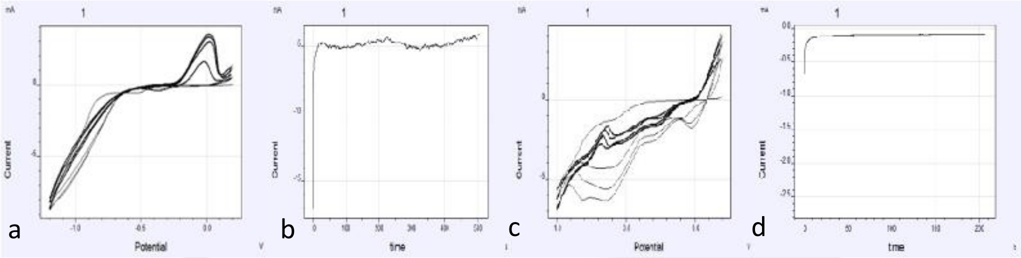

Fig. 1. Cyclic voltammograms (a and c) and chronoamperometry curves (b and d), a, PH=1.5 b, T= 80℃. C, T= 80℃.d, PH=1.5.

Conclusion

Totally, we have successfully synthesized Cu_2ZnSnS_4 (CZTS) thin films using electrodeposition method followed by different temperature and pH. It was founded that the best structure of film has been obtained in pH=1.5 and T=80℃. It is concluded that electrodeposition method is the cost effective and comfortable way to synthesize absorber layer of thin film solar cells.

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***Keywords**: Thin film solar cells; CZTS solar cell; Electrochemicaldeposition; Absorption layer.*

Silver salts effects on the TiO_2 Photoanodes in the Water splitting system under visible irradiations

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Abstract

The photocatalytic splitting of water into H_2 and O_2 has attracted considerable attention because the process presents an avenue for direct generation of an energy carrier that is easily stored and transformed into electric energy. [1]

In this paper different silver salts were deposited on a conducting support of TiO_2/ FTO electrodes through the deposition-precipitation method and have been used as visible light induced photoanode in water splitting reaction. PhotoElectrochemical measurements such as Current-Voltage and Chronoamperometry diagrams demonstrated that the Silver salts loading enhanced the visible spectral absorption of TiO_2 and consequently a higher O_2 and H_2 production, were observed.

Via some characterization techniques such as XRD, EDX and SEM, it is obvious that the thin layer of silver salts are nanostructured materials. Plus, it is obvious that the light sensitivity in the visible part of the spectrum for the prepared photoanodes is due to self-sensitization caused by reduced silver species. [2]

Keywords**:** *Silver salts, TiO_2, Photoanode, Photoelectrochemical measurements, Visible light spectrum, Water splitting*

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Electrochemical oxidation of acetaminophen in the presence of diclofenac

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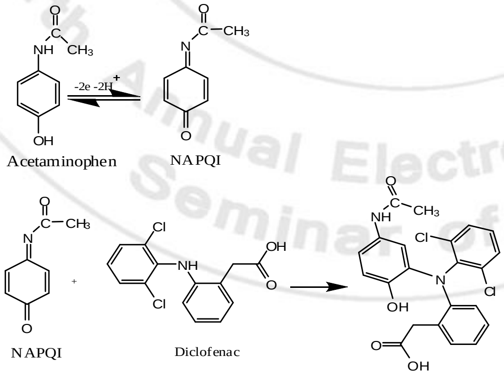
Abstract

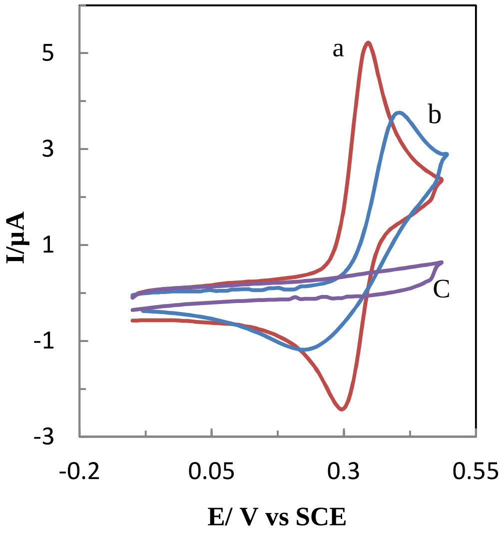
Electrochemical oxidation of acetaminophen has been studied in the presence of diclofenac in aqueous solutions, using cyclic voltammetry and controlled-potential coulometry [1]. Obtained results indicate that the *N*-acetyl-p-benzoquinone-imine (NAPQI) derived from acetaminophen participate in Michael addition reactions with diclofenac and via EC reaction mechanism convert to the corresponding product (scheme 1). In this work, we derive product with good yields based on electrochemical oxidation under controlled potential conditions in aqueous solutions, without toxic reagents and solvents at a carbon electrode in an undivided cell, using an environmentally friendly method [2,3].

Furthermore, based on an EC mechanism, the homogeneous rate constant of the chemical reaction interposed between electron transfer were estimated by comparing the experimental cyclic voltammetric responses with the digital simulated results.

Keywords: *Acetaminophen, Diclofenac, Cyclic voltammetry, Digital simulation, EC mechanism.*



Scheme 1



Cyclic voltammogram of 0.5 mM acetaminophen: a) in the absence, b) in the presence of 1.0 mM diclofenac at glassy carbon electrod, in phosphate buffer solution (pH 7.0, 0.2 M). Scan rate: 25 mV/s, T: 25±1°C

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Voltammetric sensor for determination of *N*-acetylcysteine based on electrochemical oxidation of 4,4' biphenol as a mediator

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Abstract

The electro-catalytic oxidation of *N*-acetylcysteine has been studied in presence 4,4'-biphenol, using cyclic voltammetry as a diagnostic technique. Cyclic voltammetry (CV) technique was used to investigate the suitability of incorporation of 4,4'-biphenol/4,4'-diphenoquinone redox as a mediator [1] for the electrocatalytic oxidation of *N*-acetylcysteine in buffered aqueous solution(Phosphate buffer, pH:7).

In this work, we described redox couple (4, 4'-biphenol and 4,4'-diphenoquinone) can be used as a suitable mediator for determination of *N*-acetylcysteine concentration based on the catalytic current (curve b in fig. 1).

