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Electrochemical Society of Iran
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انجمن الکتروشیمی ایران

چهاردهمین سمینار سالانه الکتروشیمی ایران

14th Annual Electrochemistry Seminar of Iran

12-13 December 2018

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Welcome to the 14th Annual Electrochemistry Seminar of Iran

Dear attendants

On behalf of organizing committee of the 14th Annual Electrochemistry Seminar of Iran, I'm delighted to welcome you all to Materials and energy research center of Iran. 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 Materials and energy research center, Alborz, Iran. It's noteworthy that the seminar includes 10 major fields including Analytical Electrochemistry, Physical Electrochemistry (theoretical), Electrochemical Synthesis, Corrosion, Bio-Electrochemistry, Nano-Electrochemistry, Computational Electrochemistry, Energy (Conversion & Storage), Electrochemistry – Industry, and Environmental Electrochemistry. We whole heartedly hope that your participation in the 14th Annual Electrochemistry Seminar of Iran in Alborz will be fruitful.

Cordially

Abouzar Massoudi

14th Annual electrochemistry seminar

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Keynote

Name	Title
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Research of Area

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Analytical Electrochemistry

Electrochemically preparation of Co-Al layered double hydroxide nanosheets on nanoporous anodic aluminum oxide /aluminum film as thin film microextraction film

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Abstract

Herein, a facile hydrothermal method was used to grow a very thin nanosheets of Co-Al layered double hydroxide (Co-Al-LDH) on an anodized aluminum foil for the first time. In this study, a hierarchical Co-Al-LDH has been fabricated via the in situ crystallization technique on nonporous anodic aluminum film. Before the hydrothermal process, the Al foil substrate was potentially anodized. The prepared film with high surface area and compact structure was used as a novel sorbent in thin film microextraction (TFME) method. After extraction, the extracting film was eluted using organic solvent to desorb the target analyte. In order to evaluate the extraction ability of the prepared film, quercetin was selected as target analyte. To investigate the capability of the prepared film in real sample analysis, different kinds of fruit juice was selected. Plackett–Burman design was used for screening the experimental factors of interest in TFME. Thereafter, the effective factors were optimized using Box-Behnken design (BBD). LDHs are an example of interesting emerging materials for extraction applications [1]. LDHs are 2D nanostructured materials consisting of positively charged, brucite-like octahedral layers of metal hydroxides and a negatively charged interlayer region containing anions and water molecules [2]. LDHs are represented by the general formula $[M^{2+}{}_{1-x} M^{3+}{}_{x} (OH)_2]^{x+} (A^{n-})_{x/n}. mH_2O$, where M^{2+} is a divalent cation, M^{3+} is a trivalent cation and A^{n-} is the interlayer anion. LDHs have a high surface area, anion exchange properties, good thermal stability and tunable and flexible interlayer spaces.

Keywords: Electrochemically preparation; HPLC; Thin film microextraction; Nonoporous anodic aluminum oxide; Quercetine,

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The synthesis of TiO_2/SWCNTs nano-composite and investigation of electrical conductivity effect

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Abstract

The nanomaterials with high surface area and unique properties are good choice for application in industry. In this study we described the synthesis of TiO_2 nanotube and TiO_2/SWCNTs nanocomposite by hydrothermal method. The synthesized nanomaterials were characterized by FESEM, EDS and XRD methods. The results showed the good synthesized of TiO2 nanotube at surface of SWCNTs. The electrical conductivity of TiO_2/SWCNTs nanocomposite was investigated by electrochemical impedance spectroscopy method and the obtained data was compared to TiO2 nanotube. The results confirmed the TiO_2/SWCNTs nanocomposite has good electrical conductivity that is useful for application as mediator for sensor investigation.

Keywords: *TiO_2/SWCNTs nanocomposite, electrical conductivity, electrochemical impedance spectroscopy*

Reference

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An electrochemical sensor based on Poly (Eriochrome Black T)/nanoporous fibers modified electrode for Electrocatalytic Determination of Ascorbic Acid

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Abstract

2-hydroxy-1-(1-hydroxy-2-naphthylazo)-6-nitronaphthalene-4-sulfonic acid sodium salt (Eriochrome Black-T, EBT) is a classical azo sulfonic acid dye, which has been often used as the spectroscopic probe for the determination of metal ion and biological molecules [1, 2]. In recent years, the electropolymerization and the biosensing application of its polymer also attract much attention. The electropolymer film coated electrodes are playing an important role in sensor field [3].

In our present investigation, a new modified electrode fabricated from the poly (EBT)/ nanoporous, by cyclic voltammetry that the whole procedures take only several minutes and can be used for quantification of ascorbic acid (AA) in different real samples. The surface and electrochemical characterization of the modified electrode was performed by field emission scanning electron microscopy, chronoamperometry, cyclic voltammetry and differential pulse voltammetry. A significant enhancement in the peak current response of AA was observed accompanied with a negative shift in peak potential at the composite modified electrode compared to the unmodified electrode. Using differential pulse voltammetry, the calibration curves for AA was obtained over the range of 0.15–100mM. The effect of pH, scan rate and concentration of AA were studied in detail. The presented methodology possesses a reliable reproducibility, repeatability and stability

in biological samples. The proposed electrode was successfully applied for AA determination in pharmaceutical formulations with promising results.

Keywords: Eriochrome Black-T, Ascorbic acid, Electropolymerization, Nanoporous

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Amperometric Determination of Hydrazine based on its Electrocatalytic Oxidation at Cu-Nanoparticles Incorporated Polymeric Film Modified Electrode

Sara Pashazadeh, Ali Pashazadeh, Younes Hashemi, Biuck Habibi*

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Abstract

Hydrazine is an important compound that has been widely used in various fields for example as a fuel for military and space vehicles and rockets, an antioxidant, a catalyst, a pesticide in agriculture, an intermediate in pharmaceuticals, a corrosion inhibitor in boilers, a reducing agent in industry, a reagent in the wide variety of chemical reactions etc. [1,2]. Recently, electroanalytical methods have been found a great attention as alternative way for the determination of hydrazine. Because electrochemical techniques have some advantages such as simplicity, low cost, good selectivity, high sensitivity, fast response, no derivatization procedure and no time consuming sample preparation procedures [3-4].

Hereupon, in this work, a promising electrocatalyst was developed based on a layer process by electropolymerization of thioacetamide on the surface of glassy carbon electrode (GCE) as a proper polymeric framework for deposition of Cu nanoparticles (CuNPs) for the first time. The prepared electrocatalyst was characterized by XRD, SEM and electrochemical techniques. Then, the cyclic voltammetry and chronoamperometry approaches were employed to characterize the electrocatalytic activity of the present nanoparticles modified electrodes toward the oxidation of hydrazine in 0.1 M NaOH solution. Electrochemical studies demonstrate that this CuNPs/PTu/GCE catalyst could have both superior electrocatalytic activity and stability for hydrazine oxidation, confirming that CuNPs/PTu/GCE should be a good material for supporting the catalyst. Anodic peak potential of hydrazine oxidation at the surface of modified electrode shifts by about 150mV toward negative values compared with that on the bare electrode. The kinetic parameters such as the electron transfer coefficient (α) and charge transfer rate constant (k) for the oxidation of hydrazine was determined utilizing cyclic voltammetry (CV). The diffusion coefficient (D) of hydrazine was also estimated using chronoamperometry. The dynamic detection range of this sensor to hydrazine was 0.3- 6 $\mathrm{mmolL^{-1}}$ at the modified electrode surface using an amperometric method. The detection limit and quantitation are 5.33 µM and 129 µM, respectively. A new voltammetric method for determination of hydrazine was erected and shows good sensitivity and selectivity, wider linear relationship, very easy surface update and good stability.

Keywords: Hydrazine, Electrocatalytic Oxidation, Polymeric Film, Determination

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Electrochemical determination of Tartrazine in food samples using nano-structure voltammetric sensor

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Abstract

Tartrazine is a usual lemon yellow azo dye and commonly suggested in food coloring [1]. As a synthetic azo dye, high level of tartrazine could be dangerous for human health. Therefore, determination of tartrazine is very important. In this study, we fabricated a carbon paste electrode modified with reduced graphene/CuO nanocomposite and ionic liquid and used room temperature ionic liquid as voltammetric sensor for determination of tartrazine. The fabricated sensor improved the oxidation current of tartrazine and reduced the oxidation of over-potential. The suggested sensor showed a detection limit 5 nM for tartrazine using square wave voltammetric method. Finally, the fabricated sensor was used for determination of tartrazine in food samples.

Keywords: *Tartrazine, reduced graphene/CuO nanocomposite, ionic liquid*

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Synergetic effect of PdNP and MWCNT as cocatalysts for enhanced electrocatalytic hydrogen evolution activity of MoS_2

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Abstract

To achieve an optimal performance, efficient electrocatalysts for HER are critical. At present, the most efficient and typical electrocatalysts for HER are Pt based compounds, which can realize excessive catalytic activity with almost no overpotential [1]. But the high cost and low abundance of Pt hinders the large-scale hydrogen production through acidic electrolyzers like polymer electrolyte membrane (PEM) electrolyzers [2]. Here, the hybrid material of MoS_2-coated Pd nanoparticles loaded on the multiwalled carbon nanotubes (Pd-MoS_2/MWCNT) was synthesized using chemical process and hydrothermal method. The nanohybrid was characterized by X-ray diffraction (XRD) patterns, Raman scattering, X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Pd-MoS_2/MWCNT showed the high activity for hydrogen evolution reaction with a small onset overpotential of 70 mV, a high exchange current density of 7.1×10^{-2} mA cm^{-1} and Tafel slope of 54 mV $decade^{-1}$ as well as an excellent stability in acid media. It was found that these catalyst exhibited excellent HER activity compared to MoS_2 nanoflower, Pd-MoS_2 and MoS2/MWCNT due to the synergistic effect of the high catalytic activity of MoS_2 nanoflowers and the excellent conductivity and large surface area of MWCNT and providing more free sites for the adsorption of H using Pd nanoparticles, exposing much more active sites and reducing intrinsic resistance. The turnover frequency per active site is also calculated. This work demonstrates the feasibility of increasing HER activity of MoS_2-based catalysts by combining $MoS_2$with MWCNT and Pd noble metal nanoparticles.

Keywords: Hydrogen evolution reaction; Molybdenum disulfide; Electrocatalyst; Multiwalled carbon nanotubes; Pd nanoparticles

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Electrochemical determination of trace Sudan (I) using lanthanium-doped ZnO nanoflowers modified graphite screen printed electrode

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Abstract

Sudan azo dyes, include Sudan (I–IV), are synthetic chemical colorants and traditionally used in industrial products [1]. In the past few years, Sudan dyes, especially, Sudan (I) is also found used as an additive in foods, such as hot chili powder, relishes, chutneys, seasonings, sauces, and ready meals because of their bright and vivid red color [2]. However, Sudan (I) was recognized as a potential carcinogen to both human beings and animals which was demonstrated through laboratory experiments and thus was classified as a category 3 carcinogen by the International Agency for Research on Cancer (IARC) [3] Therefore, the use of Sudan (I) as food additive is forbidden all over the world. To this end, it is of great importance to develop a sensitive, rapid and reliable method for the determination of Sudan (I) in foodstuffs. This article reports on a sensitive detection method for Sudan (I) based on La^{3+}/ZnO nanoflower modified graphite screen printed electrode (La^{3+}/ZnO/SPE) by differential pulse voltammetry (DPV). The La^{3+}/ZnO/SPE displayed good analytical performance for the measurement of Sudan (I). Under the optimum experimental conditions, Sudan (I) could be linearly detected in the wide concentration range of 3.0×10^{-7} to 4.0×10^{-4} M with a high sensitivity of 0.0975 μAmM^{-1}. The detection limit was down to around 2.44×10^{-9} M (S/N = 3). Finally, the method was successfully applied for the determination of Sudan (I) in real samples.

Keywords: *Sudan (I), Voltammetric sensor, Screen printed electrode, La^{3+}/ZnO nanoflower*

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Designing a modified electrode based on La^{3+}-doped ZnO nanoflowers and guar-gum application to electrochemical detection of ascorbic acid

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Abstract

The quantitative detection of drug content constitutes a permanent preoccupation for research in various fields [1]. It is well established that ascorbic acid (AA) is widely used in food, pharmaceutical industry and clinic medicine [2]. Ascorbic acid is an important antioxidant widely present in biological systems, which is an essential substance to maintain normal physiological function of human body. Abnormal contents of ascorbic acid may cause several symptoms, including fatigue, infertility and scurvy [3]. In this work, an easy method was employed to successfully develop La^{3+}-doped ZnO nanoflowers and guar-gum (GG) modified screen printed electrode (La^{3+}/ZnO/GG/SPE), and La^{3+}/ZnO/GG/SPE was applied for the electrochemically detection of ascorbic acid (AA). The electrochemical methods, such as cyclic voltammetry (CV), chronoamperometry (CHA) and differential pulse voltammetry (DPV) were used to evaluate the electrochemical performances toward ascorbic acid on the La^{3+}/ZnO/GG/SPE. Good linearship was observed for ascorbic acid in the ranges of 1.0–700.0 μM, with the detection limits of 0.03 μM. Moreover, this sensor proved favorable to simultaneously determine ascorbic acid and acetaminophen. Finally, the modified electrode has fairly good performance during the employment of real sample analysis to determine the content of ascorbic acid. These results

indicate that the La^{3+}-doped ZnO nanoflowers are supposed to be a promising material in the electrochemical determination of ascorbic acid and acetaminophen in real samples.

Keywords: *Ascorbic acid; Acetaminophen;* La^{3+}*/ZnO nanoflowers; Graphite screen printed electrode;Voltammetry*.

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Electrocatalytic oxidation of Glutation at the surface of NanoZeolite modified caron paste electrode

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Abstract

Glutathione which is present in virtually all mammalian tissues, providesreducing capacity for several reactions and plays animportant role in detoxification of hydrogen peroxide, otherperoxide, and free radicals[1]. Glutathione (GSH) is the most abundantly found non-proteinthiol in living organisms with numerous important roles in proteinand DNA synthesis, transport, catabolism, and metabolism[2]. Electrode surface modification is a field of paramount importance in the modern electrochemistry especially due to the various application possibilities of modified electrodes. In recent years, chemically modified carbon paste electrodes have received increasing attention due to their potential applications in various analysis and also due to its relative ease of electrode preparation and regeneration[3].

The aim of this research is determination of glutathione using zeolite ZSM-5 modified carbon paste electrode. Electrochemical behavior of zeolite modified carbon paste electrode which was dopped with ferrosen (FeZSM-5/CPE), zeolite modified carbon paste electrode (ZSM-5/CPE) and unmodified carbon paste electrode (CPE) were studied by using cyclic voltammetry technique. To prepare modified electrode a mixture of nanosized NiZSM-5 , graphite powder, ferrosen and paraffin oil were blended by hand mixing with a mortar and pestle. The resulting paste was then inserted in a glass tube then The electrical connection was implemented by a copper wire lead fitted into the glass tube. The unmodified carbone paste electrode (CPE), used for comparison, was prepared in the same way but omitting the zeolite and ferosen addition step. The oxidation of glutathione was studied at CPE and fe/ZSM-5/CPE by cyclic voltametric experiment in buffer

solution then obtained results was compared with each other. In the optimum condition, linear dynamic range (LDR) of glutathione by differential pluse voltammetry and cyclic voltammetry were 4.0×10^{-5}-1.0×10^{-3} and 8.0×10-5-2×10-3 respectively and the limit of detection was 8.7×10^{-7} and 1.13×10^{-6} respectively. The chronoamprometry was studied for the oxidation of glutation at the surface of proposed modified electrode. Through chronoamprometry results the catalytic rate constant for this catalytic electrooxidation was calculated to be 6.75×10^{11} $cm^3mol^{-1}s^{-1}$ From obtaining result in conclution the poroposed modified electrode was a novel, cheap and easy to use. Then it can be used for determination of glutation in pharmacutical product and pure form.

Keywords:*Glutation, zeolite (ZSM-5) modified electrod, Cyclic Voltammetry, Differential Pulse Voltammetry.*

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Electron transfer rate, active surface area and electrocatalytic performance of graphenized pencil lead electrodes

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Abstract

In this study graphenized pencil lead electrodes (GPLE) was prepared by electrochemical exfoliation of pencil lead electrode (PLE) by applying an optimized potential in acidic media. The prepared GPLE was characterized by scanning electron microscopy (SEM), X-ray powder diffraction (XRD) and electrochemical techniques. Active surface area and electron transfer rate of the prepared GPLE was improved remarkably in comparison with regular pencil lead electrode. Electrocatalytic performance of the GPLE was studied in details by determination of Bisphenol A in various real samples using differential pulse voltammetry technique. The fabricated electrode responds efficiently to Bisphenol in the linear range of 10-50 nM with the detection limit of 4.53 nM and sensitivity of 8.58 µA μM^{-1}. Low cost, simplicity of fabrication, renewability, high sensitivity and accuracy makes this electrode as a suitable choice for rapid determination of BPA in routine and clinical analysis.

Keywords: Graphenized pencil lead electrode, Electrocatalysis, Active surface area

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Preparation of miniaturized pH sensors based on metal oxide modified pencil lead electrode

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Abstract

In this study, sensitive potentiometric solid state pH sensors based on metal oxide nanoparticles electrodeposited on pencil lead electrode were reported [1-4]. The prepared electrodes were carefully characterized by SEM, XRD and electrochemical techniques. To miniaturize the prepared pH sensors, a stainless steel 304 needle was used as a reference electrode. Selectivity, response time, stability and reproducibility of the miniaturized pH sensor were studied and compared with conventional glassy pH electrode. According to experimental results, near-Nernstian slope and linearity over the pH range of 1.5-12.5 were obtained for the developed sensors. The prepared electrodes represented high ion selectivity to mono-valence and multi-valence ions with $-\log K_{\mathrm{A,B}}^{\mathrm{Pot}}$ values around 6.49. Fast response time of about 20 s in acidic medium and 50 s in alkaline medium, long-term stability and reproducibility in two months, simplicity of fabrication, low cost and accuracy makes these sensors a suitable choice for rapid pH recording in micro volume samples.

Keywords: Potentiometry; Pencil lead electrode, Miniaturized pH sensor

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Development of an aptasensor for detection of bisphenol A based on immobilization of aptamer on the nanomaterials modified gold electrode

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Abstract

Bisphenol A (BPA) is a very abundant and widely used chemical for epoxy resin and polycarbonate in plastic and paper industries. Effective detection of BPA is of vital importance in the environment and food fields. Data from multiple sources indicate that the amount of PBA to which humans are exposed may cause adverse health effects [1]. Among the different types of detection techniques, electrochemical biosensors are gaining special interest due to their remarkable sensitivity, experimental simplicity and low cost [2]. In this research, design and manufacturing of an electrochemical biosensor developed for measurement of bisphenol A. Because of the unique features of gold, this electrode is used. For the construction of this biosensor, gold nanoparticles and metal organic frameworks were used as surface modifiers due to its unobtrusive properties. Metal organic frameworks, due to its unobstructed immobilization of the aptamer on the sensor surface. Electrochemical technique used in this study are electrochemical impedance spectroscopy and cyclic voltametry. The designed aptasensor has a detection limit of 0.0066 nanomolar and a linear range of 0.001 to 10 nM, which include a wide area.

Keywords: Bisphenol A, Aptasensor, Biosensor, Electrochemical impdance Spectrometry, Cyclic Voltammetry, Metal Organic Framework.

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Electrocatalytic determination of phenylhydrazine in the presence ofhydrazine at the modified nano zeolite carbon paste electrode

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Abstract

Hydrazine and its derivatives are widely used in agriculturalchemicals (pesticides), chemical blowing agents,pharmaceutical intermediates, photography chemicals, andboiler water treatment in hot-water heating systems for corrosion control[1].Carbon paste electrode (CPE) is a special kind of heterogeneous carbon electrode consisting ofmixture prepared from carbon powder (as graphite, glassy carbon and others carbonaceous materials. Modification of cabon paste electrode using organic and inorganic materials pay much attention for electrooxidation of wide range of biological compond [2,3].

The purpose of this work is to electrocatalytic determination of phenylhydrazine in the presence of hydrazine the modified nano zeolite carbon paste electrode. The electrochemical behavior proposed electrode was investigated cyclic voltammetry and Differential Pulse Voltammetry.

A mixture of appropriate amount of nanosized NiZSM-5and graphite powder,ferrosen and paraffin were blended by hand mixing with a mortar and pestle for preparation of zeolite modified carbon paste [ZMCP]. The resulting paste was then inserted in a glass tube. The electrical connection was implemented by a copper wire lead fitted into the glass tube. The carbone paste electrode (CPE), used for comparison, was prepared in the same way but omitting the zeolite and ferosen addition step. The oxidation of hydrazine was studied at CPE and fe/ZSM-5/CPE by cyclic voltametric experiment in buffer solution then obtained results was compared with each other. The percentage of zeolite, pH, scan rate of potential were studiied. Under optimal conditions, the electrochemical behavior of phenylhydrazine (phy) in the presence of hydrazine (hy) was investigated using differential pulse voltammetry method. The linear dynamic ranges of 2.0× 10^{-5} -19×10^{-4} M and2.0× 10^{-5} -14×10^{-4} M for phenylhydrazine and hydrazine were obtained respectively. The detection limits were obtained 2.11 × 10^{-6} and 2.5 × 10^{-6} M, for (PHY) and (HY). The surface coverage coefficient (Γ^*) and diffusion coefficient (D) were calculated 1.56× 10^{-6} and 0.55 mol / cm^{-2}. Also, the electrochemical behavior of phenylhydrazine and hydrazine with a specific concentration were also investigated using a cyclic voltammetric method at different scans and the electron transfer coefficient was 0.44 and 0.42, respectively. The chronoamperometry technique was studied and the catalytic rate constant for electrooxidation of hydrazin and phenyl hydrazine were calculated to be 6.99×10^4 $cm^3.mol^{-1}.s^{-1}$ and 2.02× 10^6 $cm^3.mol^{-1}.s^{-1}$ respectively.The obtained results were show that proposed modified electrode was a sutable electrode for determination of phenyl hydrazine in the present of hydrazine.

Keywords:Phenylhydrazine,Hydrazine,Zeolite (ZSM-5) modified electrod, Cyclic Voltammetry, Differential Pulse Voltammetry.

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Development electrochemical sensor based on molecularly imprinted polymer for determination of levodopa

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Abstract

Levodopa (3,4-dihydroxyphenylalanine) also called L-dopa, is the precursor required by the brain to produce dopamine, a neurotransmitter. Levodopa crosses the protective blood–brain barrier, whereas dopamine itself cannot. Thus, levodopa is used to increase dopamine concentrations in the treatment of Parkinson's disease (PD), dopamine-responsive and dystonia. However, an excessive amount of levodopa not only helpful but also make serious side effects such as gastritis, paranoia schizophrenia and epilepsy. With dangerous side effects of levodopa with long-term use on human health, this drug should be given an accurate analysis in both pharmaceutical formulations and biological fluids [1]. Forasmuch as levodopa contain phenolic hydroxyl and amino group respectively, which is electrochemically active and can be oxidized. Thus, electrochemical methods because of their good simplicity, sensitivity, and relatively fast response, low cost and good stability are the better choice for determination of levodopa. However, the signal to noise of bare electrode is insufficient to determine the trace level of levodopa. To overcome it, molecular imprinted polymer (MIP) is considered one of the best strategy owing to its pre-determined selectivity for an imprinted template. Molecular imprinting is a technique which is used to molecular recognition via self-assembly of functional monomers around a template molecule through the interaction between their functional groups. This technology has been developed for use in sensors since it can provide enhanced selectivity and/or sensitivity. In addition, molecularly imprinted polymers (MIP) benefit from ease of preparation along with good

stability in chemical, physical and mechanical properties [2]. A considerable amount of research has been done on MIP based approach for levodopa determination. Levodopa showed a sensitive anodic peak in buffer solution of phosphate (pH=7.0) at the surface of MIP/GCE. The investigation and optimization of the effective factors on the response and electrochemical behavior of target levodopa on the surface of the modified electrode were accurately done. Levodopa response linearly within the range of 0.1-600.0 µM with detection limit of 0.05 µM. The function of this electrode in the determination of biological samples was satisfactory.

Keywords: *Molecularly imprinted polymers, Levodopa, Glassy carbon electrode, Voltammetry*

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Voltammetric determination of carbidopa using a modified glassy carbon electrode with La^{3+}/Co_3O_4 nanocubics

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Abstract

Carbidopa (CD) is one of the important catecholamine and it is used in the treatment of Parkinson's disease. Carbidopa is a drug given to people with Parkinson's disease in order to inhibit peripheral metabolism of levodopa. Carbidopa does not cross the blood-brain barrier (BBB) and contributes to the production of effective brain concentrations of dopamine from lower doses of levodopa by inhibiting the peripheral decarboxylation of levodopa to dopamine [1,2]. Therefore, it is very important to establish a sensitive method for detection of carbidopa in pharmaceutical formulations and human serum. Different techniques have been employed for the determination of carbidopa in pharmaceutical formulations. Among of these methods, electrochemical techniques offer the opportunity for portable, economical, sensitive and rapid methodologies. Among many electrodes, glassy carbon electrodes (GCEs), which are stable and robust carbon-based electrodes, have been widely used because of their high biocompatibility, low tendency for surface fouling, and relatively low level of residual current over a wide potential range. Thus, the combination of inorganic nanoparticles and sensors is one of the most exciting areas in modern analytical detection development because they offer excellent prospects for designing highly sensitive and selective sensors. As an important p-type semiconductor, cobalt oxide (Co_3O_4 in particular) has gained increasing attention because of its applications in many fields, such as sensors, gas sensing, catalysis, and lithium-ion batteries. The combination metals with metal oxide nanocomposites have a significant effect on the

catalytic activity due to the interactions and surface reactivity [3]. In this study, a new glassy carbon electrode chemically modified with La^{3+}/Co_3O_4 nanocubics was constructed and used for the sensitive electrochemical determination of trace amounts of carbidopa. This electrochemical sensor responds to carbidopa in the wide linear range of 1.0×10^{-6} to 7.0×10^{-4} M. The detection limit of 7.0×10^{-8} M was obtained at pH 7.0. The proposed sensor was successfully applied for the determination of carbidopa in real samples.

Keywords: *La^{3+}/Co_3O_4 nanocubics, Carbidopa, Glassy carbon electrode, Voltammetry*

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Fabrication of a novel nanostructure electrochemical sensor for determination of tyrosine

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Abstract

Amino acids such as tyrosine are the major targets for radical's attack. 4-Hydroxyphenylalanine or tyrosine (Tyr) is a nonessential amino acid and acts as a singlet oxygen quencher. Tyrosine plays an integral role in the synthesis of the neurotransmitter serotonin such as norepinephrine and dopamine (5-HT). Tyrosine and other amino acids play roles in inducing dementia such as Alzheimer's disease. The lack of tyrosine concentration in the body may cause albinism, alkaptonuria, depression, narcolepsy and other psychological diseases while a high level of tyrosine could cause the increase of sister chromatid exchange [1]. Therefore, it is significant to develop a simple, accurate, rapid and inexpensive sensor for the determination of tyrosine. Electrochemical analytical techniques have been a topic of interest to researchers in the biological and environmental analysis, due to simplicity, cost effectiveness, high sensitivity and the possibility of miniaturization. A screen-printed electrode (SPE) is an attractive alternative choice due to their miniaturized size, inexpensive, easy to fabricate, rapid responses and disposable, which makes them especially suitable for on-site analysis [2]. However, the signal to noise of bare electrode is insufficient to determine the trace level of tyrosine. One of the major strategies to enhance the electron exchange in electrochemical sensors and biosensors is to design new sensing layer by combining highly electrocatalytic materials with highly conductive substances. Metal oxide based nanocomposites have wide applications in

photocatalysis, gas-sensors, piezoelectric materials, and solar cells due to its features such as photosensitivity, non-toxic and low cost. The combination metals with metal oxide nanocomposites have a significant effect on the catalytic activity due to the interactions and surface reactivity [3]. A simple, selective and sensitive sensor based on La^{3+}/Co_3O_4 nanoflowers modified screen printed electrode (La^{3+}/Co_3O_4 NF/SPE) is introduced for electrochemical determination of tyrosine. Compared with the unmodified electrode, the oxidation peak current significantly improved. Under optimized experimental conditions, the oxidation peak current of tyrosine was linear over a concentration range of 5.0×10^{-7} to 7.0×10^{-4} M with a detection limit of 4.0×10^{-8} M. Moreover, the applicability of the method was demonstrated by the recovery tests of tyrosine in real samples.

Keywords: *La^{3+}/Co_3O_4 nanoflowers, Tyrosine, Screen printed electrode, Voltammetry*

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Highly sensitive determination of dopamine using screen-printed electrodes modified with 2D transition metal carbide MXene

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Abstract

Dopamine (3,4-dihydroxyphenyl ethylamine, DA), as an excitatory neurotransmitter in mammalian central nervous systems, plays an important role in several physiological activity such as mood, behavior and movement. Abnormal levels of dopamine may lead to neurological diseases, such as Parkinson's disease and schizophrenia [1]. Hence, Sensitive detection of dopamine is of great importance for the understanding and diagnostics of neurological diseases. As compared to other analytical methods, the electrochemical techniques making use of a three electrode system have drawn a particularly considerable amount of attention because of the electroactive nature of dopamine, high selectivity, high sensitivity, low cost, reproducibility, simplicity and short operational duration. Screen-printed electrodes (SPEs), which are fabricated by printing several types of inks on a specific substrate have been considered superior because of the versatile, disposable, inexpensive, good reproducibility of the results, rapid responses to analytes, easy to fabricate, and can be operated over a wide potential range. Such SPEs have been recently employed as diagnostic tools for food poisoning, diseases, and environmental pollutants. In order to improve their electrochemical performance, SPEs have been modified with nanosized materials [2]. MXene, as a new class of two-dimensional (2D) transition metal carbides (or nitrides), has been synthesized by exfoliating pristine Ti_3AlC_2 phases with hydrofluoric acid [3]. A simple, selective and sensitive sensor based on MXene nanosheets modified screen printed electrode (MXene/SPE) is introduced for electrochemical determination of dopamine. Compared with the unmodified graphite screen printed electrode, the modified electrode facilitates the electron transfer of dopamine, since it notably increases the oxidation peak current of dopamine. Under optimized conditions, the modified electrode exhibited a linear response over the concentration ranging from 0.2 to 600.0 µM, with a detection limit of 0.06 µM (S/N = 3). The proposed sensor exhibited a high sensitivity, good stability and was successfully applied for dopamine determination in dopamine ampoule, with high recovery.

Keywords: MXene nanosheets, Dopamine, Screen printed electrode, Voltammetry

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Development of a new carbon paste sensor for low level measurement of propranolol in pharmaceutical and biological samples

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Abstract

Propranolol (PPL), 1-naphthalen-1-yloxy-3-(propan-2-ylamino) propan-2-ol, is a medication of the beta blocker class. It is used to treat high blood pressure and also to prevent migraine headaches and further heart problems in angina or heart attacks. A few methods such as voltammetry [1], chromatography [2] and spectroscopy [3] have been reported for determination of propranolol. However, no potentiometric carbon paste sensor has been reported for the determination of propranolol. With respect to the unique advantages of potentiometric carbon paste sensors for drugs determination, in this study, performance characteristics of a new potentiometric carbon paste sensor for the fast, easy and selective determination of propranolol was described [4]. The constructed potentiometric sensor is based on the use of the ion association complex of propranolol-tungstosilicate as a good ionophore in the carbon paste matrix. The proposed sensor exhibited a Nernestian slope of 59.1 mV/decade for propranolol over the concentration range of 1.7×10^{-9} – 2.2×10^{-4} M, and a detection limit of 1.5×10^{-9} M. The electrode has a fast response time (9 s), satisfactory reproducibility, long life time and most importantly, excellent selectivities for propranolol relative to a variety of foreign organic and inorganic species. The effect of pH and the temperature on the potential response of the sensor was investigated. Potentiometric determination of propranolol in different pharmaceutical and biological samples such as propranolol tablet and blood serum samples were investigated by the proposed sensor.

Keywords: Potentiometry, Sensor, Propranolol, Carbon paste electrode, Drug determination

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Electrochemical determination of methyldopa in pharmaceutical samples using graphene oxide- phosphomolybdic acid/pencil graphite electrode

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Abstract

Methyldopa, (a-methyl-3,4-dihydroxyphenylalanine), is an antihypertensive agent and the best factor for the treatment of high blood pressure in pregnancy time [1]. The determination of methyldopa has been reported by several methods including titrimetry [2], chromatography [3] and spectroscopy [4]. Because of the importance of methyldopa in biological fluid, it is important to develop simple, accurate, low level and rapid method to the determination of this drug in pharmaceutical and biological samples. Electrochemical methods have advantages such as low detection limit, high sensitivity and repeatability [5]. In this study a modified pencil graphite (PGE) electrode was used as an excellent electrochemical sensor for the selective and sensitive low level determination of methyldopa in different samples. The PGE was modified with graphene oxide (GO) and phosphomolybdic acid (PMo_{12}) as a coating layer on its surface by spin coating method. The electron transfer reaction between electrolyte and electrode interfacial surface were studied using electrochemical impedance spectroscopy (EIS) in 50 mM $[Fe(CN)_6]^{3-/4-}$ with 0.1 M KCl. The obtained results showed that R_{ct} for the GO/PGE is larger than PMo_{12}-GO/PGE and much smaller than that of Bare/PGE, suggesting GO successfully enhanced electron transfer in PMo_{12}-GO modified electrode. The modifier was analysed by SEM, XRD and EDX which showed C, P, O and Mo peaks. Methyldopa can be determined by differential pulse voltammetric (DPV) technique in the linear range of 4.9×10^{-10} M to 1.0×10^{-7} M and the obtained relevant detection limit for the sensor was 1.2×10^{-10} M. The proposed sensor was used for the determination of methyldopa in pharmaceutical and urine samples.

Keywords: *Methyldopa, Electrochemical sensor, Pencil graphite electrode, PMo$_{12}$-GO /PGE.*

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A highly sensitive and selective optical sensor for the determination of mercury (II) based on a 2-((quinolin-8-ylimino)methylphenol ligand

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Abstract

In this study, a new optical chemical sensor has been produced for the selective determination of trace amounts of Hg^{2+} ions. The Hg2+ sensing system was prepared by incorporating 2-((quinolin-8-ylimino) methyl) phenol (L) as a neutral Hg^{2+} selective fluoroionophore, in the plasticized PVC membrane containing sodium tetra phenyl borate as a liphophilic anionic additive. This optode displays a calibration curve over a wide concentration range of 1.0×10^{-3} to 1.0×10^{-10} M, at pH 5.5 with a relatively fast response time of less than 40s at a wavelength of 330nm. The optode has high stability, high reproducibility and a relatively long working lifetime. The sensor shows a good selectivity towards Hg^{2+} ion respect to all lanthanide and common coexisting cations. The proposed fluorescence optode was applied successfully to determination of Hg^{2+} ion in tap and river water samples.

Keywords: Sensor, Optotod, mercury, Fluorescence.

Title area

Artificial receptors are able to transform the binding of ionic species into spectroscopic signals [1, 2]. Fluorescence because of its intrinsic sensitivity is an appropriate optical sensing method for designing the optical sensors [3–6].

Mercury is one of the most toxic elements in the world. The most toxic forms of mercury are its organic compounds, such as dimethylmercury and methylmercury.

However, inorganic compounds, such as cinnabar are also highly toxic by ingestion or inhalation. Mercury can cause both chronic and acute poisoning. Inorganic mercury may be converted to methylmercury in environment that is even more toxic than the inorganic mercury [7]. Mercury can be inhaled and absorbed through the skin and mucous membranes, if consumed by a pregnant woman, it can cause developmental delays in children [8]. So that it's critical to determine the mercury in trace amounts in different matrices.

Lately, several analytical methods have been proposed for the determination of heavy metal ions(Ag^+, Hg^{2+}, Zn^{2+}, Ni^+, ...) at low concentration level, such as; graphite furnace atomic absorption spectroscopy (GFAAS), inductively coupled plasma atomic emission or mass spectroscopy (ICP-AES, ICP-MS), and stripping voltammeter. These methods need rather expensive apparatus and are not easily adaptable for online monitoring.

Optical sensors are capable for the monitoring of toxic ions/species [9–13]. In the present work, a highly selective and sensitive optical sensor based on fluorescence measurements of 2-((quinolin-8-ylimino) methyl) phenol (figure 1) for Hg^{2+} was investigated and applied successfully for the analyses of real samples. The 2-((quinolin-8-ylimino) methyl) phenol has been used for the first time as sensing agent in the optical sensor design.

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Voltammetric determination of sunset yellow using a nanostructure modified electrode in food sample

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Abstract

In this study, NiO nanoparticles and 1-methyl-3-butyl-imidazolinium bromide as ionic liquid carbon paste electrode (NiO/NP/IL/CPE) were fabricated to determine sunset yellow (SY) in soda water and orange juice. In the first step, NiO/NP was characterized by transmission electron microscopy (TEM). The electro-oxidation of (SY) occurred at a potential about 0.7 V, which was much better in comparison with bare carbon paste electrode in phosphate buffer (pH=8) at the surface of the modified electrode. Other electrochemical techniques were also investigated including cyclic voltammetry, differential pulse voltammetry (DPV) and chronoamperometry at NiO/NP/IL/CPE. At optimized conditions for SY analysis, DPV peak currents of SY showed a wide linear dynamic ranging from 0.006 to 350 µM with a good detection limit of 4.0 nM. Finally, the proposed sensor was used for determination of sunset yellow in real samples with good selectivity and high sensitivity.

Keywords: Sunset yellow analysis, Carbon paste electrode, Soda water, Orange juice

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5-Fluorouracil electrochemical modified sensor

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Abstract

5-Fluorouracil is an antimetabolite fluoropyrimidine analog and prescribed as a drug in chemotherapy. 5-Fluorouracil is a widely used chemotherapy drug for a wide range of cancers such as breast, stomach, pancreatic, skin, gullet and bowel cancer [1].

The carbon paste electrode modified with graphene quantum dot and 1-butylpyridinium bromide was fabricated and used as electrochemical sensor for determination of 5-fluorouracil with detection limit 0.5 nM. The fabricated sensor improved the oxidation current of 5-fluorouracil and reduced the oxidation over-potential of this anticancer drugs. The novel sensor was used for determination of 5-fluorouracil in injection and serum samples.

Keywords: *5-fluorouracil, graphene quantum dot, 1-butylpyridinium bromide*

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The application of TiO_2/SWCNTs modified ionic liquid modified carbon paste electrode as sensor for determination of carbidopa and folic acid

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Abstract

Carbidopa is a drug given to people with Parkinson's disease in order to inhibit peripheral metabolism of levodopa. This property is significant in that it allows a greater proportion of peripheral levodopa to cross the blood–brain barrier for central nervous system effect [1].

In this research, a highly sensitive electrochemical sensor was fabricated by modification of carbon paste electrode with ionic liquid and TiO_2/SWCNTs as highly sensitive sensor for determination of carbidopa in the presence of folic acid.

The fabricated sensor was used for determination of carbidopa with detection limit 0.01 M. The suggested sensor was successfully used for determination of carbidopa in the presence of folic acid with good separated signals. Finally, The sensor used for determination of two compounds in drug and urine samples.

Keywords: *Carbidopa, Folic acid, TiO2/SWCNTs*

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Electrochemical determination of tert-butylhydroquinone in food samples using modified carbon paste electrode

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Abstract

In foods, TBHQ is used as a preservative for unsaturated vegetable oils and many edible animal fats. 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 extending storage life [1].

The electrochemical behavior of tert-butylhydroquinone at carbon paste electrode amplified with the 1-methyl-3- octylimidazolium tetraflouroborate and Au nanoparticles has been studied in aqueous solutions. The oxidation of tert-butylhydroquinone at the pH range of 4.0-8.0 has been investigated. At the optimum condition of pH 7.0, the tert-butylhydroquinone shows an irreversible signal at 0.24 V. The scan rate investigation confirms a diffusion process for the electro-oxidation of tert-butylhydroquinone at a surface of the modified electrode. Square wave voltammetric investigation shows a linear relationship between the tert-butylhydroquinone current and concentration within the range of 0.005-450 µM with a detection limit of 1.0 nM. The modified electrode has been applied to analyze the tramadol in injection and urine samples.

Keywords: *Tert-butylhydroquinone, Au nanoparticles, 1-methyl-3- octylimidazolium tetraflouroborate*

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Voltammetric determination of Doxorubicin using electrochemical sensor

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Abstract

Doxorubicin introduced as a useful anti-cancer drug for the treatment of breast cancer, lymphoma and bladder cancer in chemotherapy process[1]. Although doxorubicin showed a powerful ability in chemotherapy process, its high side effects, such as hair loss, nausea and immunosuppression are still a major challenge and the main problem; thus determines of its level in the human body is necessary for a chemotherapy process.

In this study, we fabricated a highly sensitive electrochemical approach base on carbon paste electrode modified with 2D nitrogen doped reduced graphene nano-sheet and 1-methyl-3-octylimidazolium chloride for determination of doxorubicin. The NrG/MOICl/CPE as an anticancer sensor displayed detection limits of 3.1 nM and 0.27 µM for doxorubicin and topotecan, respectively. The NrG/MOICl/CPE was used for determination of doxorubicin in drug and urine samples.

Keywords: *doxorubicin, 1-methyl-3-octylimidazolium chloride, 2D nitrogen doped reduced graphene nano-sheet*

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Electrochemical determination of Xanthine in food samples

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Abstract

Xanthine, is a purine base found in most human body tissues and fluids and in other organisms. A number of stimulants are derived from xanthine, including caffeine and theobromine. Xanthine is a product on the pathway of purine degradation. It is created from guanine by guanine deaminase [1].

A highly sensitive electrochemical sensor was fabricated by modification of carbon paste electrode with Fe_3O_4/SWCNTs composite and 1-ethyl-3-methyl imidazolium chloride (1E3MICl). The CPE/1E3MICl/Fe_3O_4/SWCNTs was used for determination of Xanthine with detection limit 1.0 nM. In the final step, the CPE/1E3MICl/Fe_3O_4/SWCNTs was used for determination of Xanthine in food samples.