The dependence of peak currents on pH, concentration and the potential scan rate was investigated. Under the optimum conditions the peak current was linear to the concentration of *N*-acetylcysteine in the range 50-500 μM in the cyclic voltammetry. The detection limits were determined as 8.3 μM by CV method. The diffusion coefficient of *N*-acetylcysteine and the catalytic rate constant of the reaction of 4,4'-diphenoquinone with *N*-acetylcysteine based on an EC' mechanism, was estimated using digital simulation method by comparing the experimental cyclic voltammetric responses with the calculated results. [2-3]

Finally, the electrocatalytic oxidation of *N*-acetylcysteine by 4, 4'-diphenoquinone can be employed as a new method for the voltammetric determination of *N*-acetylcysteine plasma samples.

Keywords: *N-acetylcysteine, Catalytic current, 4, 4'-biphenol, Cyclic voltammetry, Digital simulation, EC' mechanism.*

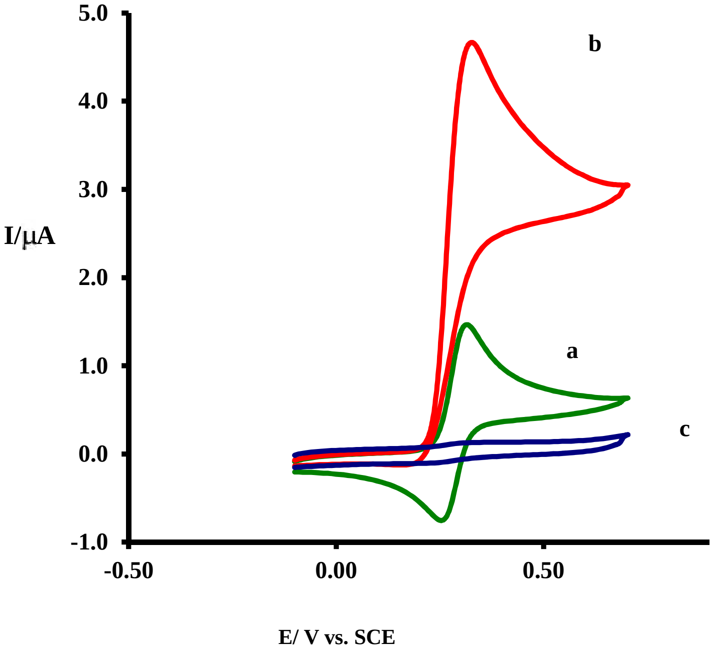

Fig1: Cyclic voltammogram of 1mM 4,4' biphenol: (a) in the absence and (b) presence of 0.2 mM *N*-acetylcysteine. (c) Cyclic voltammogram of 1 mM *N*-acetylcysteine in the absence of 4,4' biphenol, at glassy carbon electrode, in phosphate buffer solution (pH 7.0, 0.2 M). Scan rate: 10mV/s, T: 25±1°C

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Electrodeposition of Cu_2O nanoflower on the surface of FTO; Cu_2O/FTO application in hydrodynamic amperometric determination of glucose

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Abstract

Diabetes is a chronic disease causing metabolic and systemic disorders. With more than 220 million people affected, diabetes has become one of the major health afflictions worldwide, and the number of diabetes patients is expected to double in 20 years (1). Therefore, it is of significant importance to develop fast, accurate and stable technologies to detect glucose levels, both in vivo and in vitro, not only in blood but also in other sources such as foods and pharmaceuticals. There has been several efforts to fabricate nanosensors for determination of glucose using metals/metal oxides such as Cu, Ag, Pt, Cu_2O, ZnO, RuO_2, MnO_2, and TiO_2 using various fabrication techniques including sol–gel, electrodeposition and self-assembly (2). In this study, nanoflowers of Cu_2O was electrodeposited on the surface of FTO substrate. The as-prepared Cu_2O/FTO electrode was used as working electrode for hydrodynamic amperometric determination of glucose. The fabrication conditions of Cu_2O/FTO nanoflowers and determination conditions of glucose were optimized.

Fabrication of Cu_2O/FTO. Cu crystals were electrodeposited on FTO in a solution containing 0.05 M $CuSO_4$ and 0.3 M lactic acid in a typical electrochemical cell equipped with a Pt wire counter electrode and Ag|AgCl|KCl (3 M) as reference electrode. The electrodeposition was carried out with a rectangular potential pulsed mode at a potential of -2.0 V for 0.2 s, and then a potential of 0.0 V for 1 s, with various numbers pulses (10 to 150 pulses). The Cu-loaded FTO were then potentiostatically anodized in NaOH electrolyte at -0.2 V for 30 min at 25°C to fabricate Cu_2O nanoflowers on FTO (3).

Characterization of Cu_2O/FTO surface morphology. The as-prepared electrodes surface morphologies was characterize with SEM images. In the Fig. 1, the SEM images of the electrodes were presented before (a) and after (b) anodization at -0.2 V in the NaOH solution. From this Figure, the fine structure of nanoflowers was seen after anodization of electrode surfaces.

Optimization of Cu_2O/FTO electrodeposition condition. The numbers of pulses (10 to 150), NaOH concentration (0.05 to 0.5 M), anodization time (5 to 60 min), adding of SDS surfactant (0 to 0.1 M) were effective factors, so this parameters were optimized and respectively 100 pulses, 0.1 M, 30 min and 0 were optimized.

Optimization of glucose determination condition. After optimization of electrode fabrication conditions, the effective parameters in hydrodynamic amperometric determination such as applied potential, NaOH concentration were optimized and the 0.6 V applied potential and 0.2 M NaOH were used as optimized condition.

Finally, the hydrodynamic determination of glucose was performed in the optimized condition. The obtained results showed that linear dynamic range of determination was 1-4 mM and limit of detection of glucose was about 1.4×10^{-6} M.