Keywords: *Xanthine, Fe_3O_4/SWCNTs composite, 1-ethyl-3-methyl imidazolium chloride*

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Bio Electrochemistry

Determination of Optimum Temperature and Time for Electrodeposition of Gold Nanoparticles to Measure Serotonin Neurotransmitter

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Abstract

Serotonin (5-hydroxytryptamine, 5-HT) that is a monoamine neurotransmitter has an important role in various biological systems, pharmacological and psychological functions [1]. For this reason, its precise determination in biological samples can help the diagnosis of various psychological and clinical disorders [2]. So far, some methods have been developed to determine the concentration of 5-HT [1]. In this work, a simple, fast, cost-effective, rapid monitoring and sensitive electrochemical biosensor made for measurement of serum 5-HT concentration. To make biosensor, gold nanoparticle immobilized at the surface of glassy carbon electrode using electrodeposition method. Since the best procedure of electrodeposition was very important for correct performance of fabricated biosensor, for this reason, the optimum time and temperature of electrodeposition determined and the results presented in this report.

At first, the glassy carbon electrode polished by alumina slurry. Then, the gold nanoparticles (chloroauric acid; AuNPs) electrodeposited at the glassy carbon surface using constant potential electrolysis. This process performed in a deaerated $NaNO_3$ solution containing chloroauric acid;

$HAuCl_4$ and called AuNPs-GC. Then AuNPs-GC activated in a deaerated 0.5M H_2SO_4 solution by running 30 scans between 0.2 V and 1.6 V at a scan rate of 100 mVs^{-1}. All the electrochemical measurements (in presence or absence of serotonin) carried out in buffer phosphate solution using a Galvanostat/Potentiostat system (Dropsens, 400 µStat, Spain). The measurements performed using three electrode system in which an Ag/AgCl, platinum and modified glassy carbon were used as reference, counter electrode and working electrode, respectively and the cyclic voltammograms considered as biosensor responses. For determination of optimum electrodeposition time, the constant potential applied to glassy carbon for 60s, 120s and 240s. Additionally, in order to evaluation of temperature effect, the electrodeposition at fixed time (240s) carried out in 20˚C, 30 ˚C, 37 ˚C, 40 ˚C, 50 ˚C and 60 ˚C.

The results showed that the 240s and 37 ºC were the best time and the best temperature for electrodeposition of gold nanoparticles at the surface of glassy carbon electrode, respectively.

Keywords: *Serotonin, Neurotransmitter, GNP, Electrodeposition, Glassy carbon electrode, Temperature.*

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Tyrosinase - Based Biosensor for Determination of Tyrosine Using Cysteine and Chitosan Immobilization at Glassy Carbon Electrode

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Abstract

For determination of tyrosine a tyrosinase – based biosensor fabricated. For biosensor making, a glassy carbon electrode modified by gold nanoparticle electrodeposition. Then, cysteine, chitosan, and tyrosinase successively immobilized at the modified electrode surface. To evaluate biosensor performance, cyclic voltammetry separately carried out in the presence of different concentrations of tyrosine. All cyclic voltametry experiments performed in the potassium buffer phosphate, pH 7 and 25 °C and voltammograms considered as responses of constructed biosensor. Voltammograms showed that peak currents remarkably increased with rising concentrations of tyrosine. At next stage, the analytical parameters investigated using calibration curve. According to calibration curve, the linear range of biosensor determined from 30 µM to 50 µM. Detection limit and sensitivity determined 2.77 µM and 0.158 µA/µM, respectively. In addition, long-term stability

study indicated that biosensor response reduced from – 0.7 µA at beginning of the study to – 0.4 µA after two months. As a result, if this biosensor utilizes in human samples, some correction coefficient will be necessary to obtain precise results.

Keywords: *Tyrosinase Based Biosensor, Tyrosine, Electrodeposition, Gold Nanoparticles.*

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The Effects of Ascorbic Acid and Uric Acid as Two Important Interferer Agents on the Performance of Glutamate – Based Electrochemical Biosensor

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Abstract

The glutamate oxidase based biosensors have used for quantitative and qualitative determination of glutamate in food, biological samples. Since glutamate is one of the most important neurotransmitter that has an essential role in memory and learning mechanism and neurodegenerative disease (such as ischemia, epilepsy, Parkinson's and Alzheimer's diseases), therefore, in this work a glutamate oxidase based biosensor was made to measure glutamate in human serum samples. The interfere effects like ascorbic acid and uric acid as two important biological interferers that produce in human serum, are the greatest challenges for correct functions of glutamate oxidase based biosensor. For this reason we tried to clarify the role of these interferes agents on the responses and functions of made biosensors. For biosensor making, Chitosan and glutamate oxidase immobilized at the platinum electrode surface using standard procedure. In order to evaluate the function of fabricated biosensor, the voltammograms as biosensor's responses in presence of various concentration of glutamate obtained in 0.1 M buffer phosphate solution (pH 7.4). Afterward, each one of interferer agents separately added into the buffer phosphate, as a result the fabricated biosensor could record two voltammograms. One voltammogram related to

glutamate, while another one owned to each one of interferers. This investigation showed that the cathodic peak currents of interferers in which determined from voltammograms did not match with the glutamate peak current. In other words, the cathodic peak currents of interferers and glutamate occurred at different places in voltammograms and totally separated with each other. Consequently, these interferers could not disturb the performance of fabricated glutamate oxidase based biosensor

Key words: *Electrochemical Biosensors, Glutamate Oxidase, Interferer, Ascorbic Acid, Uric Acid*

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The Effects of Temperature and pH on the Responses of Glutamate Oxidase Based Biosensor

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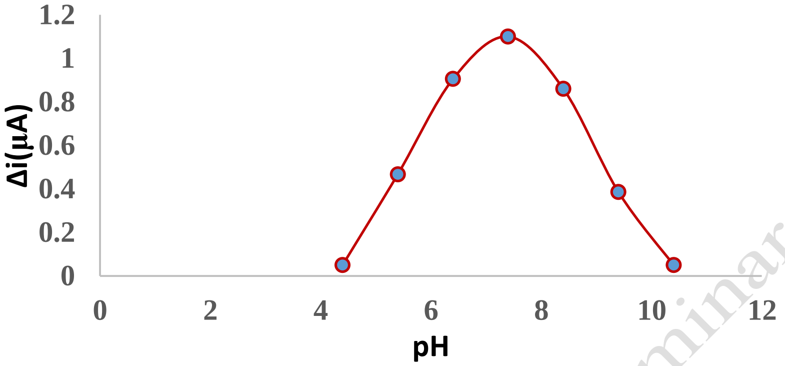
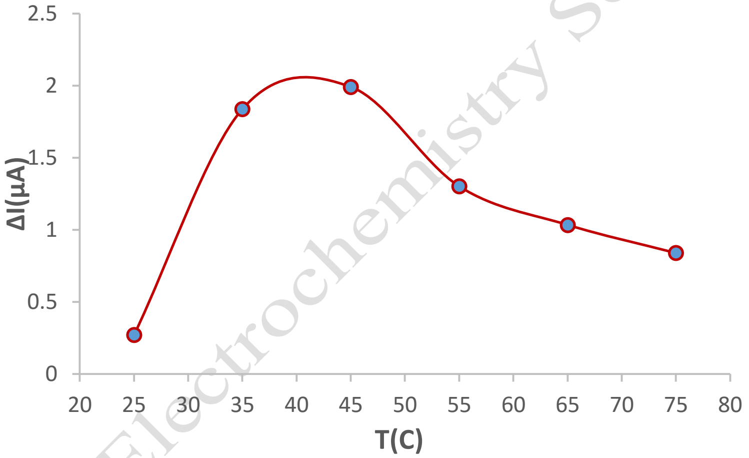
Abstract

Glutamate is the major excitatory neurotransmitter in the mammalian central nervous system (CNS). It's playing a major role in a wide variety of brain functions. However, increasing of the extracellular concentration of glutamate leads to excitotoxicity. Thus there is a need for rapid and sensitive methods to detect it in both clinical and food samples. In this research for measurement of glutamate release, a glutamate biosensor is fabricated using immobilizing of glutamate oxidase at the surface of platinum electrode. Since temperature and pH have a great effect on glutamate oxidase activity and fabricated biosensor performance, for this reason, the effects of temperature and pH on the responses of fabricated biosensor are investigated using cyclic voltametry method. The temperature effect on the responses of fabricated biosensor was evaluated between 25±1 °C and 75±1 °C and scan rate 10 mv/s using cyclic voltametry method. Also, the pH effects on biosensor's responses were evaluated in the range of 5.5 to 9.5. All experiments were performed in the buffer phosphate (0.1 M), 0.5×10^{-3} M glutamate. The results showed that the best response of fabricated biosensor was happened at 45°C and pH 7.4. So that, this temperature selected as working temperature for all further experiments. It is important to note that, pH 7.4 in which

obtained in this research, completely agrees with the optimum pH of glutamate oxidase catalytic activity.





***Key words**: Glutamate Neurotransmitter, Glutamate Oxidase, Cyclic Voltammetry, Glutamate Biosensor, Neurotransmitter, Glutamate*

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Fabrication of a very sensitive electrochemical sensor for determination of trace amounts of 2,4-dichhlorophenoxyacetic acid in soil and water samples

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Abstract

An indirect and very sensitive electrochemical determination of herbicide 2,4–dichlorophenoxyacetic acid was developed based on application of the molecularly imprinted polymer concept and using *double stranded* deoxyribonucleic acid as a biospecific substance. The sensor was prepared by electropolymerization of ortho-phenylendiamine on a modified pencil graphite electrode with chitosan and multiwall carbon nanotubes in the presence of DNA and also 2,4–dichlorophenoxyacetic as a template molecule. The current variations the concentration of 2,4–dichlorophenoxyacetic in the range of 0.01 to 10 pM and the detection limit was obtained as 0.4×10^{-14} M. This method has been successfully applied to the determination of 2,4–dichlorophenoxyacetic in the environmental water and soil samples with recovery rates ranging from 96% to 113%.

Keywords: 2,4–Dichlorophenoxyacetic acid; Deoxyribonucleic acid; Poly ortho–phenylendiamine; Molecularly imprinted polymer

Method

Electrochemical and impedance measurements were performed on Autolab electrochemical system PGSTAT 12 together with GPES and FRA 4.9 softwares, respectively. A conventional three–electrode system was used comprising platinum wire as the auxiliary electrode, Ag/AgCl/KCl (saturated) as the reference electrode and the working electrode is PGE. All leads were used with the length of 10 mm and diameter of 0.5 mm. For impedance measurements, the frequency range of 0.10 Hz to 100 kHz was employed. The AC voltage amplitude used was 5 mV and the equilibrium time was 1 min. Atomic force microscopy (AFM) and field mission–scanning electron microscopy (FE–SEM) were used by DME microscope with 95–50 E probe model and MIRA3TESCAN–XMU model, respectively. Initially, the PGE surface was modified with a mixture of chitosan and MWCNT. Then, to fabricate molecularly imprinted polymer–deoxyribonucleic acid/chitosan–multiwalled carbon nanotube/pencil graphite electrode (MIP–DNA/chitosan–MWCNT/PGE), cyclic voltammetry was used in the potential range 0 to 1.0 V vs. For extraction of the 2,4–dichlorophenoxyacetic (2,4–D) from the MIP layer, the electrode was immersed in the NaOH for 5 min.

Result and discussion

2,4–D, which is a chlorinated phenoxy compound, has been widely used as a systemic herbicide to control broadleaf weeds. This compound exhibits moderate toxicity and its application leads to serious skin and eye irritation among agricultural workers [1].

Electropolymerization of oPD on the surface of the chitosan-MWCNT/PGE was carried out using cyclic voltammetry as a film contained of PoPD was formed on the chitosan–MWCNT that had been placed on the surface of electrode. To investigate the dynamic changes of the sensor during its fabrication FE–SEM and AFM was used. The electorochemical impedance spectroscopy (EIS) and differential pulse voltammetry (DPV) were also used to characterize the constructed sensor during fabrication procedure. EIS is one method that is impressive for probing the properties of a surface modified electrode [2]. To further investigation of the sensor, differential pulse voltammograms of the construction procedure were studied in the presence $[Fe(CN)_6]^{4-}$ in 0.1 M KCl as a probe. No peak was appeared for the MIP and NIP electrodes before the template extraction. After removal of the 2,4-D the MIP electrode appeared a peak oxidation of Fe^{2+}. Since. Unlike to MIP, in the case of NIP no significant peak was found. After re-absorption of the 2,4-D, the peak declines, the space for oxidation of Fe^{2+} was decreased . This decreasing in the signal of oxidation of Fe^{2+} is proportional with concentration of 2,4-D.

The effect of some other substances was investigated on the electrode response and the sensor showed high selectivity toward 2,4–D. The different parameters that influent in results was optimized. So in this study a novel electrochemical sensor is proposed for selective detection of 2,4–D.

Conclusion

In this work, PoPD film together with DNA modified pencil graphite electrode was successfully prepared by cyclic voltammetry in acetate buffer solution (pH 4.3) on the chitosan-MWCNT/PGE surface. The fabricated sensor was applied for determination of 2,4-D in the soil and water samples with satisfactory results.

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Investigation of physico-chemical parameters effect on microbial fuel cell operation

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ABSTRACT

Microbial fuel cell (MFC) is a novel technology that can be used for electricity generation. MFC was optimized in terms of various operating conditions. To obtain a desirable performance, it is essential to understand the influential factors on the MFC. The performance of the MFC dependent on several factors such as temperature, pH, substrate concentration. The performance was analyzed under three temperatures. The various substrates that have been explored in such as acetate and glucose. The best pH obtained at 6.8. Therefore, operating conditions should be properly decided for the best operation in order to obtain power.

Keywords: MFC, pH, Substrate, Temperature

Introduction

MFC mechanism is an attractive renewable technology that can convert wastes into a directly usable form of energy. MFCs are inimitable in their ability to use bacteria as catalysts for the conversion of chemical energy to electrical energy. A MFC consists of anode and cathode compartments separated by a membrane. Microorganisms in the anode oxidize the organic substrates and produce electrons and protons. The protons are conducted to the cathode chamber through the membrane, and the electrons are carried through the external circuit. The performance of a microbial fuel cell can be influenced by several factors. In this study, the effects of operational conditions and applications having been discussed (1).

Methods

The dual-chambered MFC was made of Polytetrafluoroethylene(PTFE) with a volume of 1Liter in each chamber. The anode and cathode compartments separate by a proton exchange membrane. For better performance of the membrane, the (Nafion 115) was sequentially immersed in H_2O_2 (30%), deionized water, 0.5M H_2SO_4, and deionized water (each time for 1 h). Graphite electrodes were also used to transfer electrons, and to remove impurities from electrodes, they used 0.5 M HCl for 48 h (2).

Results and discussion

Effect of pH

MFCs operate pH values between 6 and 8. An increase in acidity will also decrease the voltage and current in MFCs. The highest voltage will be detectable when pH is obtained 6.8(2).

Temperature effects

MFCs are affected by temperature. It has been found that temperature is an essential parameter in MFC performance. The maximum voltage of MFCs at 30◦C, 50◦C and60◦C, were407.85, 428.66 and 482.15 mV and the maximum current of MFCs at 30◦C, 50◦C and 60◦C, were 0.92, 1.5 and 2.5 A. It demonstrates that the voltage and current of MFCs are seriously affected by operation temperatures (1,2).

Effects of substrates on power generation

The substrate has the dominant factor in determining performance. A broad range of substrates can be used in MFCs for electricity generation. A complex substrate helps MFCs to generate high power. The power generated with acetate (1190mV, 0.5M) was up to 42% higher than that produced with glucose (768.98 mV, 0.5M)(1).

Conclusion

One of the main characteristics which describe the performance of MFCs is the voltage of the cell which is affected by several factors such as substrate and operational parameters such as temperature, pH and etc. The optimal pH was 6.8. High temperatures can speed up power. Maximum voltage and electric current were measured to be 1190 mV and 3.1 A.

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Polyphenylenediamine/OH-MWCNTs Nano-composite Based Sulfamethoxazole-MIP Electrochemical Sensor for Analysis of Biological and Pharmaceutical Samples

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Abstract

Molecular Imprinting Technology (MIT) is a technique to design artificial receptors called Molecularly Imprinted Polymers (MIPs). In the two past decades, the preparation of MIPs and their applications have attracted the interest of many research groups with different interests [1]. MIPs were introduced in 1931 [2]. MIPs are synthesized by copolymerization process of the functional monomers and a cross-linking agent in the presence of template molecules. The extraction of template molecules results in creation of cavities with specific binding sites bearing defined shape, size and functional groups for the analyte. These cavities are potential to trap the template selectively from the mixtures containing closely related molecules [3].

In this communication the potential of a sulfamethoxazole-molecularly imprinted polymer, prepared by using polyphenylenediamine, triphenylamine, OH-functionalized multi-walled carbon nanotube (OH-MWCNT) composite for modification of the carbon paste electrode (CPE) to fabricate a selective sulfamethoxazole electrochemical sensor is reported. Electrochemical behavior of sulfamethoxazole on the investigated modified electrode and the optimization of parameters affecting sulfamethoxazole determination by the sensor were studied by using cyclic voltammetry technique. The calibration curve for sulfamethoxazole determination was obtained by incorporating the fabricated sensor as working electrode in differential pulse voltammetry systems. It was confirmed that the anodic peak current increased linearly with the analyte concentration in the range 1.0×10^{-6}–9.0×10^{-3} mol L^{-1} with a limit of detection 4.5×10^{-7} mol L^{-1}. The inter-day and intra-day relative standard deviations of the developed sensor for the determination of 10^{-4} mol L^{-}

[1] sulfamethoxazole, were determined as 3.45 and 7.44%, respectively. The selectivity of the proposed sensor was tested by determination of sulfamethoxazole in binary solutions containing sulfamethoxazole/glucose, sulfamethoxazole/lactose and sulfamethoxazole/ascorbic acid. The modified carbon paste electrode was successfully applied for the determination of sulfamethoxazole in some biological and pharmaceutical samples. The reliability of the method was examined by independent analysis of the samples using HPLC.

Keywords: *Sulfamethoxazole; Molecularly imprinted polymer; Polyphenylenediamine; Multi-walled carbon nanotube; Electrochemical sensor*

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Nano Electrochemistry

Synthesis and Characterization of Pd Nanocatalysts Based on N-Doped Graphene for Methanol Oxidation in PEM Fuel Cells

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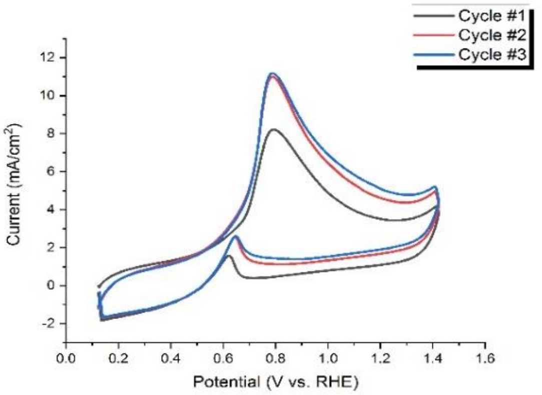
Abstract

The Pt nanocatalysts are the most promising material in anodic catalysis for polymer exchange membrane fuel cells. The Achilles' heel of these types of catalysis is the intense CO-poisoning that hinders the activation sites of the Pt-catalysis[1]. In these respects, the research efforts have been done to develop highly active and cost-effective new electrocatalyst. Two main factors that should be considered corresponding to them are: (i) the well-designed architect of nanoparticles on a structured substrate and (ii) advanced materials for the support [2]. Pd-catalysis is chosen as a cheaper substitute to oxidize methanol, decorated on N-doped graphene. Shifting the Fermi energy to a more positive level happens due to the substitution of N into graphene structure and the outcome is a better electronic conductivity. Utilization of urea as a nitrogen source and the hydrothermal method, helped the graphene oxide to have a hydrogel of NrGO. Impregnation of 20% Pd on this porous substrate resulted in Pd/NrGO. XRD analysis is a good evidence of different Pd facets, i.e. (111), (200) and (220) are related to 39.31^0, 44.86^0 and 66.47^0 respectively. The cyclic voltammetry of this catalyst shows a great improvement in methanol oxidation in comparison to Pt/C. The onset peak of MOR in Pt/C is 1.0 V[3] while Pd/NrGO shifts it to 0.62 V and with consideration of commercial catalyst in mind, the synthesized catalyst increased I_f from 0.9 V[3] to 11.18 V.



Methanol Oxidation voltammogram for Pd/NrGO. Electrolyte: 1 M KOH+ 1M CH_3OH. Scan rate: 20 mV/s. Reference Electrod:Ag/AgCl

Key Words: Methanol Oxidation, NrGO, Pd electrocatalysis

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Glucose electrochemical oxidation at modified electrode with ZnO based nano catalyst

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Abstract

In this work, at first we synthesized 1 % Ag doped ZnO with hydrothermal method as electro-active catalyst for glucose oxidation. ZnO nanostructure was prepared using monosaccharide templates. The effect of dopant concentration and synthesis conditions such as temperature on the structural morphology and electro-catalytic properties of final product was studied. The electrochemical oxidation of glucose was evaluated by GCE modified with synthesized Ag doped ZnO nanostructures. The scan rate effect, voltammetric parameters and electrolyte type on the electro-oxidation response of glucose was studied. Obtained results revealed improvement of glucose electro-oxidation response that confirmed the applicability of the prepared modified electrode for glucose bio fuel cells.

Keywords: Fuel cell, Electrocatalyst, Hydrothermal, ZnO, Glucose, Electro oxidation.