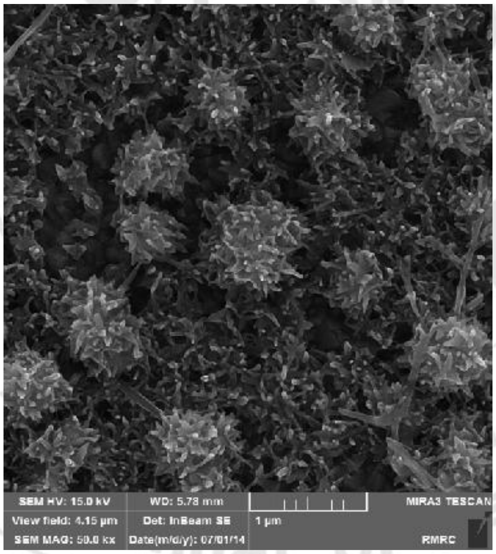

Fig. 1 SEM image of Cu_2O/FTO

Keywords: *Electrodeposition, Cu_2O/FTO, Glucose, Hydrodynamic determination, Nanoflowers*

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The Influence of Applying Constant Potential on the Optical Properties of Nickel Oxide Thin Films Deposited by Electrodeposition

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1. Introduction

Nickel oxide (NiO) is a stable wide band gap material and can be used as a transparent p-type semiconducting layer, which has many applications in optical industrials [1]. In this paper, we have studied the influence of applying constant potential on the optical properties of NiO thin films deposited by electrodepesition on fluorine tin oxide (FTO)-glass for use in optical filters.

Keywords: *Nickel Oxide, Electrodeposition, Optical Properties*

2. Methods

A transparent FTO coated glass was used as a substrate with sheet resistant of 20-30 Ω/cm^2. Before deposition, the FTO substrate was cleaned for better films adhesion [2]. Then, nickel oxide thin films were electrochemically deposited onto FTO coated glass substrate using chronoamperometric (potentiostatic) technique. Electrodeposition of NiO films was carried out using a three-electrode (PGS 2063+) with FTO-glass as working electrode, a platinum foil as a counter electrode and saturated calomel electrode (SCE) as reference electrode. The films were deposited from bath solution containing 0.1 M nickel sulphate ($NiSO_4.6H_2O$), 0.1 M sodium acetate (CH_3COONa) and 0.1 M sodium sulphate (Na_2SO_4) at PH 6.8 and deposition temperature of 50°C for 300 s with using different applying constant potential versus SCE (i.e. 0.9 V, 1.1 V, 1.3 V, 1.5 V, 1.7 V, 1.9 V).

3. Results and Discussion

Optical spectra were obtained on a spectrophotometer (Shimadzu (UV-1800)) at room temperature. Fig. 1 shows the (a) transmittance spectra, (b) absorbance spectra and (c) reflectance spectra of NiO films on FTO-glass for different applying potential. The results shows as the applying constant potential increases, the transparency decreases and absorption increases. The absorption in UV-Vis region is attributed to absorption in NiO band gap [1]. It is known that the correlation between absorption coefficient and optical band gap E_g

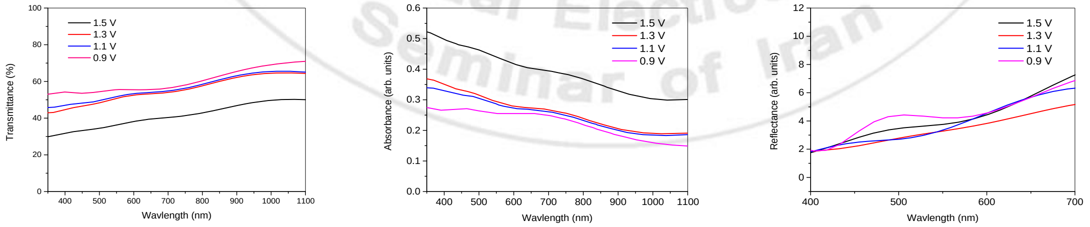

Fig. 1: (a) the transmittance spectra, (b) the absorbance spectra, (c) reflectance spectra of NiO films on FTO-glass for different applying potential.

can be determined by the equation $(\alpha h\upsilon)^n = A(h\upsilon-E_g)$ [3]. Hence, the optical band gap for the absorption peak can be obtained by extrapolating the linear portion of the plot of $(\alpha h\upsilon)^n$ versus hυ to $\alpha = 0$.

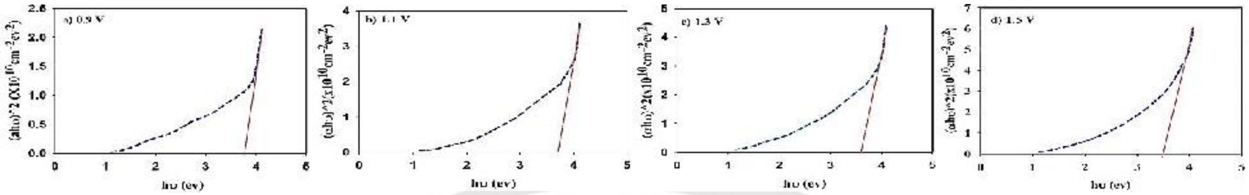

Fig. 2: $(\alpha h\nu)^2$-hν curves of NiO layers deposited on FTO-glass for a) 0.9 V, b) 1.1 V, c) 1.3 V, d)1.5 V

Fig. 2 shows $(\alpha h\upsilon)^2$ versus hυ plots for the sample on different potential applying. For all samples, the optical absorption in the edge region can be well fit by the relation $(\alpha h\upsilon)^2 \sim h\upsilon - E_g$, which shows that NiO films deposited on FTO-glass have the direct band gap. The band gap of NiO films deposited on FTO-glass for each constant applying potentials at 0.9 V, 1.1V, 1.3V, 1.5V are 3.75 eV, 3.68 eV, 3.62 eV, 3.49 eV, respectively. The obtained results are similar to the value (3.55 eV) reported by Boschloo and Hagfeldt [4]. As it is clear from the optical band edge results, by increasing the applied potential an obvious red shift occurs. There are many reports concerned with quantum size effects in low dimensional semiconductor system. It is well known that the semiconductor nanoparticle energy gap decreases with increasing the grain size, which leads to a red shift of the optical absorption edge and have been observed in many semiconductor nanoparticle systems [3]. It is a probable reason for the absence of red shift. However, the optical properties of a semiconductor can also be modified by mechanisms other than the quantum size effect. For example, the NiO films can interact with surrounding walls of the FTO-glass and this interaction can also alter the optical properties.

4. Conclusions

Deposited NiO film on FTO-glass were prepared by using an electrochemical deposition method. The optical absorption band gap of NiO films for constant applying potential 0.9 V, 1.1V, 1.3V, 1.5V were measured 3.75 eV, 3.68 eV, 3.62 eV, 3.49 eV, and red shift of the optical band edge was observed; With increases applying constant potential, the transparency decreases and absorption increases. The Sample related to 1.5 V showed more absorption and The Sample related to 0.9 V showed more transparency.

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PdNi electrocatalysts with enhanced catalytic activity for oxygen reduction in acid media

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Abstract

Carbon-supported Palladium-Nickel (PdNi) alloyed electrocatalysts with different Pd/Ni atomic ratios was used for oxygen reduction reaction (ORR), in acid media. This bimetallic catalyst was synthesized via the metallic reductive precipitations of the nitrate precursors with Ethylene Glycol (EG). The characterization of the electrocatalysts using X-ray diffraction (XRD) showed bimetallic nanoparticles having a narrow size ranged 5-3 nm with face-centered cubic (fcc) hexagonal structure. Cyclic voltammograms and polarization curves from rotating-disk electrode measurements showed significantly higher activity on PdNi than observed on Pd catalyst, with a mechanism involving four electrons transfer to water formation. The PdNi/C alloy electrocatalysts are inactive for the adsorption and oxidation of methanol. Therefore, bimetallic alloyed Pd-Ni catalysts can act as a promising methanol-tolerant ORR catalyst in a direct methanol fuel cell (DMFC).

Keywords: Palladium-Nickel alloy, electrocatalysts, Oxygen reduction reaction, Acid Media, Direct methanol fuel cell.

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the study of surface fractality composite film poly pyrrol with different surfactants on copper plate with electrochemical technic.

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***Keywords**: copper plate, Fuel cell, surfactant, electropolymerization, fractal*

Introduction

Fuel cells are one of the most promising power sources which among of different types of fuel cells, the proton-exchange membrane fuel cell, PEMFC, has advantages like relatively low operating temperature and water producing as the only byproducts of its overall electrochemical reaction in addition to high energy densities, high efficiencies and fast start-up which are common characteristics of all types of fuel cells [1,2]. copper plates are a multifunctional part of a PEMFC. Metallic copper plates have received considerable attention due to better mechanical properties, good machining, high electrical conductivity, gas impermeability, acceptable material cost, improved manufacturability and applicability to mass production there are several reports on the dependency of morphology and properties of polypyrrol to the electrochemical deposition methods [3]. To achieve different morphology, polypyrrol was electropolymerized on the surface commercial by galvanostatic, potentiostatic and potentiodynamic methods and alo, sodium dodecylsulfate, Dodecyltrimethylammonium bromide (DTAB) and Triton X-100 (TX100) were used in electropolymerization bath as anionic, cationic and nonionic surfactant additives, respectively.

Experimental

A solution of pyrrol and H2SO4 was used as the electrolyte of electrodeposition bath. surfactant using cases, the appropriate amounts of Dodecyltrimethylammonium bromide(DTAB), Sodium dodecyl sulfate(SDS) and triton X-100(TX100). was added to the electrolyte to make a solution of 0.001M of them. A piece of 1 cm*15 cm of was polished with 300 to 900 grit emery papers. A standard three electrodes cell was used for electropolymerization containing of an Ag/AgCl electrode, a platinum grid and the piece as the reference, auxiliary and working electrodes, respectively. The electrochemical studies of the coated were carried out in solution of 0.05M H2SO4 and the above standard three electrodes cell unless the working electrode was the polymer coated Copper. Electrochemical impedance spectroscopy was widely used for determining of series and polymer film resistances and fractal dimensions of PPY films as criteria of surface roughness. The corrosion resistance was found out by polarization curve analysis. The corrosion studies and electropolymerization experiments were executed by a autolab 4.9 Electrochemical interface and Electrochemical impedance spectroscopy studies were carried out by a autolab 4.9.

Results and discussions

Electrochemical impedance spectroscopy was widely used for determining of series and polymer film resistances and fractal dimensions of PPY films as criteria of surface roughness. The corrosion resistance was found out by polarization curve analysis. Potentiodynamic polarization curves, electrochemical impedance spectroscopy and were used for investigating the properties of polypyrrol-coated as copper plate materials for fuel cell.

The polymerisation reaction is very complicated and the mechanism of electropolymerisation is still not fully understood. The generally accepted mechanism is that in the first step the neutral monomer is oxidised to a radical cation followed by aromatisation and oxidation of the dimer during oxidative electropolymerization, which anode has a positive charge Sodium dodecyl sulfate(SDS) micelles extensively are attracted by the electrode because of the electrophoretic interactions and its aniline containing with a higher local concentration can undergo the polymerization process with a lower overpotential. While Dodecyltrimethylammonium bromide(DTAB) micelle goes far away the anode surface and for achieving to the repulsion between the micelle and electrode surface and undergoing the pyrrol containing of the micelle into the reaction, a higher over potential should apply. Finally, uncharged Triton X-100 (TX100) micelle does not influence by electrical field and therefore the same behavior will be observed for both chronoamprograms of individually aniline and pyrrol + Triton X-100 (TX100) solutions.

hematiccopperly behavior a(an anionic and b) a cationic surfactant during electropolymerization

The potentiodynamic polarization curves for all samples comparing with bare in contact with a 0.05M H_2SO_4 solution are depicted in figure. Corrosion parameters like i corr , E corr and Tafel slops obtained by Tafel extrapolation method, which was taken place using Corrware software.