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Determination of Vitamin B6 in Food Samples Using Nanostructure Based Electrochemical sensor

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Abstract

A highly sensitive and fast response electrochemical sensor based on ZnO/CNTs and 1-ethyl-3-methyl imidazolium tetrafluoroborate room temperature ionic liquids carbon paste electrode (ZnO/CNTs/ 1-E-3-MITFBr/CPE) is proposed for the determination of vitamine B_6 in real samples. At first step, we study application of the ZnO/CNTs nanocomposite for the preparation of carbon paste electrode modified with ionic liquid as a suitable and high conductive binder. The electro oxidation of vitamine B_6 occurs at a potential about 850 mV at a surface of ZnO/CNTs/ 1-E-3-MITFBr/CPE and this mount is better than the bare carbon paste electrode at the optimized condition. In continuous, other voltametric techniques such as syclic voltametry, chorono amprometry and differencial pulse voltammetry are studied. The differencial pulse voltametry (DPV) peak currents of vitamine B_6 show good linear dynamic range (0.05-650 µM) with a detection limit of 0.01 µM. Finally, the proposed sensor was used as highly selective sensor for determination of vitamine B_6 in real samples.

Keywords: vitamine B_6 analysis, Voltammetric sensor, Food samples, Modified electrode

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High sensitive voltametric nanosensors for determination of Xanthine in the prensece of Caffeine in fish samples

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Abstract

Caffeine is a central nervous system stimulant of the methylxanthine class. It is the world's most widely consumed psychoactive drug. Unlike many other psychoactive substances, it is legal and unregulated in nearly all parts of the world. The most prominent is that it reversibly blocks the action of adenosine on its receptor and consequently prevents the onset of drowsiness induced by adenosine. Caffeine also stimulates certain portions of the autonomic nervous system. In this work, CuO/CNTs nanocomposite with room temprature d ionic liquid carbon paste electrode fabricated for determination of xanthine in the presences of caffein in food samples. Nanopowders was characterized by SEM, and TEM. The results obtained confirm the presence of CuO in nanopowders produced during chemical precipitation. In continuous, Electrochemical behavior of caffein and xanthine at the CuO/CNTs/IL /CPE had been investigated in phosphate buffer solution (PBS) by cyclic voltammetry (CV).other voltametric techniques such as chronoamperometry (CA) and differential pulse voltammetry (DPV) were investigated. The experimental results shows wide linear dynamic range and ofcourse good detection limit was found to be 5.0 nM. The proposed sensor was successfully applied for the determination of xanthine in the prensece of caffein in fish samples.

Keywords: Food sample analysis, Voltammetry, Caffein, Xanthine

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Electrochemical label free immunosensor for the determination of PSA biomarker

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Abstract

Prostate cancer is the most common cancer in men in the world and is the second leading cause of death from men's cancer in the world. Detectable level of prostate specific antigen in (PSA) human serum reveals the intensity of cancer. It is believed that the consideration of the concentration range of cancer biomarkers and cells in the early stage of the cancer and metastases in the development of novel diagnostic technology is prominent [1]. Due to increasing wide response range, high selectivity and sensitivity for determination of PSA tumor marker in different samples, we introduced this proposed immunosensor.

Keywords: *Electrochemical immunosensor, PSA, Nanocomposite, SWV, CV*

Methods

In this research, graphene oxide (GO) was synthesized using the modified Hummer's method from commercial graphite powders [2], then the reduction process with $NaBH_4$ was done. Then, the nano-composites (rGO-AuNPs) were synthesized by reduced graphene oxide and gold nanoparticles and used for modifying of the surface of electrode. PSA antibodies were added to the modified electrode and the electrochemical behaviors of immunosensor were considered by applying cyclic voltammogram (CV) and square wave volatammogram (SWV).

Results and discussion

The SEM images of nano-composites (rGO-AuNPs) are illustrated in Fig. 1. Fig. 2 shows the CV varies at each immobilization stage in 0.1 M KCl containing 5 mM $Fe(CN)_6^{3-}$ at scan rate

100 mV s^{-1}. After the modification of the GC surface, the current response clearly increased in comparison with the bare GC, due to the increasing of the effective surface area. After the antibody was dropped onto the surface of modified electrode, the current response obviously declined owing to creating the barrier and decreasing active sites for electron transfer procedure of $K_3Fe(CN)_6$. The fabricated immunosensor was utilized to survey the relationship between the SWV peak current and PSA concentration. The equation of the calibration curve is I(μA) =0.3329 log C(ng ml^{-1})+22.013 (R^2=0.9968). The detection limit (LOD) was calculated 0.06 ng ml^{-1}.

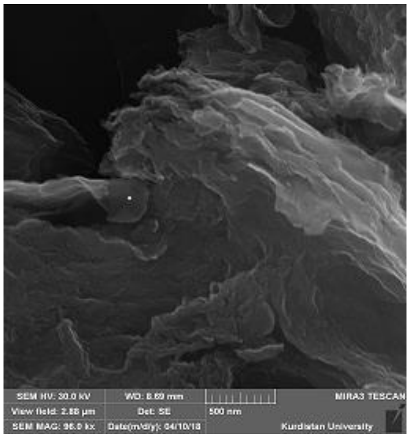

Fig. 1. SEM images of (rGO-AuNPs)

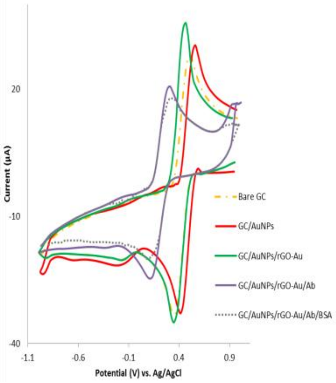

Fig. 2. CV response

Conclusion

The proposed immunosensor is a beneficial sensor for detection of PSA because of being label free with the simple materials

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An Electrochemical Nanostructured Sensor For Determination of Ferulic Acid in Food Samples

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Abstract

CuO/CNTs nanocomposite and room temperature ionic liquid carbon paste electrode (CuO/CNTs/IL/CPE) were fabricated to determine ferulic acid in corn milk, wheat flour, and corn cider samples. At first, CuO/CNTs was characterized by transmission electron microscopy (TEM). In continuous, The electro-oxidation of ferulic acid investigated in phosphate buffer at the surface of modified electrode which was much better in comparison with bare carbon paste electrode. Other electrochemical techniques were also examined including cyclic voltammetry, differential pulse voltammetry (DPV) and chronoamperometry at CuO/CNTs/CPE/IL. At optimized conditions for ferulic acid analysis, voltametric peak currents of ferulic acid showed a wide linear dynamic range with a good detection limit of 5.0 nM. Finally, the proposed sensor was used for determination of ferulic acid in real samples with good selectivity and high sensitivity.

Keywords: ferulic analysis, carbon paste electrode, corn milk, corn cider

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Fabrication of vanillin electrochemical sensor using glassy carbon electrode modified with Au@Pd /PMo12 nanohybrid

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Abstract

Vanillin is a widely used edible spice with strong milky flavor, it can be found in the seeds of vanilla or be synthesized. The determination of this food additive is very important in food samples due to high side effect of it in high level.

In this research, we fabricated a highly sensitive electrochemical sensor based on glassy carbon electrode modified with Au@Pd /PMo_{12} nanoparticle (Au@Pd /PMo_{12} /GCE) for determination of vanillin in food samples. The Au@Pd /PMo_{12} /GCE showed the good catalytic activity for electro-oxidation of vanillin and reduced the oxidation over-potential of vanillin in aqueous solution. The as-prepared electrode was successfully used for analysis of vanillin with limit of detection 6.0 nM. Finally, the proposed sensor was used for determination of vanillin in food samples.

Keywords: *vanillin, Au@Pd /PMo_{12} /GCE, electrochemical sensor*

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Au nanoparticle decorated on carbon ceramic electrode as a novel platform for sensitive detection of hydrogen peroxide in human urine

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Abstract

There are a lot of interests in determination of hydrogen peroxide in analytical tasks because of great importance of hydrogen peroxide in different fields, such as food, clinical, pharmaceutical, industrial and environmental analyses. So development a high sensitive, selective and economical method for hydrogen peroxide determination is a challenge in many research groups.

In this study gold nanoparticles were electrodeposited on the surface of carbon ceramic electrode for the determination of hydrogen peroxide in human urine. Morphology and composition of the resulting electrode was characterized by scanning electron microscopy (SEM). The electrode displayed excellent response to the electro-reduction of hydrogen peroxide which is linearly related to its concentration in the range from 0.2 μM to 1200 μM. The detection limit of the developed sensor was 0.12 μM, and the sensitivity was 949 A M^{-1} cm^{-2}. The modified electrode was used to determination of hydrogen peroxide in hair coloring creams as real samples.

Keywords: Gold nanoparticles, Carbon ceramic electrode, Hydrogen peroxide

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Chitosan/porous reduced graphene oxide as active hybrid material for the electrochemical detection of ciprofloxacin

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Abstract

Ciprofloxacin is an antibiotic used to treat a number of bacterial infections [1]. This includes bone and joint infections, intra-abdominal infections, certain type of infectious diarrhea, respiratory tract infections, skin infections, typhoid fever, and urinary tract infections [2,3]. In this study, a new matrix based on a chitosan-porous reduced graphene oxide hybrid (CS-prGO) was prepared and characterized. Modification of a glassy carbon electrode (GCE) with CS-prGO (CS-prGO/GCE) using drop casting allowed for the selective analysis of ciprofloxacin with a limit of detection of 45 nM with a linear range between 0.1-100 μM by differential pulse voltammetry (DPV). In addition, the analytical performance of the proposed sensor was successfully conducted for the determination of ciprofloxacin in real samples, making CS-prGO/GCE electrodes promising interfaces for bio-electrochemical applications.

Keywords: *Ciprofloxacin, Chitosan, Reduced graphene oxide, Electrocatalysis*

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Synthesis of Pt nanoparticles on reduce graphene oxide by gamma radiation in order to methanol electrooxidation

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Abstract

Because of wide range of applications such as wastewater treatment, biosensors, electrochemical sensors, energy storage systems and fuel cells, investigations have been focused on the synthesis of supported metal nanoparticles [1]. The properties of these materials are strongly related to the method of preparation and it is one the major topics studied in direct methanol fuel cell (DMFC) [2]. Different reducing agents have been reported for the synthesis of metal nanoparticles but there is still a need to find eco-friendly, easy and effective method to produce nanoparticles with a more homogeneous size and shape [3, 4]. To this reason at this study, the ability of synthesis nanoparticles Platinum (Pt) on reduce graphene oxide (rGO) by gamma radiation method at room temperature and ambient pressure was considered. The reduction of Pt/rGO was confirmed by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and cyclic voltammetry. Pt nanoparticles were successfully dispersed on the surface of graphene sheets (Fig.1, 2). The obtained materials displayed the face-centered cubic (fcc) structure of Pt with mean nanoparticles sizes of around 5.578 nm (Fig.1, 2). A value of 1.056 cm^2 of the electrochemical surface area (ECSA) was obtained for Pt/rGO in acid medium with 50 mV/s scan rate. The experimental results reveal that this procedure offers a facile, economic, green route for develop electrocatalysts without using additional reducing agent or producing undesirable by-products.

Keywords: *Gamma-ray, Pt nanoparticles, rGO support, Reduction, radiation process.*

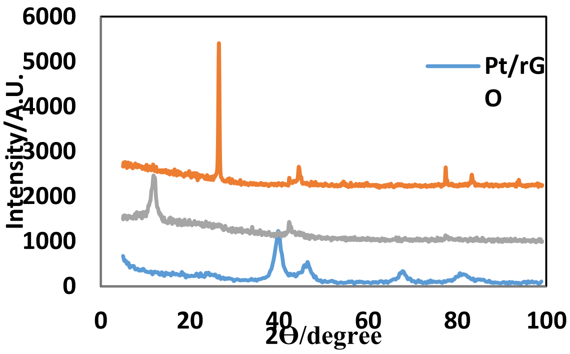

Fig. 1: X-ray diffraction patterns of graphite, GO and Pt/rGO

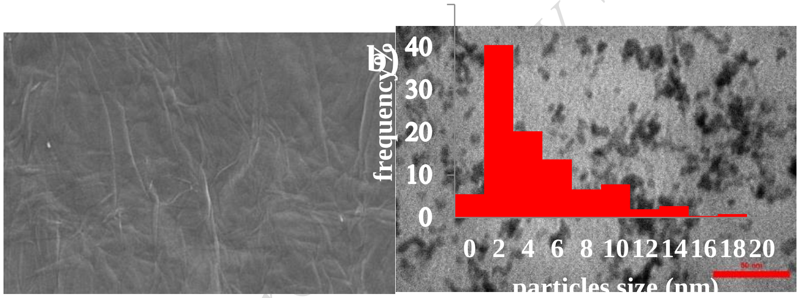

Fig.2: a) SEM image of GO at 200 nm magnification. b) TEM image of Pt/rGO obtained by gamma irradiation

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Synthesis of RGO/CNT nanocomposite

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Abstract

In this work, graphene oxide (GO) was synthesized through Hummer's method and reduced to graphene (RGO) through thermal reduction. Then, a composite was prepared from GO and functionalized carbon nanotube namely GO/CNT under ultrasonic irradiation and finally was converted to RGO/CNT by heating. The physical characterization of synthesized composite was accomplished using X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and N_2-adsorption-desorption techniques. The specific surface area of the composite was 564.48 m^2 /g.

Graphene with the merits of high electron transfer rate, large surface area, high conductivity as well as thermal and chemical stability has been tested as a promising cathodic material for Li–air batteries due to its very high discharge capacity and high round-trip efficiency. Carbon nanotubes (CNTs) have also been investigated as cathodic materials for nonaqueous Li–O2 batteries because of their high chemical and thermal stability and high conductivity resulting from their unique structures.

Keywords: nanocomposite, synthesis, Graphene, CNT, Li–O2 batteries

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Preparation of reduced graphene quantum dots for electrocatalytic applications

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Abstract

In this study reduced graphene quantum dots (rGQD) were electrodeposited on the surface of pencil lead electrode for electrocatalytic applications. Scanning electron microscopy, electro- chemical impedance spectroscopy and cyclic voltammetry techniques were used for characterizing the prepared electrodes. The prepared electrode was studied in detail in Potassium hexacyanoferrate(III) solution and active surface area was calculated and compared with other electrodes. The developed electrochemical sensor responds efficiently to Adenine over the concentration range 0.2-120 µM with the detection limit of 112 nM and suitable sensitivity. High performance of the developed sensor is attributed to the large surface-to-volume ratio, excellent biocompatibility of rGQD and abundance of hydrophilic edges as well as hydrophobic plane in rGQD which enhances electrocatalytic performance of the modified electrode.

Keywords: Reduced graphene quantum dots; Pencil lead electrode, Adenine.

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Application of molecularly imprinted polymers in electrochemical biosensors based on carbon nanomaterials

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Abstract

Over the recent years, Molecularly imprinted Polymers (MIPs) have attracted the attention of many scientists because of their outstanding ability to be used as natural receptors, high stability, low cost, and easy preparation in electrochemical biocomponents. These polymers are built by creating three-dimensional hollow spaces in which monomers and crosslinkers bind together in the presence of the target molecule as the desired analyte, and the target molecule, through its specific functional groups, forms a monomer- The crosslinker is attached, and this feature increases these polymers selectivity significantly. In addition to polymers, various nanomaterials such as graphene and carbon nanotubes are also used in electrochemical biosensors. In this paper, in addition to various techniques for making the electrode using molecularly imprinted polymers and carbon nanomaterials, and their mechanism of action, various aspects of the use of these polymers in electrochemical biosensors have been investigated. By understanding how these polymers work in the electrochemical biosensors, we can say that in the future we will see further advances in this technology.

Keywords: *Molecularly imprinted Polymers, Biosensors, Carbon Nanomaterials, Electrochemical Biosensors*

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Design of Selective Hydrogen Gas Sensors using Electrospun CoO Nanofibers

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Abstract

Metal-oxide-semiconductor (MOS) gas sensors have gained special focus driven by their diverse applications in air-quality detection, inflammable-gas inspection, environmental monitoring, healthcare, defense, security, so on [1].

In this paper, we synthesized cobalt (II) oxide nanofibers. Cobalt Oxide (CoO) nanofibers were fabricated by electrospinning a hybrid solution, which is a mixture of the $CoCl_2.6H_2O$ sol precursor, poly vinyl pyrrolidone (PVA), polyvinyl alcohol (PVA) and solvent. By calcining at three Temperatures 100, 200 and 300 °C the polymeric components were decomposed and a structure of CoO nanofibers was obtained. The structure and morphology of different nanofibres were characterized by various techniques such as FT-IR, XRD, SEM and EDX. The FT-IR spectrum confirms the synthesis of cobalt (II) oxide and The XRD spectroscopy confirms the cubic crystalline structure of CoO [2]. The sensing results indicate that electrospun CoO nanofibers is a promising material for sensing of 25 ppm H_2 even at room temperature and have good reversibility. Nanofibers CoO had highly selectivity and do not respond to 25 ppm of ethanol, methanol, chloroform, Benzaldehyde, acetone. CoO nanofibers with high surface area and porous configuration are advantageous to achieve high and quick gas response via effective and rapid diffusion of analyte gas onto the sensing surface.

***Keywords**: Nanofibers, Sensors, Semiconductor, Cobalt (II) Oxide*

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Improved Carbon Monoxide Sensing Properties of CuO Electrospun Nanofibers

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Abstract

Sensitivity and selectivity of gas sensors have improved with the use of Metal-oxide semiconductor [1]. It is well-known that chemical gas sensor performance features such as time response, stability, selectivity, durability, sensitivity, reproducibility and reversibility are largely influenced by the properties of the sensing materials used [2].

The electrospinning process was used for CuO nanofibers synthesis. We used a polymeric solution, which is a mixture of the $CuCl_2$.6HO, Poly vinyl pyrrolidone (PVP) and polyvinyl alcohol (PVA) and solvent. eventually, nanofibers were calcined to remove organic compounds at temperatures of 400°C for 2h. The structure and morphology of nanofibers were characterized by various techniques such as FT- IR, XRD, SEM and EDX. The FT-IR analysis was performed to confirm the presence of characteristic vibrational peaks pertaining to CuO nanofibers. The XRD spectroscopy confirmed the crystalline structure of CuO monoclinic [3]. During the gas sensing experiment, response and selectivity of CuO-based sensors for detection of CO were studied. The sensors responses were measured in presence of 350 ppm CO at the 175°C. The short response time and the short recovery time and excellent repeatability were the features of these sensors. Also these sensors had good selectivity and give a very small response to ethanol, methanol, acetaldehyde, aldehyde and n-hexane. Consequently, nanofibers CuO, due to porous configuration, is an attractive proposition for advanced CO measurement.

***Keywords**: Nanofibers, Semiconductor, Gas sensor, CuO*

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Determination of Cabergoline with Using Modified Screen Printed Electrode

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Abstract

In the present work, a screen printed electrode modified with Co_3O_4 nanoparticles (Co_3O_4/SPE) was investigated for its ability to serve as a sensor towards cabergoline. The Co_3O_4/SPE was found to exhibit an electro-catalytic activity for the electrochemical oxidation of cabergoline in 0.1 M phosphate buffer solution (pH 7.0). Cyclic voltammetry and differential pulse voltammetry were employed to study the electrochemical properties of the modified electrode. The electrochemical oxidation of cabergoline occurs at +0.6 V with a limit of detection found to be 0.2 µM and with linear range of 1.0 µM to 70.0 µM. The prepared modified electrode showed high sensitivity, stability and good reproducibility in response to cabergoline, confirming its usability for the accurate determination of trace amounts of cabergoline in pharmaceutical and clinical preparations.

Keywords: Cabergoline, Electrochemical Reaction, Co_3O_4 *nanoparticles, Differential Pulse Voltammetry.*

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Modified Screen Printed Electrode for Electrochemical Determination of Carvacrol

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Abstract

In the present work, a fast electrochemical sensor for determination of carvacrol was developed based on Co_3O_4 nanoparticles modified screen printed electrode. Carvacrol could be determined directly by electrochemical oxidization with the modified electrode. Co_3O_4 nanoparticles increased electrochemical response to carvacrol. Experimental variables, such as the deposited amount of the modifier suspension, pH of the supporting electrolyte and the potential scan rate were optimized by monitoring the electrochemical responses of carvacrol. Under the optimum conditions, the modified electrode showed a wide linear dynamic range of 10.0–500.0 μM with a detection limit of 1.5 μM for the voltammetric determination of carvacrol. The prepared modified electrode showed high sensitivity, stability and good reproducibility in response to carvacrol, confirming its usability for the accurate determination of trace amounts of carvacrol in pharmaceutical and clinical preparations.

Keywords: Carvacrol, Electrochemical Reaction, Co_3O_4 nanoparticles, Differential Pulse Voltammetry.

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Electrochemical Aptasensor for detection of prostate specific antigen based on reduced graphene gold nanocomposite

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Abstract

Prostate cancer is the second most cause of cancer related mortality in man worldwide[1] . The early cancer detection is crucial for improving survival rate and effective prognosis[2]. Prostate specific antigen (PSA) as the prostate cancer biomarker is a promising tool for cancer early detection[3]. In this work, we report a label-free electrochemical aptamer-based biosensor for amperometric and impedimetric detection of PSA based on reduced graphene oxide/Au (rGOAu) nanocomposite.