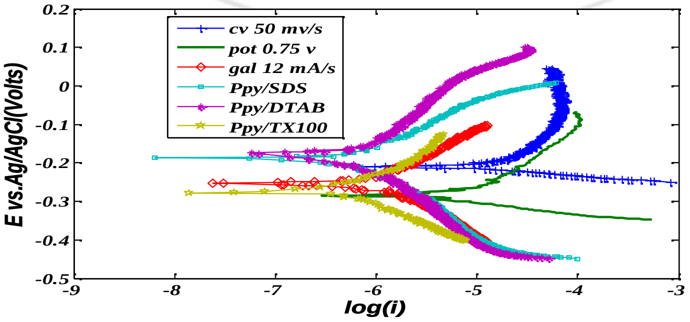

Fig. Potentiodynamic polarization curves of uncoated and PPY-coated electropolymerized in different conditions in 0.05M H_2SO_4 solution

was calculated and fractal dimension as criterion of surface roughness was determined for all PPY films. Comparing of fractal dimension values shows that by using surfactants during electropolymerization fractal dimension causes an enhancement in fractal dimension and consequently formation a smoother PPY film.On the other words, in surfactant cases an impact PPY film is produced. Among of surfactants which have been used in this work, Sodium dodecyl sulfate (SDS) make a more compact film compared to Dodecyltrimethylammonium bromide(DTAB) and Triton X-100 (TX100). This may relate to adsorption of SD - species on the surface of PPY film and making a more organic media for better penetration of pyrrol molecule to the surface of electrode and also achieving of electrode surface from inside its micelle, a micro reactor with a higher concentration of pyrrol compare to the bulk. also, the surface roughness of PPY which prepared by electrodeposition at constant current density of 15 mA/cm 2 is higher than other samples which prepared by potentiostatic and potentiodynamic methods.

Conclusion

Our studies showed that the properties of electropolymerized PPY -coated depends to its morphology which itself influences by not only the electrochemical method of polymerization but also the type of surfactant added to the electropolymerization bath To achieve different morphology, poly pyrrol (ppy)was electropolymerized on the surface copper by galvanostatic,potentiostatic and potentiodynamic methods and also composite ppy with sodium dodecyle solphate(sds), Dodecyltrimethylammonium bromide(Dtab),and tuition X100(Tx100) were used in electropolymerization bath as anionic, cationic and non ionic surfactant additives, respectively. Potentiodynamic polarization curves show corrosion rate for different plate. Our study for fractal dimension showed that sodium dodecyl solphate (Sds) makes a more compact poly pyrrol (ppy) film with low corrosion rate in the study we calculate fractal dimension for all copper plate with composite ppy and related this quantity with surface roughness and surface fractality.

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Pd-Ni and Pd-Co nanoparticles supported on carbon as an effective catalyst for oxygen reduction

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Abstract

Alloying is a strategy that has been used to find non-Pt electrocatalysts that are effective and less expensive for the oxygen reduction reaction (ORR) [1]. Mixing two or more metals can result in a catalyst that has distinct properties from its monometallic components. For example, it has been found that the addition of metals that bind oxygen strongly (Co, Ni, etc.) can lower oxygen binding to more noble metals (Pt or Pd) and improve their ORR activity [2]. In this work, we investigate the effect of alloy composition in Pd-Ni and Pd-Co nanoparticles on the ORR activity. Nickel (II) chloride ($NiCl_2$), palladium (II) chloride ($PdCl_2$) and sodium borohydride ($NaBH_4$, 99.99%) were purchased from Sigma-Aldrich. Carbon (Vulcan XC-72 R) was provided by the Cabot Corporation. 50 mg of carbon was ultrasonically dispersed in de-ionized water. $PdCl_2$ and $NiCl_2$ (1:1) or $PdCl_2$ and $CoCl_2.6H_2O$ (1:1) was added and the total metal content was 20 wt%. Then 10 mL of $NaBH_4$ solution in excess was added. The solid particles were separated by filtration, washed and dried. The catalyst inks were prepared by mixing 30 mg of catalysts with 2-propanole, de-ionized water and 5wt% nafion solution. After the painting of catalyst inks on the carbon felt, the final electrodes were dried at 120 ^{o}C for 1 h. The electrochemical measurements were carried out using three-electrode compartment. An Ag/AgCl electrode was used as the reference electrode and platinum as the counter electrode. Cyclic voltammetry (CV) was applying a scan rate of 20 mV s^{-1} between 1 and +1 V vs. Ag/AgCl in the O_2 and N_2 saturated NaOH solution. EIS measurements were performed over a frequency range of 100 KHz to 0.01 Hz. The CV plots of Pd-Ni/C and Pd-Co/ C are shown in Fig. 1. The ORR peaks of Pd-Ni/C and Pd-Co/C are achieved at 0.3 and 0 V vs. Ag/AgCl, respectively. In the oxygen saturated solution, the water reduction is happened in more positive potential for both electrodes, in the comparison of nitrogen saturated one. Polarization curves are produced at a scan rate of 1 mV s^{-1} and the kinetic parameters were extracted by the Tafel equation (Fig. 2). The Tafel slopes and current densities of Pd-Ni/C and Pd-Co/C electrodes were 128 and 131 mV/decade and 6.2 × 10^{-3} and 5.6 mA cm^{-2}, respectively. A Tafel slope of 120 mV per decade shows that the first electron transfer is rds. The EIS measurement is done at ORR potentials of electrodes based on CV plots. The charge transfer resistance of Pd-Ni/C and Pd-Co/C electrodes are 8 and 14 Ω cm^2. These results lead us to conclude that Pd-Ni/C alloy catalysts acts more powerful than Pd-Co/C one. According to Volcano plots the ORR activities of Ni particles are higher than Co one. So, by alloying Pd with Ni, the ORR activity is enhanced.

Keywords: Palladium, Alloy, Electrocatalysts, Oxygen reduction reaction

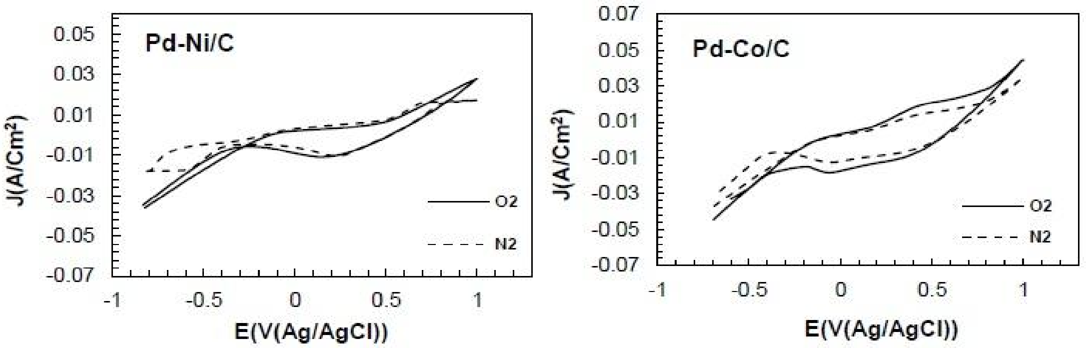

Fig. 1. Cyclic voltammograms of Pd-Ni/C and Pd-Co/C electrodes in O_2 and N_2 saturated 0.1 M NaOH solution with 20 mV s^{-1} scan rate.

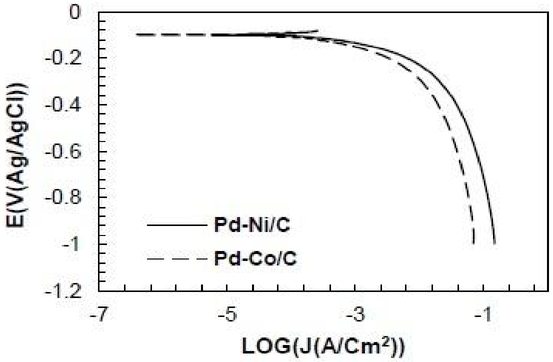

Fig. 2. Tafel polarization curves of Pd-Ni/C and Pd-Co/C electrodes in O_2 saturated 0.1 M NaOH solution with 1 mV s^{-1} sweep rate

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Platinum–manganese oxide as catalysts for DMFC and the importance of order of electrodeposition

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Abstract

Over the past few decades, direct methanol fuel cells (DMFCs) have generated tremendous interest owing to their advantages. However, the successful commercial application of DMFCs is still hindered by several technological challenges, including poor kinetics due to catalyst poisoning [1]. Pt-based electrocatalysts have been suggested with an aim to mitigate such poisoning effect [2]. Among these various promoters, metal oxides are considered as the best due to their low cost [3]. El-Deab et al suggested that novel nanoparticles-based binary catalyst composed of Pt and manganese oxide directly electrodeposited onto GC for the efficient electrooxidation of formic acid[4] and CO[5]. According to our knowledge there is not any research for investigating methanol oxidation on Pt-MnOx which is electrodeposited on carabon paper. In the present study, MnOx has been chosen as a second component in these condition and the influence of the order of electrodeposition of the two species on the electrocatalytic oxidation of methanol is investigated. Carbon paper (Carbon Toray 090) was used as the working electrodes and MnOx and Pt were electrodeposited on it. Electrochemical measurements were performed in a compartment three-electrode using a computer controlled electrochemical analyzer. A Pt electrode and an Ag/AgCl/KCl(sat.) were employed as the counter and reference electrodes, respectively. All potentials in this investigation will be displayed in reference to the Ag/AgCl. All chemicals used in this investigation were of analytical grade (Merck).Four electrodes were prepared by electrodeposition on carbon substrate: MnOx, Pt, Pt on MnOx and MnOx on Pt. For MnOx and Pt on MnOx electrodes, MnOx was electrodeposited onto the carbon paper substrate by anodic electrodeposition in an electrolyte solution of 0.5M H_2SO4 +0.5M $MnSO4.4H_2O$ under potentiostatic condition of 1.15 V for 25 min at 45^0C. For MnOx on Pt, MnOx was electrodeposited under the same condition only for 1 min. For Pt bare and Pt on MnOx, Pt was electrodeposited by cathodic LSV electrodeposition in an electrolyte solution of 0.2M H_2SO4 +2mM $H_2PtCl6.6H2O$ at 5 mV/s between -0.5 and 0. 5V at room temperature.Fig1

(A-D) shows a SEM micrograph of the electrodes and the presence of these particles were characterized by EDS spectrum in Fig 1 (E-G). Fig(2-a) shows CVs measured in 0.1 M H_2SO4. The CVs clearly reveal the characteristic features due to hydrogen adsorption/desorption, double layer charging, oxide formation, and oxide reduction on Pt surface. Although the region of H_2 ads/des is the same for all electrodes but the current densities are different. The presence of MnOx decreases the coverage of Pt, the peaks might be damp (Fig2-MnOx on Pt) but the deposition of Pt on different supports make some changes (Fig1-C-D,F-G) so, the catalytic activities are affected.

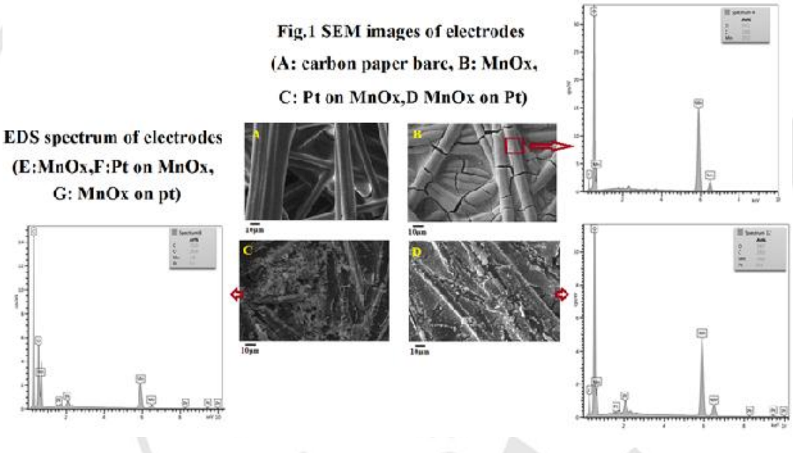

Fig.1 SEM images of electrodes (A: carbon paper bare, B: MnOx, C: Pt on MnOx,D MnOx on Pt)

EDS spectrum of electrodes (E:MnOx,F:Pt on MnOx, G: MnOx on pt)

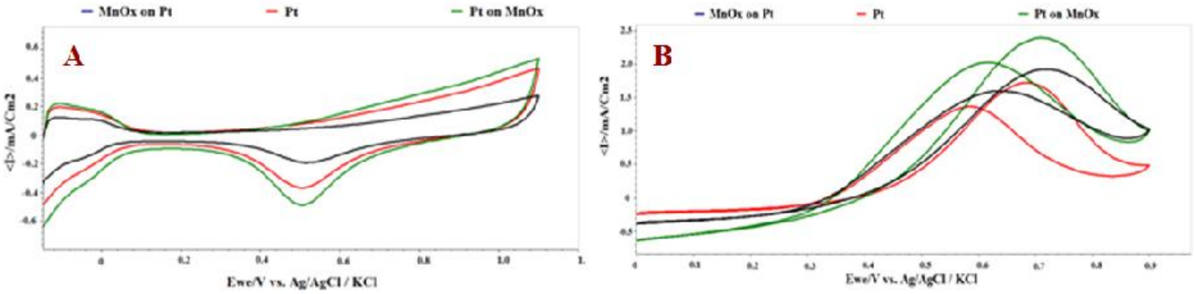

Figure 2-. CVs in 0.1 M H2SO4,B-CVs in 0.5M CH3OH+0.1 M H2SO4 (at a scan rate of 50 mV/s with bubbling nitrogen)