Materials and methods

Modified rGOAu electrode was employed to increase the sensitivity of PSA detection, using PSA aptamer. First, the graphene oxide was synthesized by a modified Hummer method. Then the $HAuCL_4$ and graphene oxide were simultaneously reduced through a chemical reduction method and rGOAu nanocomposite was obtained. The thiolate PSA aptamer was incubated with rGOAu nanocomposite in 4˚C for 24 h and was conjugated with rGOAu through self-assembly of Au-S groups. Then aptamer/rGOAu was combined with nafion polymer and the aptamer/rGOAu/nafion were sedimented on the surface of the glassy carbon 2 mm electrode. Finally, the performance of the fabricated biosensor was investigated by using an Ag/AgCl reference electrode and a platinum counter electrode in two different ranges of antigen concentrations including 0.1-0.9 ng/ml and 2.5-10 ng/ml. potassium hexacyanoferrate ($K[FeCN_6{}^{3-/4-}]$) and carbon dot copper (Cu/CD) were used as redox probes. A hydrothermal method was used for Cu/CDs synthesis using di ammonium hydrogen citrate as the source of carbon. The interaction of aptamer with PSA have been studied by the cyclic voltammetry (CV), square wave voltammetry and electrochemical impedance spectroscopy (EIS).

Results and discussion

To monitor the fabrication of aptasensor, the CV and EIS tests were employed in K [FeCN6 $^{3-/4-}$]. Figure 1a illustrates the EIS characterization of the aptasensor. For the bare electrode an small semicircle was observed in Nyquist plot and a low charge transfer resistance (R_{ct}) was measured to be 209.065 Ω. After modification of electrode with rGOAu the R_{ct} value decreased to 133.922 Ω, indicating that the generated layer is accelerating the electron transfer due to its high electron conductivity. After the modification of electrode with rGOAu/nafion, the R_{ct} value increased to 260.4366Ω, because nafion polymer act as a barrier against electron transfer. The R_{ct} value increased dramatically to 415.5144 Ω, as the aptamer was added to the rGOAu/nafion, which is due to the electrostatic repulsive of negative charge phosphate backbone of the aptamer and the negative ions in the electrolyte. Finally by introducing the PSA with the concentration of 2.5 ng/ml the R_{ct} value reached to 436.9666 Ω, which is due to the resistance increase on the electrode surface. The results are in accordance with the results obtained by CV measurements. The analytical performance of the aptasensor was examined with CV, SW and EIS. Figure 1b illustrates the SW results of PSA in the range of 2.5-10 ng/ml. By increasing the PSA concentration the redox signal of K [FeCN6 $^{3-/4-}$] decrease. Figure 1b also shows a trend in the changes of PSA concentration against current. The results are in accordance with the results obtained by CV and EIS measurements. The CV and SW measurements were also done in Cu/CD solution. Figure 1c shows the SW measurement of PSA concentrations in the range of 2.5-10 ng/ml in Cu/CD solution. As the PSA concentration increase the redox signal of Cu/CD decrease. Figure 1c also shows a trend in the changes of PSA concentration against the current. The results are in accordance with the results obtained by CV measurements. Under optimal conditions, the aptasensor exhibits a linear range from 0.1 to 10 ng/mL, with a limit of detection as small as 0.05 ng/ml. The present aptasensor is highly selective and sensitive and shows satisfactory stability and repeatability.

Conclusion

These results indicate that the reported aptasensor has great potential in detection of PSA.

Keywords: aptamer, electrochemical aptasensor, graphene gold, prostate cancer, PSA

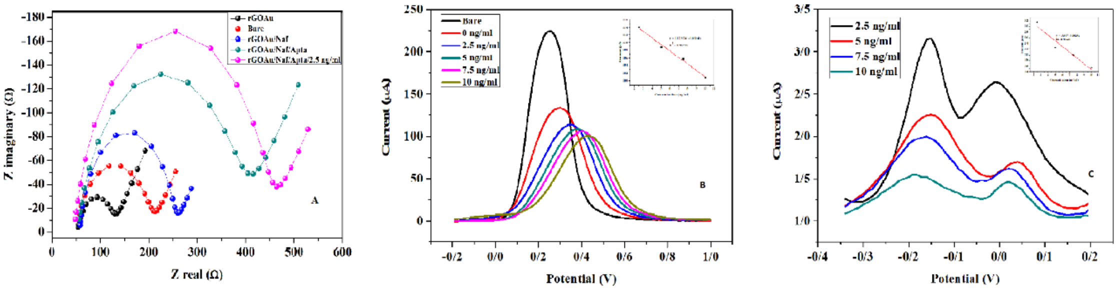

Figure1-. Electrochemical impedance spectroscopy of the different electrode in PBS (10mM, pH=7.4) solution containing 2mM Hexacyanoferrate (A). Square wave voltammetry responses and calibration curve of the aptasensor after incubating in PSA/PBS solution containing (2.5, 5, 7.5, and 10 ng/ml) and the linear relationship between the current and concentration of PSA in 2mM Hexacyanoferrate (B).and in 40mg/ml Cu/CD(C).

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Synthesis of Titanium Oxide nanotubes with microplasma electrochemical method

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Abstract

This work is devoted to synthesis of the Titanium Oxide nanotubes on a titanium foil has been done by atmospheric-pressure argon microplasma-assisted electrochemistry in an organic electrolyte with electrolytes composed of ethylene glycol, acid fluoride, and water. FESEM images were indicated that, due to the cathode structure, length and diameter of the nanotubes enhanced from 1.3 to 3.8 µm and 20-25 nm to 50-70 nm when the microplasma current increased from 3 to 7 mA, respectively.

Keywords: TiO_2 nanotubes, Atmospheric pressure microplasma, Electrochemistry, Material characterizations.

Introduction

Among the conductor-based nanoparticles, titanium oxide (TiO_2) has drawn strong interest for its potential use in gas sensing, photo catalysis, solar cell, electrochromic devices], water cleaning and biocompatibility improvement [1, 2]. It is well known that properties and performance of TiO_2 depend strongly on its structure and morphology as the nanoparticles, nanotubes, nanorods, nanowires, and nanoleaves, in a mesoporous layer [3, 4]. These characteristics may also participate in improving the performance of the device by increasing its efficiency or permitting new reaction pathways. This research paper revolves around the TiO_2 nanotube synthesis by using the micro plasma assisted electrochemical.

Method

Titanium foil with 0.5 mm in thick was set (as the anode) inside the reaction cell containing an electrolyte (consisting of ethylene glycol solvent with addition of 0.2 wt.% hydrofluoric acid (HF) and 2 vol.% DI water) at room temperature. At first, the surface of Ti foil was polished with 400, 600 and 1200 grit silicon carbide abrasive paper, then ultrasonically cleaned in acetone, ethanol and deionized water for 15 minutes respectively and finally dried in air at room temperature. After the microplasma-assisted electrolysis, the samples were rinsed with distilled water and acetone for 10 minutes and then were annealed at 250º C, 350º C and 500º C in air for 1 h. The reaction time was 60 minutes in different process conditions. The morphology of the Ti foils was analyzed by field emission scanning electron microscope (Model TE-SCAN-MIRA3).

Result

Morphological characteristics of Ti foils after plasma-treated in aqueous solution show in Fig. 1. These images confirm the formation of nanotubes on Ti foil. As seen, diameter of the nanotubes increased from nearly 20– 25 nm to 50–70 nm, when the current density enhanced from 3 mA to 7 mA.

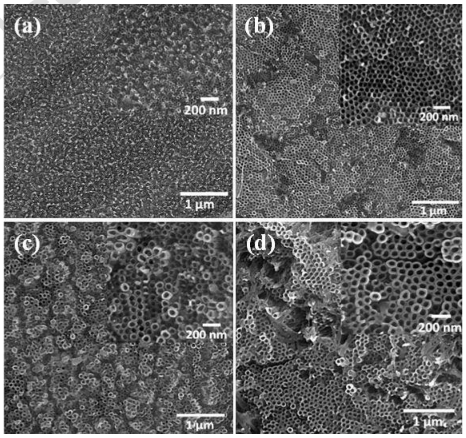

Figure 1: FE-SEM images of plasma treated samples at (a) 3 mA, (b) 4 mA, (c) 5 mA and (d) 7 mA current (in air, for 1 hour).

Conclusions

The use of the microplasma as a cathode in the electrochemical method in comparison with other cathodes accelerates the processes involved in the TiO_2 nanotube synthesis. In particular, we have demonstrated that the diameters and length of TNT can be tuned by changing the microplasma parameters such as discharge current.

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Design and Fabrication of microplasma-electrochemical device for synthesis of nanoparticles

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Abstract

Recently, microplasma electrochemical method has attracted considerable attention in a wide variety of applications from bacterial inactivation to nanoparticle synthesis in liquid phases. In the typical conventional electrochemical cell, reactions take place between solid electrodes and the ionic liquids an electrolyte. In microplasma electrochemical method, plasma discharges is coupled to electrochemical systems to induct reactions without using a solid electrode in the solution. In this new method, microplasma-liquid interactions can be accelerated the electron transfer rate and accordingly enhance the rate of metallic oxide.

Keywords: Atmospheric microplasma, Electrochemistry, Microplasma-liquid interactions, Optical emission spectroscopy.

Introduction

The microplasma operates at atmospheric pressure as the cathode in electrode geometries where at least one dimension is less than 1 mm^2. Microplasmas are defined as spatially confining plasmas with dimensions below about a millimeter or less that are different from conventional plasmas at lower pressures. This new class of plasma organization has fascinating features such as small physical size, atmospheric pressure stability and equilibrium thermodynamics [1-4]. Microplasma usually contains ultraviolet (UV) radiation, excited species, and charged particles, which interact with surface of the liquid. The plasma-liquid interface becomes a reaction region where many particular chemical and physical processes occur under the electron /positive ion irradiation from the plasma [5].

Method and Results

Figure 1 shows a schematic view of the microplasma electrochemical setup. To ignite an atmospheric pressure direct-current (DC) plasma on the liquid surface, a stainless steel capillary tube as a cathode (0.5 mm inside diameter, 0.7 mm external diameter and 9 cm length) was located at 5 mm above the liquid surface and 3 cm away from Ti foil (anode). Ar gas flow was kept at 200sccm and the applied voltage to the capillary tube was 2 kV (reduced to 1.2 kV). The plasma was kept stable by a ballast resistor (RA = 100 kΩ). The total applied voltage between the two electrodes and the microplasma current was measured using a high voltage probe (Tektronix P6015A) and resistor Rc (Rc = 100 Ω). A characteristic of microplasma Optical emission spectroscopy (OES) is often used as an ordinary technique to determine the discharge parameters, especially in plasma treatment on material surfaces. The emission spectrum was measured above and near the solution surface. It showed that, in addition to Ar lines, N2 second positive band (337.1 nm, 357.7 nm), OH molecular band (between 306.4 – 308.9 nm), atomic hydrogen (656.3 nm) and atomic oxygen (546 nm, 590 nm 726 nm, 777 nm and 911 nm) have been detected. The relative strengths of the spectral lines changed with changing discharge current. As the plasma discharge current increased to 7 mA, there were no significant changes in the intensities of Ar lines, while the intensities of some spectral emissions such as OH and O were increased. A possible explanation for this phenomenon is that an increase of discharge current delivered to the plasma is absorbed by electrons and ions. When the discharge current is enhanced, the electron density in the plasma increases. Because of a higher flux of the electrons on the solution surface, an increase is observed in the amount of gas species such as hydrogen peroxide, hydrogen, O and OH. In the following sections we investigated further effect of the produced species by the plasma on the experimental results.

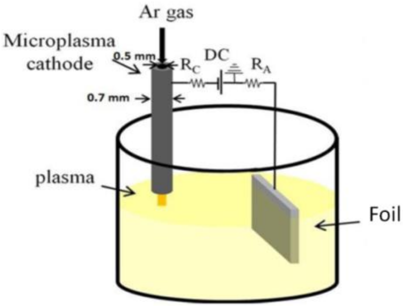

Figure 1: a schematic view of the microplasma electrochemical setup

Conclusion

Consequently, microplasma-liquid interactions produce the active species such as electrons, ions, excited OH, metastable Ar, and nitrogen-related species. Some of these highly reactive species such as plasma-generated electrons have been used to reduce the metal cations similar to a standard electrochemical cell. In these structures, the anode can participate in the synthesis such as oxide or be an inert electrode such as Pt with the metal salt in the electrolyte providing the material for the NP synthesis.

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Manufacture of electrochemical nanobiosensor for detection of bacterial Lipopolysaccharide

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Abstract

Here in, an aptasensor was designed to electrochemical detection of Lipopolysaccharide (LPS). Thiol-modified aptamer exhibiting high affinity (Kd = 11.9nM) to LPS was immobilized on a glassy carbon electrode using reduce graphene oxide gold nanocomposite as transducer and carbon quantum dot magnesium (Mg.CQDs) as reduce probe. A good linear relationship of the current and the LPS concentration was demonstrated in a broad dynamic detection range of 0.1–0.9pg/ml and low detection limit 0.01pg/ml.

Introduction

Lipopolysaccharide is one of the main components of the outer wall membrane of all gram-negative bacteria. Bacterial Lipopolysaccharide molecules known as endotoxin in some sources**.**

LPS with high chemical stability due to the death of gram-negative bacteria cells, as well as some Live bacteria are secreted and released into the environment(Miao 2013). the LPS molecule reaches the human immune system through the lung, high mortality rates due to shock induced by endotoxin is still a major clinical problem(Wen, Yang et al. 2009), Septic shock is the first cause of death in ICU.in this study, aptamer was used Due to its specific properties, easy chemical synthesis with low cost for detecting endotoxin (LPS) in complex environments(Yu, Liang et al. 2016). The technique of this nanobiosensor is much faster with high sensitivity and a much higher specificity than conventional methods for detecting LPS at a lower cost, and also the operatory is very simple and also the use of graphene- gold hydride to increase sensitivity and Mg.CQDs as label free redox probes.

Materials and methods

Initially, the electrode surface was polished by alumina powder, and a cyclic voltammetry (CV) in 2mM K4Fe(CN)6 was applied to ensure that the electrode surface was cleaned. Next, the reduce graphene oxide gold nanocomposite solution that was synthesized by a modified hummer method and a chemical reduction method, which was incubated with aptamer in 4^0C for 24h, then was Incubated with Nafiune for 15 minutes. After that dropped 6.5 microliter of solution on the electrode surface. So the prepared aptasensor was incubated in 10mM pH 7.4 PBS containing various concentration of LPS at room temperature for 35 min each. After washing with PBS to remove the nonchemisorbed LPS. this study first investigated the affinity of the aptamer to evaluate the selectivity of the aptasensor, by use 5×10^4 ng/ml Bovine serum albumin, 2.5×10^4 ng/ml Fetal bovine serum, and 110 mg/dl glucose. Carbon quantum dot magnesium was synthesized via a hydrothermal method by harnessing di ammonium hydrogen citrate as carbon source and $MgCL_2.6H2O$ as magnesium source. To ensure the attachment of lipopolysaccharide to the aptamer, the electrochemical impedance was performed at 32 frequency points in the range of 100-100K Hz for characterization. square wave voltammetry at the potential range of -0.4_1 V were carried out in a conventional three-electrode cell with a glassy carbon electrode an Ag/AgCL and a platinum plate as the working, reference and counter electrodes in 2mM K4Fe(CN)6 solution and carbon quantum dot magnesium for different concentrations of LPS.

Results and discussion

The surface properties of the glassy carbon electrode at each modification Step were characterized electrochemically. The EIS results in hexacyanoferrate are shown in (Fig.1.A). After the immobilization of aptamer, and the redox peak currents decreased further which indicates the aptamer was successfully attached on the electrode surface. The aptasensor showed a high selectivity to LPS despite the presence of fetal bovine serum (FBS), glucose and bovine serum albumin (BSA), promising option for detecting LPS often present in a complex media.

The square wave voltammetry results in 2mM hexacyanoferrate and in carbon quantum dot magnesium are shown in (fig.1.B) and in (fig.1.C).

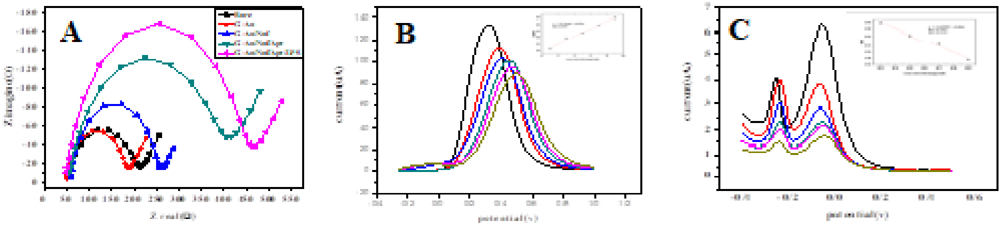

Figure 1. electrochemical impedance spectroscopy of the different electrode in PBS (10mM, pH=7.4) solution containing 2mM hexacyanoferrate(A). square wave voltammetry responses and calibration curve of the aptasensor after incubating in LPS/PBS solution containing (0.1,0.3,0.5,0.7and 0.9 ng/ml) and the linear relationship between the current and concentration of LPS in 2mM hexacyanoferrate(B).and in 40mg/ml Mg.CQDs(C).

Conclusions

In this study, the electrochemical nanobiosensor based on aptamer and Mg.CQDs was developed and used to detect LPS at a concentration range (0.1pg/ml to 0.9 ng/ml) in the present of Glucose, FBS and BSA. The developed aptasensor has a high affinity for LPS, a low detection limit (0.01pg/ml), a good linear relationship with LPS concentrations, new redox probes, simple operation and low cost of production.

Key words: *electrochemical nanobiosensor, Aptasensor, LPS, Endotoxin, Mg.CQDs, Graphene /Gold*

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Voltammetric sensor based on electrode modification with carbon nanotube-nickel nanoparticle hybrid for determination of a novel anti hepatitis C drug, Daclatasvir

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Abstract

Daclatasvir (DCV) is a first confirmed HCV nonstructural protein 5A replication complex inhibitor, which is applied in the treatment of chronic hepatitis C that causes considerable morbidity and mortality and liver related complications [1]. So its determination and monitoring is very important issue in clinical and medical fields. This work explains simple, easily modified electrochemical sensor for sensitive detection of DCV, in which DCV oxidized at glassy carbon electrode (GCE) surface modified with carbon nanotube-nickel nanoparticle hybrid. CNTs coated with Ni NPs expected to show different physical properties than using them individually and may have synergetic effects [2]. Electrochemical studies were accomplished by cyclic voltammetry (CV). Elemental analysis and morphology of synthesized nanoparticle hybrid was characterized with energy dispersive X-ray spectroscopy (EDX) and scanning electron microscopy (SEM), respectively. MWCNTs and Ni NPs illustrated satisfactory synergic electrocatalytical properties in DCV oxidation which leads to sensitive detection in real samples such as tablet and human serum. Limit of detection (LOD) and linear rang were 15.82 nM and 0.024-300 µM respectively which in comparison to other reported studies about determination of DCV were satisfying results.

Key words: Electrochemical sensor; Daclatasvir; carbon nanotube-nickel nanoparticle hybrid

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Nano-textured photovoltaic structures with solar energy capability

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Abstract

The goal of this project is to investigate the production of photovoltaic nanostructured textiles and the possibility of producing electric energy from this intelligent substrate to supply energy appropriate to everyday needs. Because of the sensitivity of environmental issues and the reduction of energy dependence on fossil fuels, global attention has been drawn to the use of renewable energy, including solar energy. The sun, as an endless source of energy, can be a solvent of energy and environmental problems. The development of smart textiles requires a multidisciplinary approach involving several knowledge, such as circuit design, intelligent materials, microelectronics and chemistry, which is combined with a profound understanding of textile construction.

The ability to fabricate nanostructured photovoltaic textures was one of the issues that involved the minds of scientists and researchers, and led them to explore their efforts to produce monolithic materials that could be used by the sun and the photovoltaic effect of electricity. It generates this power supply to a device that comes with a person and needs electrical current.

The components of a conventional organic solar cell are often heavy, fragile and rigid. Recent innovations and inventions in the field of photovoltaic equipment provide access to flexible solar cells with human capability, which can act as an independent system for providing energy in emergencies. The process of electrospinning, which can be used to generate electricity from the

sun, is at the forefront of research. Hence the papers presented by scholars and researchers in this regard were the best option for writing this article.

Keywords : Energy, Nanostructured, Photovoltaic ,Solar, Sun, Textiles

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Effect of grain refinement on electrochemical behavior of Fe-18.5%Cr ferritic stainless steel in 0.1 M HNO3 solution

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Abstract

In the present study, the electrochemical behaviors of coarse-grained and fine-grained ferritic stainless steel in 0.1 M HNO_3 solution were investigated using a series of electrochemical analyses. The potentiodynamic polarization curves for these two types of microstructures showed similar trends. It was also observed that grain refinement decreases the corrosion current density and increases the corrosion potential. Electrochemical impedance spectroscopy (EIS) analysis revealed that grain refinement increases the polarization resistance of ferritic stainless steel. Finally, it was concluded that the corrosion and passivation behavior of the investigated ferritic stainless steel in the 0.1 M HNO_3 solution is improved by refining the grain structure.