According to Fig.2 double layer capacitance of MnOx on Pt is larger, reflecting that surface area of MnOx/C is larger than carbon paper. So the order of deposition would have an important role in the catalytic activity.The promoting activity of Pt in the presence of MnOx for the methanol electrooxidation reaction was investigated by CVs measurements (Fig2.B). The high peaks with high reactivation current clearly show the promoting activity of MnOx for methanol electrooxidation compare with Pt. Moreover, the onset potential on the Pt on MnOx sample is lower than that for the MnOx on Pt which shows the importance of order of deposition. The

modification of Pt anodes with manganese oxide results in improvement of the activity for methanol electrooxidation. Results show higher promotional activity of the MnOx on Pt in compare with Pt bare. The higher catalytic activity of Pt on MnOx compared to its mirror image reveals that the order of the electrodeposition is an essential parameter.

Keywords: DMFC, Manganese oxide, methanol oxidation, order of electrodeposition

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Multiwalled Carbon Nanotube Supported PtRuPd as a Electrocatalyst for Ethylene glycol oxidation reaction in Fuel Cells

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Abstract

The activity of the Ethylene glycol (EG) oxidation reaction of a multiwalled carbon nanotube (MWCNT)-supported PtRuPd catalyst was investigated by Cyclicvoltammetry, X-ray diffraction (XRD), Scanning Electron Microscope (SEM) and Energy Dispersive Spectrometer (EDS). The PtRuPd nanoparticles with 1:1:1 and 1:2:1 and 1:1:2 atomic ratios (with same morphological structures) were deposited on the MWCNTs .Cyclicvoltammetry results demonstrated that the MWCNT supported PtRuPd(1:1:2) catalyst exhibited a higher mass activity (mA mg-1 of PtRuPd) for the Ethylene glycol oxidation reaction than other ratios.

***Keywords**: Multiwalled Carbon Nanotube ¤Fuel Cells ¤Ethylene glycol*

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Application of Copper (II)-based Metal Organic Framework Synthesized by Electrochemical Method for Oxygen Reduction Reaction

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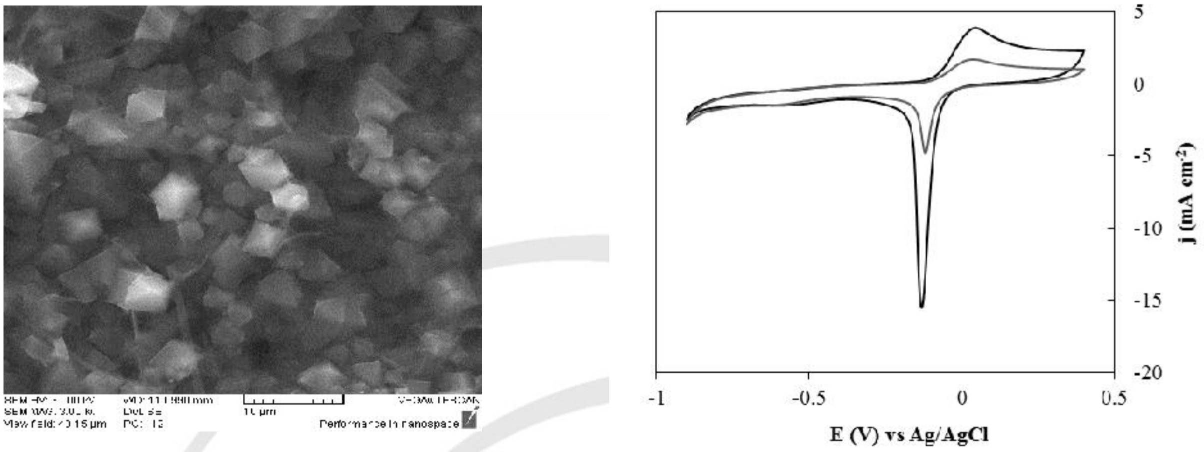
Abstract

Metal–Organic Frameworks (MOFs) attract a lot of attention from the scientist community because of their extremely high porosity and tunable chemical composition. They have applications in gas storage, separation, and catalysis[1,2]. Routine synthesis of MOFs involves solvothermal methods, microwave-assisted, mechanochemical, sonochemical and electrochemical synthesis [3,4]. Among these methods, electrochemical synthesis has two main advantageous. This method require a few minutes time for synthesis comparing to other methods which require several hours or days for synthesis. Also in electrochemical method usually the synthesis is accomplished at room temperature.

In this work, copper (II) benzene-1,3,5-tricarboxylate (Cu BTC,BTC=1,3,5-tricarboxylate) was synthesized by electrochemical method (Fig. 1) and its performance as electrocatalyst for oxygen reduction reaction (ORR) was studied in 0.5 M H_2SO_4, phosphate buffer 6 (PBS6) and 0.1 M NaOH solutions, which the best result was obtained in PBS6. At the optimum condition the ORR was compared with a Cu BTC synthesized by solvothermal method. The ORR results shown that in comparison to solvothermal MOF, the electrosynthesised MOF has very higher current density for ORR, while the overvoltage is

Keywords: *Metal–Organic Framework, solvothermal method, electrochemical synthesis, copper (II) benzene-1,3,5-tricarboxylate, electrocatalyst*



A B

Figure 1. A) SEM image of the HKUST-1 coating electrochemically deposited on a copper electrode, B) Typical CVs obtained at Cu-BTC- synthesized by solvothermal method (gray) and synthesized by electrochemical method (black) in 0.10 M phosphate buffer solution (pH 6.0) with the scan rate of 50 mV s^{-1}.