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Energy

Electrochemical study of glucose oxidation on Pt/NiO Nanoparticles at neutral media

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Abstract

Non-enzymatic glucose biofuel cells (GBFCs) has been renewed interest because of good long-term stability and adequate power density [1, 2]. Noble metals such as Pt have been commonly used as electro catalytic material for glucose oxidation reaction. Platinum is very rare and expensive, Pt doped metal oxide catalysts have been mainly utilized in the practical fuel cells to solve these problems [3]. In this research, nickel oxide nanoparticles synthesized with a simple hydrothermal method and characterized with X-ray diffraction (XRD) and Scanning Electron Microscope (SEM). For evaluating electrochemical activities of synthesized electrocatalysts, the electrodes were fabricated on carbon paper with Pt (with various amounts) doped NiO, PTFE and activated carbon powder in reaction layer of prepared electrodes. Based on obtained results of cyclic voltammetry (CV) and linear sweep voltammetry (LSV),10% Pt doped NiO showed high electro catalytic activity for glucose oxidation in 5 mM solution of glucose and in phosphate buffer solution (pH 7.4) at room temperature. In addition, electrochemical surface area of this electrocatalyst reached 128 $m^2 g^{-1}$, which was higher than that of commercial Pt/C electrocatalyst (32.45 $m^2 g^{-1}$). Such low-cost electrocatalyst can be suitable candidate for glucose fuel cells.

Keywords: Pt/NiO, fuel cell, Glucose oxidation.

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Development of Dimethyl Phosphate and Vinyltriethoxysilan as an Electrolyte Additive for Lithium Ion batteries

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Abstract

The novel electrolyte additive lithium dimethyl phosphate (LiDMP) has been synthesized and characterized. Incorporation of LiDMP (0.1% wt) into LiPF6 in ethylene carbonate (EC) / ethyl methyl carbonate (EMC) (3:7 wt) results in improved rate performance and reduced impedance for graphite / LiNi1/3Mn1/3Co1/3O2 cells. Ex-situ surface analysis of the electrodes suggests that incorporation of LiDMP results in a modification of the solid electrolyte interphase (SEI) on the anode. Lithium-ion batteries (LIBs) have attracted attention due to their potential to facilitate the rapid development of mobile electronic devices, electronic vehicles and energy storage. However, the high flammability of carbonate-based electrolytes has long been one of the most important obstacles for the further applications of these types of batteries. To develop safer advanced batteries, herein we use an environmentally-friendly additive, vinyltriethoxysilane (VTES), to suppress the flammability of a carbonatebased electrolyte.

Keywords: Lithium Ion batteries, Dimethyl Phosphate, Vinyltriethoxysilan, Electrolyte Additive

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Electrochemical Study of electrodeposited Ni on modified glassy carbon electrode for glucose oxidation reaction

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Abstract

Glucose biofuel cells (GBFCs) could produce a clean and safe energy for a next generation portable devices [1]. It has a high energy content which is promise a low cost electrochemical power sources. The performance of GBFCs is determined mainly by the anodic reaction [3]. Due to this, anode electrocatalyst is a limiting part of GBFCs. Ni is a good catalyst for glucose oxidation reaction (GOR), even better than Pt [2]. In this work GOR was investigated on modified glassy carbon electrode with electrodeposited Ni. For electrodeposition process, the cyclic voltammetry as simple electrochemical method was applied in an acidic aqueous solution. The effect of cycle number in cyclic voltammetry electrodeposition process was studied on performance of prepared electrodes for GOR. The performance of prepared electrodes was studied by electrochemical method like as cyclic voltammetry (-1.2 – 0.8 V vs. Ag/AgCl saturated KCl, scan rate 20 mV/s) and linear sweep voltammetry (-1.2 – 0.2 V vs. Ag/AgCl saturated KCl, scan rate 1mV/s) in glucose 3 mM and phosphate buffer solution (PBS) 0.10 M. Beneficial from this catalyst GOR takes place with current density of 1.04×10^{-5} mA cm^{-2} at 0.0 V vs. Ag/AgCl saturated KCl at optimized condition.

Keywords: Glucose biofuel Cell, Nickel, oxidation reaction, cyclic voltammetry, Electrodeposition.

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Antifouling Effect of ZnO on Ethanol Oxidation by Silver-Palladium Bimetallic Electrocatalyst

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Abstract

Fossil fuels will be finished and their prices are increasing. Therefore, there are many attempts to replace them with clean and renewable energies. Direct alcohol fuel cells are one of the interesting novel power sources has been extensively studied for stationary and portable miniature electric devices due to their high efficiency and low emissions of pollutants. However, there are some challenges to developing this type of fuel cells. Fouling of the catalyst layer in the alcohol fuel cells is a challenge, which reduces the catalyst performance and lifetime. In this study for the first time, the effect of zinc oxide (ZnO) as an antifouling agent for ethanol oxidation reaction (EOR) in alkaline media on the palladium-silver bimetallic catalyst is investigated. ZnO rods is electrochemically deposited at a short time and at a constant current on the carbon cloth (CC) substrate and then palladium and silver are electrodeposited simultaneously at room temperature and at a short time on the ZnO rods (AgPd/ZnO/CC). Cyclic voltammetry tests show the ethanol oxidation on the proposed anode is more complete and the CO-stripping experiments show ZnO can reduce the catalyst layer poisoning considerably. Also, the onset potential and ethanol oxidation peak position are significantly more negative than AgPd/CC, which means the EOR is easier on the proposed electrode.

Keywords: Zinc oxide, Ethanol oxidation, Palladium-silver bimetallic catalyst, Fuel cell, Carbon fiber cloth

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Electrochemical behavior of carbonaceous aerogel supported nanocatalysts

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Abstract

Fuel Cells are devices for converting chemical energy of the fuel to electrical energy. One of the most important parts of a fuel cell is the catalyst layer which is responsible for the oxidation of the fuel. So far, many studies have been carried out on the synthesis of catalyst types and bases and various carbon structures have been employed as catalyst supports.

Carbon aerogel is one of the emerging materials that can potentially be an ideal choice for catalyst base due to its high surface area and porous structure. In this study, carbonaceous aerogels based on carbon nanotubes were synthesized by sol-gel method and characterized by various techniques like FESEM, XRD, BJH. The density of the aerogel was 0.18 g/cm^3. The BET surface area was measured to be 491 m^2/g with a mean pore diameter of 14.9 nm and total pore volume ($p/p_0=0.98$) of 1.8 cm^3/g. Then, Pt and Ru nanoparticles were deposited on the support by impregnation method and the support was characterized by FESEM, XRD and ICP methods. Finally, to study the electrochemical behavior of the catalysts, cyclic voltammetry and chronoamperometry tests were performed and the results were compared with the commercial ones.

Keywords: *Aerogel, Nanocatalyst, Electrochemistry.*

Influence of fast charging protocols on the cycle life of commercial lithium-poly batteries

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Abstract

The rate and shape of the charging current indubitably affect the charging time and the ageing rate of a battery. Depending on the application requirements, it is possible to use high-charging current in order to decrease the charging time. However, the influence of fast-charging current profiles should be investigated to identify their impact on battery functionality over time.

The effect fast-charging current profiles on the cycle life of commercial lithium-poly batteries under different state of charge (SOC) ranges was studied using two methods[1, 2] :(1) Constant Current(CC) Charging, (2) Multistage Constant Current (MCC) Charging. Firstly, all of the batteries were charged to 4.2V and then followed by a constant voltage (CV) charging until the current declined to 0.05 C. Batteries cycled under three cycling ranges 0%-60%, 20%-80% and 40%-100% of SOC [3].

The results revealed that fast-charging MCC-CV protocol has a more important role in decreasing the degradation rate compared to the fast-charging CC-CV protocol. The battery was cycled at 0%-60% SOC perform far better than the other batteries in terms of retaining the capacity.

Keywords: cycle life ,fast-charging, Lithium-Poly batteries, SOC range

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Magnesium ion batteries: New candidates for energy storage

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Abstract

Energy is not only the driving force of global economy, but also a vital basis for human life. Development of energy storage technology is one the most important challenges of modern society. [1]

As an important electrochemical energy storage devices, metal ion battery can be used as renewable energy. Improvement of portable electronic devices become more widespread in rechargeable batteries especially metal ion batteries which show appropriate performance and efficiency. [2]

A lot of investigations are accomplished to develop electrodes and electrolytes in metal ion batteries and thier cycling stability, rate ability and final capacity.

Li-ion batteries (LIBs) are widely utilized in mobile electronic devices and electric cars due to their high energy density, cycle stability and energy efficiency .Between non-lithium ion batteries, sodium-ion and magnesium-ion batteries (NIBs & MIBs) are promising alternatives, due to the high abundance of their resources and safety. [1]

Magnesium resources are more abundant (1.94%) than lithium (0.006%).Moreover Mg, being divalent and denser, is theoretically capable of delivering a higher volumetric energy density (3833 mA h cm^{-3}) than Li (2061 mA h cm^{-3}). [3]

To compete with recent lithium ion batteries (LIBs), energy density, high voltage and capacity of magnesium ion batteries (MIBs) should be developed. [3]

The development of rechargeable MIBs, however, still faces scientific challenges related to anode-electrolyte-cathode incompatibility and impervious layer formed on metallic Mg surface in most polar organic electrolytes. [4]

However, most of anode materials suitable for LIBs can’t react electrochemically with Mg due to the complicated nature of divalent Mg^{2+} cation, and only a few alloying-type materials have been reported, such as Bi, Sn, Sb, Pb, In, and their alloys. In addition, a few insertion-type materials including $Li_4Ti_5O_{12}$, $FeVO_4$, Li_3VO_4, TiO_2-B and layered $MgNaTi_3O_7$ was reported as alternative anode materials for MIBs. Compared with insertion-type materials, alloying-type anode materials are particularly attractive for both Li/Na/K/Mg-ion batteries owning to their high specific capacity and superior cycling performance in appropriate conditions. [4]

Keywords: Energy storage, Magnesium ion batteries, anode

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Influence of sodium gluconate concentration on the microstructure of Mn–Co-CeO_2 electrodeposition

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Abstract

The reduction in the operating temperature of solid oxide fuel cells (SOFCs) from 1000 °C to 600–800 °C leads to the potential for using lower cost metallic interconnects materials such as stainless steel. However, excessive growth of chromia and chromium evaporation can lead to cathode poisoning, and thus shorten the required service life for the SOFC stack. In order to solve the mentioned problems, protective and conductive coatings can be employed. Manganese-cobalt coatings are promising candidates for SOFC interconnect applications because of their high conductivity and good oxidation resistance [1-3]. In the present study, the effect of sodium gluconate on the microstructure of manganese-cobalt-CeO_2 was investigated.

One-compartment cell was used for DC electrodeposition process. All experiments were carried out in 100 ml electrolytes prepared with deionized water. Bath electroplating with composition of 0.5 M $MnSO_4$ + 1 M H_3BO_3 + 0.1 $CoSO_4$ M + CeO_2 40 g/L + 0.1 M $(NH_4)SO_4$ at pH 2 and current density of 600 $mA.cm^{-2}$ was used to electrodeposition of Mn-Co-CeO_2 coating. The effect of sodium gluconate concentration ($NaC_6H_{11}O_7$) on the microstructure was characterized by means of scanning electron microscopy (SEM), and energy dispersive X-ray spectrometry (EDS).

In order to investigate the effect of sodium gluconate in the solution, different amounts of $NaC_6H_{11}O_7$ (0.35 M, 0.7 M and 1.4 M $NaC_6H_{11}O_7$) in the electrolyte solution were studied. Figure1 demonstrates the surface morphology of as deposited Mn-Co-CeO_2 coating in bath with different concentration of sodium gluconate. Results showed that the increase of sodium gluconate concentration caused to the increase of cathodic current efficiency. Also results demonstrated that

the variation of sodium gluconate concentration had significant effect on the grain size, uniformity and adherence of the coating. Based on the EDX results at low amount of sodium gluconate (0.35 M) the amount of manganese was low. It is because of low chelating agents to chelate with manganese [2].

At higher amount of sodium gluconate (1.4 M and higher) the amount of cobalt, manganese and oxygen was not very different from 0.7 M gluconate. So 0.7 M gluconate in the electrolyte solution is sufficient for obtaining approximately equal amount of manganese and cobalt in the coating composition. Also the grain size in 1.4 M gluconate is larger than 0.7 M which probably one causes of growing such coarse grains, is the higher deposition rate. Such relative coarse grains obtained from 1.4 M sodium gluconate solution is harmful during SOFC operation [4].

Keywords: *Electrodepositon, SOFC, Mn-Co-CeO$_2$ coating, Microstructure, Sodium gluconate.*

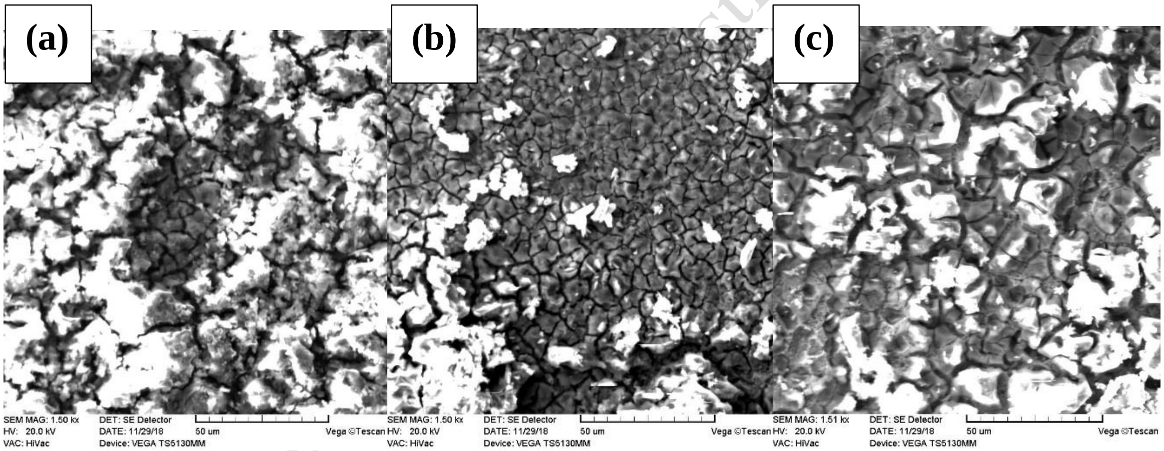

Figure1: surface morphology of as deposited Mn-Co-CeO$_2$ coating in bath with gluconate concentration of (a) 0.35M, (b) 0.7 M and (c) 1.4 M

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Fascinating Oxygen Reduction on ZIF-derived Fe-N co-doped Carbon composite with graphene

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Abstract

Oxygen reduction reaction (ORR) is the key reaction at the cathode of fuel cells for next-generation electrochemical energy conversion. The sluggish kinetics of ORR makes it the rate-determining step of the whole cell in most cases, thus efficient electro-catalysts are required. Taking advantage of these features, MOFs could serve as both metal and carbon source as well as self-sacrificial templates to prepare complex nanostructures such as porous carbon supported metal nanoparticles and porous metal oxides through thermal conversion [1].

In this study a simple Zn/Fe bimetallic zeolitic-imidazolte frameworks (ZIF) composite with graphene oxide (GO), carbonization method is utilized to synthesize a Fe-N-C hybrid with hierarchical nitrogen-doped porous carbons [2].

Combining MOFs with graphene oxide (GO), their derived carbon composites exhibit enhanced electrochemical performance due to the increased electrical conductivity and density of active sites. However, most of the composites show the unsatisfactory structure and property because of the weak interactions between MOFs and GO, as well as the fast growth kinetics of the MOFs caused nanoparticles aggregation[3].

Since high temperature can enhance the degree of graphitization and also increase the conductivity of catalysts to elevate ORR activity, porous carbon catalysts derived from MOFs must undergo a high-temperature pyrolysis [2].

Due to the synergetic effect of bimetal doping the ORR activities of bimetallic MOF-derived porous carbon catalysts are often better than that of single Zn (or Co, Fe) containing MOF-derived ones [3]. In order to investigate the electrochemical properties of the synthesized catalyst, cyclic voltammetry, linear sweep voltammetry and chronoamperometry techniques were used. The results reveal that Fe doping during the ZIF-8 synthesis stage was vital to gain the unique morphology and well dispersed active sites. Furthermore, a high ORR activity of the as-prepared material in both acidic and alkaline media was observed that was attributed to the generated mesoporous, nanostructure derived from MOFs, the proper nitrogen source and the high conductivity of the graphene carbon matrix.

Keywords: *Oxygen reduction, Metal Organic Famework, fuel cell, N-doped graphene*

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An over view of Tin-polypyrrole structured anode for lithium-ion-batteries

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Abstract

lithium-ion batteries are one of most important type of energy storage systems that have been investigated extensively, owing to their advantages of environmental friendliness, high energy density and long cycle life. Tin (Sn) based materials as anode for LIBs has attracted most of attentions due to its high specific capacity; however pulverization and poor cycling hinders its vast application. Conductive polymers can buffer the strain resulting from volume change in lithium ion insertion and extraction process. polypyrrole as one of the conductive binder not only can improve electrons transportation but also acts as a dispersant and prevent agglomeration

Tin-polypyrrole based anodes has been prepared by both chemical and electrochemical pathways with different kind of morphologies. This composites are able to reduce above mentioned problems.to cater rapid development in Sn-based anodes, here the structural design principles and overall compare of similar compositions will be presented; to facilitate future practical implementations in next generation of Tin-polypyrrole anodes.

Keywords: *Lithium-ion-batteries,anode,Tin,polypyrrole*

Type of anode	Synthetic method	Characterization	Cycle	Capacity
rGO/SnO_2/ppy [1]	**In-situ-chemical polymerization**	**XRD,Raman,BET SEM**	**800**	**280 f/g**
Core shell SnO_2@ppy [2]	**Hyrothermal Insitu-polymerization**	**XRD,FESEM,TEM TGA,FTIR**	**100**	**484.4 mAh/g**
SnO_2 nanorods array-polypyrrole coverage [3]	**Hydrothermal electroposition**	**SEM,FTIR,EDS XRD**	**300**	**701**
CPN@SNS_2 [4]	**polymerization Hydrothermal**	**XRD,SEM,TEM,BET TGA,XPS,Raman**	**100**	**699.2 mAh/g**

Some related articles

Reference

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The performance of CMC in a Co-based metal organic framework in lithium ion batteries

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Introduction

The Energy storage is a critical but weak link in the chain of sustainable energy applications. Developing high-capacity battery systems without sacrificing the safety, cost, power, and stability standards remains a formidable challenge, and requires optimized performance of every battery component. Besides other elemental parts in batteries, such as electrodes and the electrolyte, an efficient binder is critical to maintain both the electronic and mechanical integrity of battery electrodes.[1] The traditional binders, which interacts with electrode materials via weak Van der Waals forces and consequently lacks the necessary capabilities (e.g., the suppression of significant volume variations, the interface maintenance etc.), could not fulfill the high demands of batteries with high energy density.[2] Metal-organic frameworks (MOFs) are an emerging class of porous crystalline materials, prepared from self-assembly of metal ions and organic bridging ligands. Their highly ordered periodic porous structures give superior surface areas up to 7000 m^2/g, which is not attainable by traditional porous materials. In addition, high thermal stability, tunable pore property, and various chemical reactive sites have attracted great attention from many different areas, including gas storage, chemical sensor, catalysis, proton conductor and LIBs.[3] Here we used Co-based MOF with CMC as binder in a half cell.

Keywords: Li ion battery, anode, binder, MOF, capacity.

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Ternary nanocomposite of conductive polymer/ graphene/ metal oxide as efficient electroactive materials in energy storage materials

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Abstract

This study gives an overview of the synthesis, surface and electrochemical investigations over ternary nanocomposite of conductive polymers in the development of new supercapacitors. They utilize both Faradaic and non-Faradaic procedures to store charge, leading to higher specific capacitance and energy density, higher cell voltage, longer life cycle and moderated power density. Owing to a unique combination of features such as superb electrical conductivity, corrosion resistance in aqueous electrolytes, highly modifiable nanostructures, long cycle life and the large theoretical specific-surface area, the use of ternary nanocomposites as a supercapacitor electrode material has become the focus of a significant amount of current scientific researches in the field of energy storage devices. In this regard, synthesis, characterization and performance of different ternary nanocomposites of p-type conductive polymer/graphene/metal oxide are discussed in detail. In terms of electrochemical measurements, galvanostatic charge–discharge evaluation, EIS (electrochemical impedance spectroscopy) and CV (cyclic voltammetry) were employed for conducting an enquiry into supercapacitive performance of synthesized nanocomposite of poly orthoaminophenol. These remarkable results demonstrate the exciting commercial potential for high performance, environmentally friendly and low-cost electrical energy storage devices based on ternary nanocomposite of conductive polymer/graphene/metal oxide [1-3].

Keywords: Conductive polymer, metal oxide, graphene, ternary nanocomposite, pseudocapacitor

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Fabrication of High Activity Electrocatalysts For Oxygen Reduction Reaction By Silica-Protection Of Zeolitic Imidazolate Framework (ZIF)-Derived

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Abstract

Oxygen reduction reaction (ORR) is one of the essential electrochemical reactions for the energy conversion and storage devices such as fuel cells and metal-air batteries. However, a large amount of Pt is required for catalyzing the kinetically sluggish ORR at the air cathode, therefore greatly limiting their large scale implementation. Recently, metal-organic frameworks (MOFs), constructed from bridging metal ions and ligands, have emerged as a new type of attractive precursors for the synthesis of PGM-free catalysts, which has led to encouraging performance improvement. In this work we report a highly efficient Co based catalyst for the oxygen reduction reaction (ORR) with highly dispersed Co-N_x sites on N-doped carbon. We synthesized the core-shell ZIF8/ZIF-67 and silicon- core-shell ZIF8/ZIF-67. Silicon protection strategy proved highly effective in preventing the irreversible fusion and aggregation of Co,N-CNF during the high-temperature pyrolysis step used in Co,N-CNF manufacture. Compared to unprotected core-shell ZIF8/ZIF-67 an enhanced electrocatalytic activity was obtained in the case of the silicon-core-shell ZIF8/ZIF-67 with optimized composition and temperatures.

Keywords: Oxygen Reduction Reaction(ORR), Silica-Protection, Zeolitic Imidazolate Framework (ZIF), core-shell

Investigation of alcohols oxidation on silver as an electro-catalyst in alkaline solution by electrochemical method

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Abstract

In this research, oxidation of different alcohols (methanol, ethanol, 1-propanol, 2-propanol, ethylene glycol, glycerol, 1-bothanol and 2-bothanol) was studied in alkaline medium on silver catalyst surface by cyclic voltammetry method. The results show that some of the alcohols in the presence of alkaline solution exhibit excess oxidation on silver electro-catalysts, as evidenced by their higher peak current densities, lower onset potentials and better anti-poisoning properties which originated from the tailored geometric and electronic structures of silver.

Keywords: Alcohols, Catalyst, Electrochemical, Silver.

1. Introduction

Alcohol electro-oxidation reactions have many uses such as in direct alcohol fuel cells, which are electrochemical power generators especially for portable applications [1]. Liquid fuels, such as alcohol molecules, are more advantageous than gaseous fuels. For instance, they are more easily stored and transported, and their high theoretical energy density is also arrestive [2,3]. In this research, oxidation of alcohols containing one or more than two –OH was studied on silver catalyst surface in alkaline medium via cyclic voltammetry method.

2. Experimental

All the chemicals were analytical grade of Merck origin. The electrochemical measurements were done by a computer-controlled potentiostat/galvanostat (AutoLab, PGSTAT302N) contained a three-electrode system of Ag/AgCl-saturated KCl, a platinum wire and a silver as the reference, counter and working electrodes, respectively.

3. Results and discussion

Fig. 1 depicts the cyclic voltammograms of pure silver electrode in a solution of 0.5 M NaOH containing 0.3 M of different alcohols (methanol, ethanol, 1-propanol, 2-propanol, ethylene glycol, glycerol, 1-bothanol and 2-bothanol) at a scan rate of 10 mVs^{-1}.

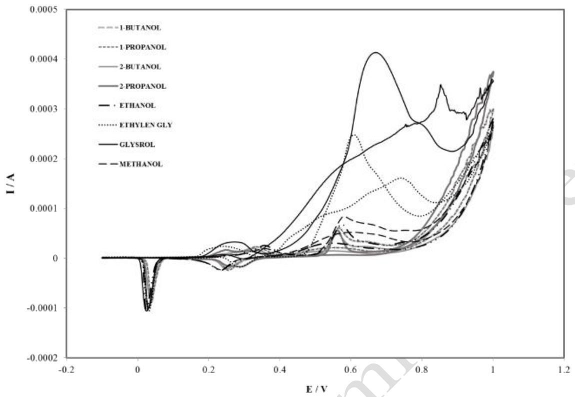

Fig. 1. Cyclic voltammograms in the presence of 0.3 M of different kinds of alcohols on silver electrode in 0.5 M NaOH solution. Scan rate: 10 mV s^{-1}.

4. Conclusion

Our studies have shown that silver has an enhanced catalytic behavior for glycerol electro-oxidation in alkaline solution compared with the other alcohols.

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Metal oxide composites derived from Metal Organic Framework (MOF)

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Abstract

Metal−organic frameworks (MOFs), a new class of porous crystalline materials, have attracted enormous attentions in many applications over the past two decades because of their high surface area, tunable porosity and controllable structures[1].

Recently, MOFs have been shown to easily transform into metal oxides, metal oxide/carbon, and metal oxide composites after heat treatment, which has drawn great attention for energy conversion and storage applications. Furthermore, MOFs are not restricted to only the exploitation of single metal oxides but can also be used to prepare a variety of metal oxide composites[2]. Thus, herein one Metal based iron oxide derived metal-organic frameworks are fabricated through a general facile strategy. The intrinsic hollow nanostructure can shorten the lengths for both electronic and ionic transport, enlarge the surface areas of electrodes, and the improve accommodation of the volume change during Li insertion/extraction cycling[3]. The hybrid multielements characteristics allow the volume change to take place in a stepwise manner during electrochemical cycle. Therefore, as-prepared metal oxide electrode exhibits outstanding performance as anode materials for lithium ion batteries. As an anode material for LIBs, the capacity retained 1770 mAh g-1 after 25 cycles at a current density of 200 mAh g-1

Keywords: Metal-Organic Frame Work, Metal Oxide, Li-ion Battery

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Investigation of dead-ended anode PEM fuel cell performance under different operating conditions

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Abstract

Dead-ended anode proton exchange membrane fuel cell is increasingly being used in some special applications due to its need for simpler and lower cost subsystems. However, the performance of such a fuel cell is more affected by the operational parameters and conditions than the traditional proton exchange membrane fuel cells. Therefore, realizing the most effective parameters and determining their optimum values are essential. In the present study, electrochemical impedance spectroscopy is used to examine the effect of operating conditions on the performance of a dead ended anode fuel cell. cell temperature, operating current densities, cathode humidity and hydrogen pressure are selected to assess their effects on the fuel cell performance. The results show that the performance enhances by increasing the cell temperature up to 60°C and the the performance enhances by increasing cathode humidity

up to 50% and hydrogen pressure up to 15psi . The experimental results also show that the performance decreases by further increasing of the temperature up to 70°C and the performance decreases by further increasing of the cathode humidity up to 80% and hydrogen pressure up to 20psi and The results show that the performance always decreases by increasing of the operating current density from 300 mA.cm^{-2} to 500 mA.cm^{-2}.

Keywords: Proton exchange membrane fuel cell (PEMFC), Dead-ended anode (DEA) , Electrochemical impedance spectroscopy (EIS) , Nitrogen crossover.

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Recent progress in cathode materials and structures for Nonaqueous lithium–oxygen batteries

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Abstract

New energy technologies are needed to resolve current issues of energy production including environmental degradation, raw material shortages and increasing energy demand. Metal-air batteries, especially aprotic Li-O2 batteries, offer an alternative which have higher theoretical energy density (≈3600 Whkg−1) and are more environmentally-friendly when compared to widely used Li-ion batteries.[1] these batteries still suffer from many critical issues, such as low capacity, poor cycle life, and low round-trip efficiency, rendering the practical application of these batteries rather sluggish. Cathode catalysts with high oxygen reduction reaction (ORR) and evolution reaction (OER) activities are of particular importance for addressing these issues and consequently promoting the application of Li–O2 batteries. To handle the above problems, many researchers have been endeavoring to develop efficient ORR and OER electrocatalysts to improve the performance of Li-O2 batteries. In the last decade, numerous ORR and OER catalysts emerged. Overall, the catalysts include porous carbon materials [2], transition metal oxides [3] and nitrides [4], precious metals [5], and perovskite- or pyrochlore-based compounds [6]. This paper reviews, the role of the cathode in nonaqueous Li–air batteries including the cathode reaction mechanisms and the properties and morphologies of cathode materials in recent advancements of these batteries.

Keywords: Li-O2 batteries, Cathode, Oxygen electrocatalysis, Electrochemical performance

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Pseudocapacitive Characteristics of Vanadyl hydroxide for energy storage

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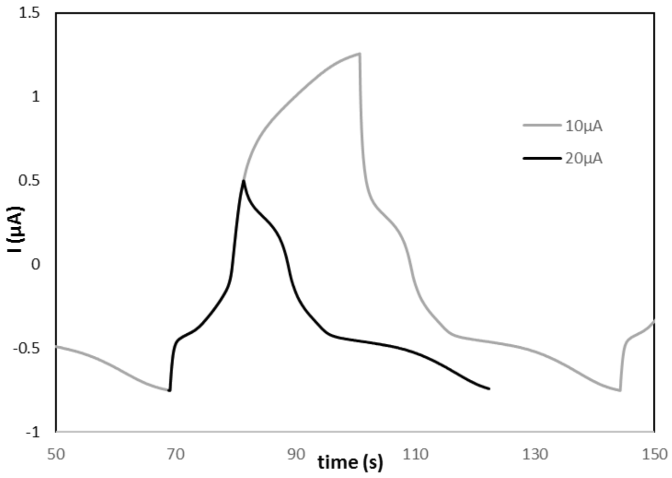
Abstract

An adequate alternative for fossil fuels are batteries, fuel cells and supercapacitors, which is placed in the category of electrochemical energy storage (ESS), and powering the electrical grid by the linking of these technologies with renewable energy sources such as solar and wind [1, 2]. One of the difference between electrochemical energy systems is in power and energy density, so that fuel cells have higher energy density and supercapacitors have higher power density [2]. The combination of electrochemical energy systems like fuel cells/supercapacitors or batteries/supercapacitors can achieve high power and high energy together [2]. This property can be seen in pseudocapacitance with faradaic mechanism as like as batteries and deliver energy faster than batteries, will have potential to both high energy and power density in the same material [2]. With attention to pseudocapacitance mechanism, three mechanisms have been proposed: Underpotential deposition, Redox pseudocapacitance and Intercalation pseudocapacitance.

In this work, we formed a thin film of $VO(OH)_2$ on platinum working electrode by the cathodic deposition method which released hydroxides from the surface of working electrode, react with VO^{2+} cations contained in the vanadyl sulfate solution and produce brownish yellow vanadium hydroxide colloidal particles that stick to the surface of the electrode. Electrochemical tests of this work was carried out by using vanadyl hydroxide working electrode prepared by the above method, Ag/AgCl as reference electrode and platinum auxiliary electrode in 0.5 M sodium sulfate solution.

Cyclic voltammetry in different scan rates from 2 to 500 mV.s^{-1} and different pH (2 to 12) accomplished in range of -0.8 to 1.1 V to investigate pseudocapacitive mechanism. Then Galvanic charge-discharge test fulfilled in 5, 10, 20, 50 and 100 µA to compare with each other and estimate the specific capacitance as shown in figure below. According to figure, with decreasing the current density and increasing time of each charge or discharge cycle the specific capacitance increase. Also, in each charge or discharge cycle, two redox reactions are observed that related to the change of different oxidation numbers of vanadium species. Besides, the device exhibited a good cycling stability with capacitance retention of 87.8% after 1000 charging-discharging cycles.



Keywords: Energy storage, Pseudocapacitive mechanism, Supercapacitor, Vanadyl hydroxide

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Oxidation activation energy of manganese-cobalt-cerium oxide coated AISI 430 steel for SOFC interconnect application

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Abstract

The formation of oxide scales is one of the critical issues for applying Fe–Cr alloys in solid oxide fuel cells (SOFCs) operated at 773 K–1073 K (intermediate operation temperature SOFCs) [1-2]. The growth of oxide scale is dominated by the diffusion of elements (cations and oxygen) in the scales and the microstructures of scales [3]. One of the most effective approaches to improve the interconnect properties is to apply surface coatings to provide better conductivity, reduced scale growth and Cr volatility. Manganese-Cobalt coatings are promising candidates for SOFC interconnect applications because of their high conductivity and good oxidation resistance. In this study, the electrodeposition method was employed to coat manganese, cobalt and cerium oxide onto AISI 430 steel.

For the direct current (DC) electrodeposition process, a one-compartment cell was used. Platinum foil was used as the anode and it was placed in the same compartment as the working electrode. All experiments were carried out in 100 ml electrolytes prepared with deionized water. Ammonia hydroxide or 20 vol% H_2SO_4 was used to adjust the electrolyte pH. Bath electroplating with composition of 0.5 M $MnSO_4$ + 0.10M $CoSO_4$ + CeO_2 40 g/L + 1 M H_3BO_3 + 0.7 M $NaC_6H_{11}O_7$ + 0.1 M $(NH_4)SO_4$ at pH 2 and current density of 600 $mA.cm^{-2}$ was used to electrodeposition of Mn-Co-CeO_2 coating.

Oxidation resistance of manganese-cobalt-CeO_2 coated and uncoated samples was studied at 800 ºC for 100 h. The corrosion resistance was remarkably reduced by the application of coating layer. The bare substrate had a weight change of 0.407 $mg.cm^{-2}$ after 100 h of isothermal oxidation, while

the coated samples had a weight change of 0.181 mg.cm^{-2}. The coating effectively protected the substrate from the corrosion at high temperatures. In order to measure the oxidation activation energy of Mn-Co-CeO_2 coating, uncoated and coated samples were subjected to isothermal at 800 °C, 900 °C and 1000 °C for 20 h. [4].

The parabolic rate constants (*k*p), can be fit into an Arrhenius expression to determine the activation energies for the oxide formation process on each of the samples (Fig. 1). Activation energies were calculated 118 and 49 kJ mol^{-1}h for uncoated and Mn-Co-CeO_2 coated specimens, respectively. The lower activation energy for the Mn-Co-CeO_2-coated samples would imply that oxide formation is easier during isothermal oxidation. This is an interesting result, considering the fact that the oxides on the Mn-Co-CeO_2 coated samples are thinner than the oxides on the uncoated AISI 430 samples.

Keywords: *Oxidation, SOFC, Electrodeposition, Mn-Co-CeO_2 coating, Activation energy.*

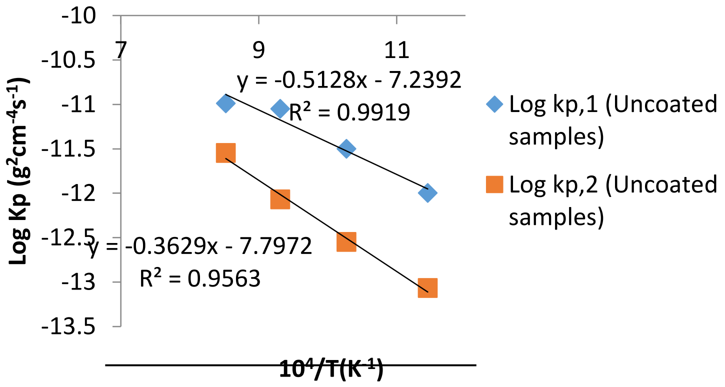

Fig. 1. Plots of log(kp) vs. 1/T for uncoated and Mn-Co-coated Crofer 22 APU steel.

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Preparation of cobalt oxides nanoparticles modified exfoliated graphite for oxygen evolution reaction

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Abstract

In this study cobalt oxide nanoparticles were electrodeposited on the surface of exfoliated graphite graphenized as a low cost and efficient electrocatalyst for the OER [1-3]. The prepared cobalt oxide modified exfoliated graphite was carefully characterized by scanning electron microscopy, energy-dispersive X-ray spectroscopy and cyclic voltammetry techniques. The cobalt oxide modified exfoliated graphite exhibits excellent performance in electrocatalytic water oxidation in alkaline media due to synergistic effects arising from the exfoliated graphite and cobalt oxide nanoparticles. The prepared electrocatalyst represents low OER overpotential of 1.51V (vs. RHE) at the current density of 10 mA cm^{-2} and Tafel slope of 141 mV dec^{-1} in 1 M KOH solution. The cobalt oxide modified exfoliated graphite was highly stable and capable for maintaining catalytic activity for at least 4 h.

Keywords: Cobalt oxide nanoparticles, exfoliated graphite, Water splitting

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Synthesis of cathodic material of lithium ion battery by NMC composition using the middle nucleation method in co-precipitation process

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Abstract

In this study, the middle nucleation method in co-precipitation process was used to synthesize lithium ion battery cathode precursor with NMC compound. In order to improve the performance of the battery in the lithiation process, the precursor is mixed with larger amounts of lithium to increase the lithium ion penetration coefficient in the cathode structure. In this method, nuclition and spherical growth of carbonate precursor was performed by pH and reaction bed control. The XRD results indicate that the middle nucleation method leads to better crystallization of the precursor. The SEM results also indicate that particle size distribution is more appropriate than conventional co-precipitation process. The results of the battery charging/discharging test made with synthesized cathode have a capacity of 195mAh/g at a discharge rate of 0.5C, It also has better cyclic stability than similar samples (discharge capacity at a discharge rate of 0.5C after 30 cycles of 185 mAh/g). EIS results show that the internal impedance of the battery compared with similar samples has decreased. In total, it can be noted that the use of co-precipitation process by middle nucleation method with excess lithium has been found to be a suitable method for the preparation of a lithium-ion battery cathode.

Keywords: *Lithium ion-battery, NMC compound, Co-precipitation process, Middle nucleation method*

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Synthesis and characterization of titania nanotubes as an anode material for lithium ion microbatteries

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Abstract:

Titania nanotubes fabricated by potentiostatic anodization of titanium in aqueous solution. Morphology and crystalline structure of titania nanotubes was characterized by field emission scanning electron microscope (FESEM) and energy dispersive X-ray spectroscopy (EDS). The characterizations showed that titania nanotubes well aligned, uniform and impurity free. Electrochemical performances of as-prepared anode were obtained by cyclic voltammetry (CV) and chronopotentiometery (CHP). First charge and discharge capacities are 0.058mAh/cm^2 and 0.045mAh/cm^2 respectively.

Keywords: TNTs; Anodization; Lithium-ion microbatteries; Electrochemical characterization

Introduction

Lithium ion batteries with high energy density and power density are the technology of choice for portable electronics, hybrid electric vehicles and electric vehicles[1].

Due to the increasing of greenhouse effect and air pollution, eliminating gasoline powered transportation and utilizing hybrid electric vehicles (HEVs) and electric vehicles (EVs) can exert a huge influence on air quality. HEVs and EVs can store energy from sustainable energy resources such as the wind and solar power[2,3].

Graphite is the first anode which used in lithium ion batteries, although it is abundant but it suffers from low capacity and rate capability. Titania nanotubes can further improved the rate capability and capacity at the same time[4].

In spite of numerous studies in titania nanotubes, there are few studies on titania nanotubes applications on microbatteries. Herein, we synthesize and characterize titania nanotubes and the reported data is based on surface area.

Materials and Methods

Titanium sheets (99.7% purity) was purchased from Iran Tejarat Company. Hydrofluoric acid (HF) of MERCK company (38%-40%) were purchased from Mina Tajhiz Aria. Deionized water was used during experiments. Average titania nanotubes diameter was estimated by Digimizer software.

Titania nanotubes were synthesized via anodization. They were cleaned with ethanol and deionized water and dried in air. Titanium sheet was used as anode and pure platinum (Pt) mesh as cathode. Electrolyte used in this process contained 1 wt% HF. Anodization were carried out at constant voltage condition. The voltage was set on 20V in 20 minutes. After anodization the samples were rinsed with deionized water and dried by drier. Finally to crystallize TNTs, They were calcinated in 400°C for 1h.

Electrochemical measurement

The electrochemical performance of as-prepared titania nanotubes was evaluated using a coin cell, in which titania sheet without any binder or back contact was used as working electrode and Li metal as counter electrode. The electrolyte was 1 M LiPF6 dissolved in a mixed solvent of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 in weight). The cell was assembled in an Argon-filled glove box at room temperature.

Results and Discussion

Characteristics of sample

Figure 1 shows EDS results presenting the Ti and O elements. The Ti Lα, O Kα, Ti Kα and Ti Kß peaks respectively at 0.5, 0.5, 4.5 and 5 KV represent the existence of TiO_2 compound without any impurity such as F^- element. FESEM images of synthesized titania nanotubes demonstrate that titania nanotubes are well aligned and uniform due to proper polishing of surface. There is no sign of breakage and wall dropping which shows that the applied voltage is appropriate for nanotubes formation. The average inner and outer diameters are 75 nm and 87nm respectively.