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Synthesis of nano zinc oxide by anodic dissolution method

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Abstract

In this study, ZnO nanoparticles were synthesized using an anodic dissolution method. This method is based on the anodic dissolution of zinc in the presence of an amine which acts as a supporting electrolyte. An electrochemical cell, containing a plate of stainless steel as the cathode, a sacrificial zinc anode and an aqueous solution of different salts, was used for all experiments. In this study the effect of different salts such as C16H36BrN, C16H36IN, C16H36N4 and C16H36CN on the structural and optical properties of the products was explored. The experiments were performed under 0.05 A in a potentiostat mode. ZnO nanoparticles were synthesized with C16H36N4 by anodic dissolution method. Fourier transform infrared spectroscopy results showed that the products have been covered by the surfactant. Finally the results obtained by scanning electron microscopy showed a nano flake morphologhy.

Keywords: *Anodic dissolution, ZnO nanoparticles, structural and optical properties*

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Fabrication of Nano-porous silicon by electrochemical etch of high resistivity silicon wafer

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Introduction

Porous silicon (PS) has attracted much attention as promising semiconductor materials for optical and electronic device applications. [1,2]. Electrochemical anodic etching method is an effective technique to produce uniform pores on the surface of P-type silicon wafer. Several parameters are used to optimize the characterization of surface of a porous layer, such as etching time, current density and concentration of etching solution [3,4,5]. In this research, resistance effect on two wafers with resistivity 10 Ω.cm and 0.04Ω.cm was investigated in constant conditions.

Methods

Firstly, the both wafer cleaned by RCA method. Then a Silver thin film coating deposited on backside P-type Si- wafer by using DC Sputtering (PVD – DSR1, IRAN). The electrolyte solution was HF: EtOH: H_2O with volume ratio 1:2:2. A Teflon cell electrochemistry was used for the electrochemical etching process. The Si wafer <100> as positive electrode connected on power supply under constant current density mode. A 40 mA constant current density and 10 min of etching time duration at the same conditions were applied to both wafers. The shape and size of pores were observed under FESEM (Field Emission Scanning Electron Microscopy) analysis.

Results and discussion

The fabrication of PSs was done by electrochemically etch when a constant current was applied to the both wafers and potential profile changes with time for 10 min. were plotted in figure 1. The range of potential variation is between 153.4 V to 116.8 V for 10Ω.cm resistance wafer, while the range of potential variation for 0.04Ω.cm resistance wafer is between 84 to 62.4 V.

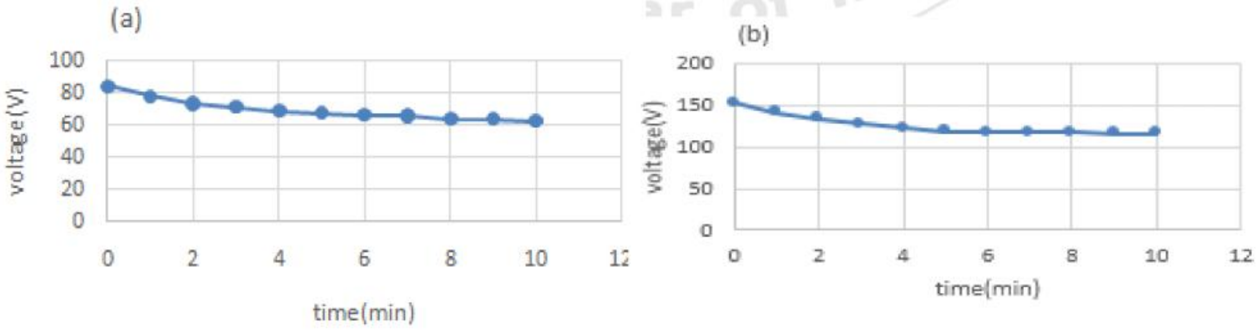

Figure. 1. Profile of potential versus time (a) P-type Si wafer <100> with resistivity 0.04 Ω.cm (b) P-type Si wafer <100> with resistivity 10 Ω.cm.

The samples morphologies were studied also by FESEM analysis. Figure 2-a shows that the 40mA current is applied to the wafer surface with lower resistance leads to an initial rupture formation, then over the time the honeycomb cavities with very low depth and average pores diameter of 336.49 nm (figure 2-b) have been formed. While high resistance wafer under the same conditions in the nanometer range is porous. The pore diameters observed are between 14.37 to 97.48 nm that show good porosity (Figure 2-c)

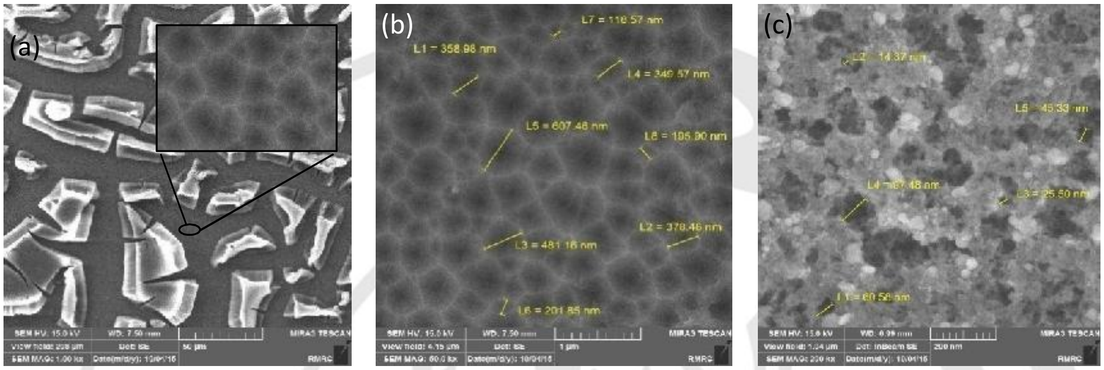

Figure.2. (a) rupture formation on the wafer surface with resistivity 0.04 Ω.cm (b) honeycomb cavities formation with macro pores diameter (c) mesoporous formation on the wafer surface with resistivity 10 Ω.cm.

Conclusions

We used electrochemical anodizing process for fabrication nanoporous silicon layers. The both samples were under constant conditions 40 mA and 10 min. FESEM pictures showed that the porosity is formed uniformly in P-type Si wafer with resistivity 10Ω.cm rather than in P-type Si wafer with resistivity 0.04 Ω.cm.

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Keywords: *Porous Silicon, Electrochemical Etch, Nano-Porosity, FESEM.*

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