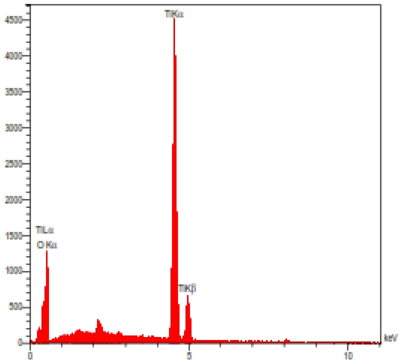

Fig. 1. EDS spectra of titania nanotubes

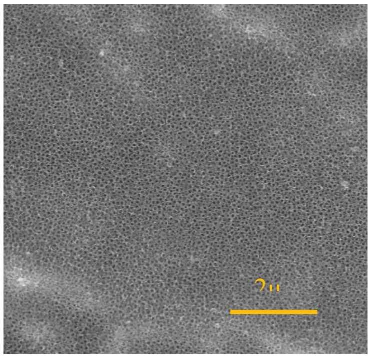

Fig. 2. FESEM of anodized titania nanotubes in 20V, 20min in 25kx magnification

Electrochemical behavior of sample

Electrochemical behaviors of as-prepared titania nanotubes were obtained for sample with 20V, 20min anodization condition. Cyclic voltammetry obtained at scan rate of 1mV/S. figure 4 shows that lithiation occurs at 2.16V (Li/Li$^+$) and delithiation process occurs at 1.66V. lithiation/delithiation in TNTs is formulated as below:

$$xLi^+ + xe^- + TiO_2 \leftrightarrow Li_xTiO_2$$

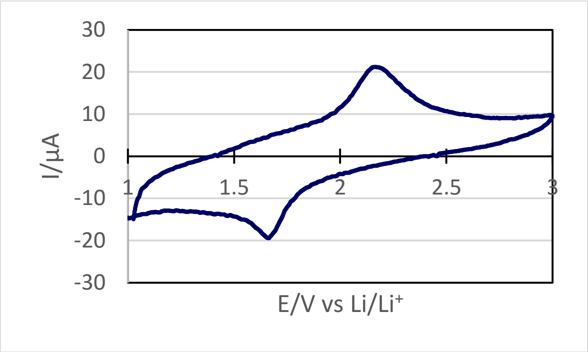

Fig. 3. CV of as- prepared titania nanotubes at 1mV/S

Fig.5 shows the initial capacity of titania nanotubes. charge and discharge capacity in 1st cycle is 0.058 and 0.045 mAh/cm^2 respectively. 2nd cycle is 0.026 and 0.028 mAh/cm^2 which is decreased in compare with 1st cycle which is due to SEI formation in electrode/electrolyte interface and it is almost matched with corresponding cyclic voltammetry

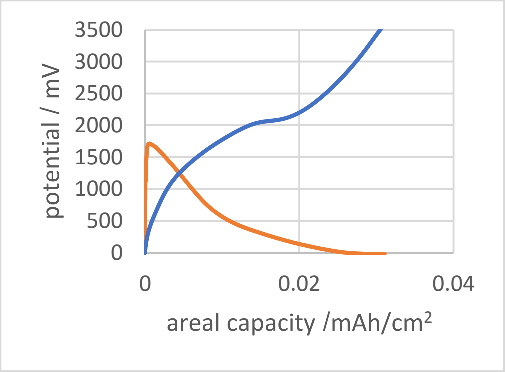

Fig. 4.2nd Charge and discharge plot of titania nanotubes by Chronopotentiometery (CHP) method

Conclusions

Titania nanotubes was synthesized via anodization in aqueous solution successfully. Characterization of morphology and chemical structure was done by FESEM and EDS. The electrochemical performances was evaluated by charge-discharge plateau and cyclic voltammetry plot. The first charge and discharge capacities are 0.058 and 0.045 mAh/cm^2 respectively. Cyclic voltammetry shows that lithiation occurs at 2.16V (Li/Li$^+$) and delithiation process occurs at 1.66V

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The effect of plasticizer on ionic conductivity of the electrospun PEO-based electrolytes applicable in lithium ion batteries

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Abstract

Herein, fabrication of all-solid-state PEO-$LiClO_4$ nanofibrous electrolytes by using an electrospinning process was reported. The effect of propylene carbonate (PC) on morphology and electrochemical properties of the electrospun electrolytes was evaluated. The results showed that the average diameter of the nanofibers was decreased with the addition of PC. In addition, flat-shaped nanofibers were obtained in the absence of PC. Ion conductivity of 0.05 $mS.cm^{-1}$ was approached with the addition of PC into the nanofibrous electrolytes. Moreover the as-spun electrolyte showed good cycling stability after 20 cycles.

Keywords: *Li ion battery, Electrospun electrolyte, Ion conductivity, Propylene carbonate, Plasticizer.*

Introduction

In recent decades, solid polymer electrolytes (SPEs) have appeared as a safe alternative for liquid electrolytes of lithium ion batteries (LIBs) which provides fabrication of all-solid-state and flexible LIBs. SPEs are basically consisted of a host polymer and a lithium salt which are commonly prepared using a film casting technique. Low ion conductivity is the major drawback associated with SPEs which have limited them to be applied in practical applications. Ion conductivity of the SPEs is significantly affected by crystalline regions and glass transition temperature. Addition of high dielectric constant plasticizers such as propylene carbonate leads to the reduction of crystallinity and Tg and therefore conductivity improvement. Recently, electrospinning has been introduced as an efficient method of SPE's fabrication. Compared with film electrolytes, highly-porous structure of the electrospun SPEs, assists ion transfers and improves ion conduction. In this study, the effect of plasticizer on the morphology and conductivity properties of the electrospun PEO-based electrolytes were evaluated.

Materials and methods

PEO (Mw=300000) and lithium perchlorate ($LiClO_4$) with concentrations of 8.5 wt. % and 0.007 wt. % were mixed in acetonitrile, simultaneously. Various ratios of propylene carbonate (PC) were added to the mixture and stirred for 6 hours before electrospinning. Nanofibrous electrolytes were fabricated using an electrospinning method. Feed rate of $0.5 ml.h^{-1}$, voltage of 18.5 kV, distance of 15 cm were kept constant during electrospinning. A scanning electron microscope was used to study morphological properties of the nanofibers. The electrochemical measurement was carried out on a stainless steel electrode| the nanofibrous electrolyte| stainless steel electrode cell, in a frequency range of 10 kHz to 1 Hz.

Results and discussions

Morphological structures of the electrospun electrolytes containing various PC ratios are shown in figure 1

. Flat-shaped nanofibers were formed in the absence of the PC which is due to due to the formation of thicker fibers and more essential time for evaporation of the solvent. However, with the addition of PC, thinner fibers were fabricated due to the changes in the viscosity and conductivity of the electrospun solutions.

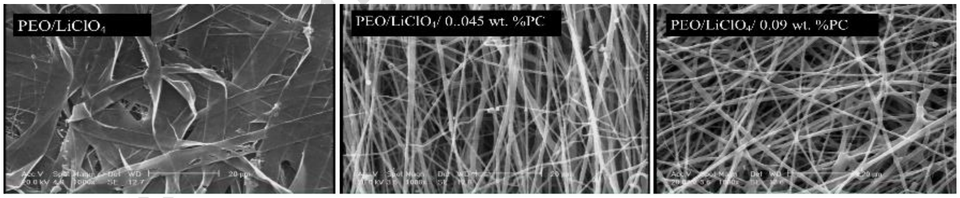

Figure 1. SEM images of the nanofibrous electrolytes.

Figure 2a shows the Nyquist plot of the as-spun electrolytes. As it is apparent, the impedance was declined with the addition of PC. With the addition of plasticizer, PC molecules were placed between the polymer chains, increase amorphous regions and improve salt dissociations. In addition, plasticizers decrease Tg and therefore enhance ion conductivity. Capacity retention of the electrospun electrolyte plasticized by PC with cycle number is shown in figure 2b. As can be seen, the fabricated electrolyte showed almost good cycling stability which can be due to appropriate interfacial contact between as-spun electrolyte and the electrode.

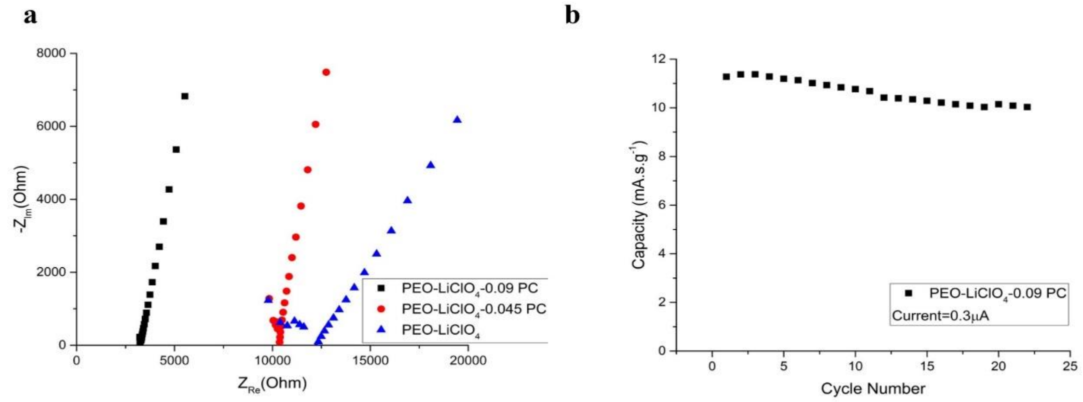

Figure 2. A.C. impedance of the electrospun electrolytes.

Conclusion

In conclusion, PEO-LiClO$_4$ nanofibrous electrolyte was fabricated using an electrospinning method. The effect of PC ratio was evaluated on morphology and electrochemical characteristics of the electrolytes. Results showed a reduction in nanofiber's diameters with the addition of PC into the nanofibrous electrolytes. In addition, ion conductivity of 0.05 mS.cm^{-1} was obtained with the addition of 0.09 wt. % PC. Furthermore, the electrospun electrolyte showed good cycling stability.

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Conductivity study of the electrospun PEO-based electrolytes incorporated with TiO2 nanoparticles for use in Lithium ion batteries

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Abstract

In this study, all-solid-state PEO-based nanofibrous electrolytes were fabricated by an electrospinning method. $LiClO_4$ and ethylene carbonate (EC) were applied as lithium salt and plasticizer, respectively. The effect of TiO_2 nanoparticles were studied on the morphology and ion conductivity of the as-spun electrolytes. The results showed reduction of average diameter of the nanofibers with introduction of TiO_2 to electrospun electrolytes. In addition, ion conductivity of about 0.08 $mS.cm^{-1}$ was obtained with the addition of 3 wt. % TiO_2 to the electrospun nanofibers.

Keywords: *Li ion battery, Electrospun electrolyte, Ion conductivity, TiO_2 nanoparticle.*

Introduction

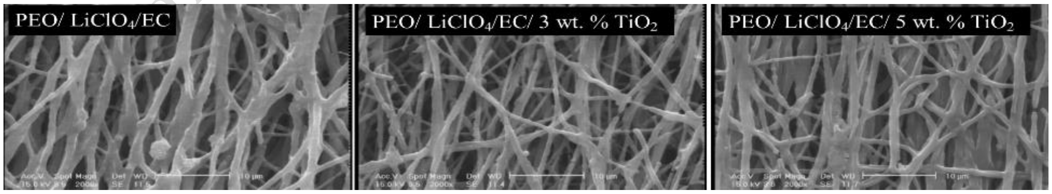
The development of lithium ion conducting solid polymer electrolytes (SPEs) is of current interest for use in portable devices and electric vehicles. SPEs provide the possibility for the fabrication of light weight and flexible devices with enhanced safety. However, insufficient ion conductivity suppressed their applications. Basically, SPEs are fabricated through a film casting method. SPEs comprise a polymer matrix and a lithium salt. Polyethylene oxide (PEO) is the most suitable matrix which can easily dissolve various lithium salts and additives. In SPE structures, ion conductivity increases with reduction of crystallinity regions and glass transition temperature (Tg). Incorporation of inert fillers such as titanium dioxide (TiO_2), etc. into the polymer matrix is a common method for improving the ion conductivity. In 2017, Freitag et al. indicated that compared with film casting method, an electrospinning process could be more efficient for the fabrication of SPEs. Highly-porous structure of nanofibers facilitates ion paths and enhances ion conductivity. In this study, the effect TiO_2 nanoparticles on the morphology and electrochemical properties of the electrospun electrolytes were evaluated.

Materials and methods

PEO, lithium perchlorate ($LiClO_4$), nano-sized TiO_2, ethylene carbonate (EC) and acetonitrile were obtained. Appropriate ratios of TiO_2 nanoparticles were sonicated in acetonitrile for 30 min (50 Hz). Then PEO (7 wt. %), EC (0.045 wt. %) and $LiClO_4$ (0.01 wt. %) were added to the solution and stirred for 4 hours. Nanofibrous structures were fabricated using an electrospinning method in following conditions: feeding rate of 0.5ml.h^{-1}, voltage of 18.5 kV, distance of 15 cm. Morphological properties were studied using a scanning electron microscope. The electrochemical measurement was carried out on a stainless steel electrode| the electrolyte| stainless steel electrode cell using the electrochemical impedance spectroscopy method, in a frequency range of 10 kHz to 1 Hz.

Results and discussions

Figure 1 shows the SEM images of the as-spun electrolytes. As it is apparent smooth and bead-free nanofibers were formed during electrospinning. Average diameter of the nanofibers were decreased with incorporation of TiO_2 into the nanofibers which can be attributed to the changes in the viscosity and ion conductivity of the electrospinning solutions.



PEO/ $LiClO_4$/EC

PEO/ $LiClO_4$/EC/ 3 wt. % TiO_2

PEO/ $LiClO_4$/EC/ 5 wt. % TiO_2

Figure 1. SEM images of the electrospun electrolytes.

Figure 2 shows the Cole-Cole plot of the electrospun electrolytes. As can be seen, the impedance was declined with the addition of 2.5 wt. % TiO_2 fillers. However, the impedance was increased with the addition of 5% wt. TiO_2 fillers. With the incorporation of the inert fillers, filler particles are placed between the polymer chains, reduce crystallinity and inhibit the orientation of the polymer chains and therefore increase ion conductivity. Although, with the addition of fillers over an optimum ratio, filler agglomerations occur which block the ion path and hence reduce the ion conductivity.

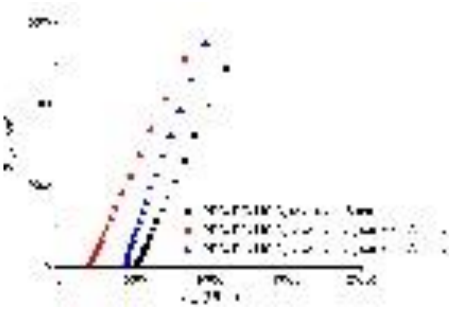


Figure 2. A.C. impedance of the electrospun electrolytes.

Conclusion

In summary, nanofibrous PEO-based electrolytes incorporated with TiO_2 ceramic filler were fabricated via an electrospinning method. The effect of TiO_2 ratio on the characteristics of the electrospun electrolytes were studied results showed reduction of the nanfiber's diameter with increase in TiO_2 ratio. In addition, ion conductivity of about 0.08 mS.cm^{-1} was obtained with the addition of 3 wt. % TiO_2 nanoparticles.

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Enhancing photoelectrochemical water splitting by Nickel-doped WO3 photoanode under visible light irradiation

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Abstract

Since its discovery by Honda and Fujishima in 1972, photoelectrochemical (PEC) water splitting has been intensively studied as a unique and effective approach to generating renewable energy from sunlight [1]. Monoclinic tungsten trioxide (WO_3) was recognized as one of the “ideal” materials for solar-driven water splitting because of its photosensitivity, good electron transport property, and photostability against acid corrosion [2,3].

This work describes the fabrication of Nickel-doped tungsten oxide (WO_3) photoelectrode by facile and cost-effective electrodeposition method at low temperature to improve the charge separation for enhanced photoelectrochemical water splitting. Photoelectrochemical measurements of the WO_3 and Nickel-doped tungsten oxide (WO_3) photoanodes were carried out under visible light illumination, in 0.5 M Na_2SO_4 solution with saturated calomel electrode (SCE) as a reference and a platinum wire as the counter electrode. The Ni-doped WO_3 photoanode was shown to greatly improve the PEC water splitting compared to WO_3 photoanode.

Keywords: *Charge separation, Electrodeposition, Photoelectrochemical water splitting*

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Enhanced efficiencies of lithium-air batteries using CNT/MnO2 nanocomposite cathodic materials

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Abstract

The rechargeable Li-O_2 batteries have attracted a considerable interest because of their theoretical energy density which is higher than 11000 Wh/Kg [1,2]. The energy density of Li-O_2 batteries is 5-10 times greater than those of lithium ion batteries [3,4]. This high energy density makes them a good candidate in totally electric cars, hybrid cars, and advanced electrical devices [5]. High theoretical energy density of this battery is due to the fact that the active cathodic material is not stored in battery and is supplied from air [6]. Thus, owing to the low weight of lithium metal, this battery is lighter compared to other electrode material based energy storage devices [7]. A CNT–60% MnO_2 nanocomposite was prepared and applied as the cathode material in the Li-O_2 battery. The Electrochemical Impedance Spectroscopy (EIS) and discharge–charge cycles were also studied for all the cathodes fabricated using various CNT–MnO_2 nanocomposites. The synthesized CNT–60% MnO_2 compound had a capacity of about 4600 mA.h/$g_{totalcathode}$ at a current density of 1000 mA/$g_{totalcathode}$. The battery fabricated using the optimum nanocatalyst revealed over-voltages equal to 0.20V and 0.87 V for discharge and charge, respectively, having a cycleability using the current density of 100 mA/$g_{totalcathode}$.

Keywords: Li-O_2 batteries, Electrochemical Impedance Spectroscopy (EIS), CNT–MnO_2 nanocomposite, Cycleability, Capacity, Current density.

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Synthesis and characterization of CNT/MnO_2 nanocomposites for application as active cathode materials in lithium-air batteries

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Abstract

Miscellaneous catalysts have been utilized as air cathodes such as noble metals like Pt, Au [1], and transition metal oxides like MnO_2, Fe_2O_3, Co_3O_4 and their mixtures [2,3]. Since these catalysts are expensive (like noble metals) or have low electrical conductivity (like metal oxides), the CNT composites with metal oxides are applied to overcome the low conductivity and corrosion drawbacks [4]. A series of CNT–MnO_2 nanocomposites containing different values of MnO_2 were prepared for application as the cathode materials in the Li-O_2 batteries to obtain the optimum rate. The optimum theoretical ratio of MnO_2 to the CNT used in synthesis was 60% (w/w_{carbon}) but the TGA analysis confirmed that the exact MnO_2/CNT ratio in the optimum catalyst was 41% (w/w_{total}). The CNT–60% MnO_2 nanocomposite was characterized by FE-SEM, TEM, XRD, EDS, TGA, FT-IR, and N_2 adsorption-desorption analyses. The XRD pattern of CNT–60% MnO_2 nanocomposite contained most of the peaks related to both the standard XRD pattern of MnO_2 (PDF number 44-0141) and those of the MWCNT structure. The FE-SEM micrograph of the pristine MWCNT indicated that the CNT diameters were almost equal for both CNT and CNT/60%MnO_2 composite (~30–40 nm) but in case of composite, the formation of MnO_2 particles was evident on the CNT surface. The TEM image of the CNT/60% MnO_2 nanocomposite revealed that the CNTs were covered with very fine MnO_2 particles forming a layer around the CNT (core-shell system) with the synthesized nanocomposite had a diameter of about 25 nm and the diameter

of CNT was ranged between 10–15 nm. The N_2 physisorption analysis showed a lower surface area for the CNT/60%MnO_2 composite (80 m^2/g) compared to that of the pristine CNT (103 m^2/g) which was attributed to the deposition of the MnO_2 nanoparticles over the CNT surface. The average pore volumes for the CNT and CNT-60% MnO_2 are 0.2097 and 0.1462 cm^3/g, respectively. All of the CNT/MnO_2 nanocomposites were intended to be applied as the cathode materials in the Li-O_2 batteries in order to achieve the optimum rate.

Keywords: *CNT–MnO_2 nanocomposite, TEM, XRD, TGA analysis, Cathode materials, Li-O_2 batteries*.

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Application of RGO/CNT nanocomposite as cathode material in lithium-air battery

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Abstract

In this work, RGO/CNT synthesized to be used as the cathode material in the lithium-air battery. The electrochemical efficiency of composite was evaluated through charge-discharge cycleability and electrochemical impedance spectroscopy (EIS) analysis. Results showed a capacity of 9000 mA·h/g at 100 mA/g. Also, the cycleability of the prepared electrode was examined during 50 cycles. Both constant current and constant current-constant voltage discharge methods were applied to improve the efficiency of lithium-air battery. XRD pattern of cathode made from CNT/RGO at 10th cycle using CC and CC-CV methods at current density of 200 mA/g. No product is detected at 10th cycle for the cathode used CC-CV method indicating the complete charging process. Contrarily, for the system charged by the CC method, some peaks attributed to lithium peroxide and lithium carbonate are witnessed that are related to defects and redox reactions of carbon. No lithium peroxide and lithium carbonate peaks are observed in the CC-CV charging process.

It was indicated that the CC-CV method was beneficial which was verified by the EIS and XRD analyses. Results exhibited an appropriate electrochemical performance for this composite to reduce and generate oxygen in aprotic medium.

Keywords: Cathode, RGO/CNT nanocomposite, EIS, lithium-air battery, capacity

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Influence of silica colloidal on the performance of gel valve-regulated lead-acid batteries

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Abstract

The gel electrolyte is a key factor modify the performance of lead-acid batteries. Two conventional gelators, colloidal and fumed silica, are studied. A gel electrolyte is prepared by mixing the Silica colloidal and Na_2SO_4 with sulphuric acid. The electrochemical properties illustrate that the gel electrolyte can suppress the oxygen evolution reaction, reduce the resistance to charge transfer at open circuit potential (increasing in OCP), increase the initial capacity, reduce water loss, demonstrating that it is a promising gel electrolyte for lead acid batteries.

Electrochemical behavior and battery performance under 100% DoD were investigated. Increasing the SiO_2 concentration led to quicker gelling times and hard gels. The cyclic tests indicate the proper performance of the gel electrolyte.

Keywords: Silica colloidal, open circuit potential, Deep of Discharge, gel electrolyte

Reference

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Gelled-electrolyte technology for valve-regulated lead-acid batteries

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Abstract

In recent years, the valve-regulated lead-acid (VRLA) battery has been developed into a versatile and acutely dependable energy-storage device. When given a accurately determined battery design technology for the required product application, the VRLA battery will offer the end user, some, if not all, of the following characteristics: high current capability; good reliability under cyclic, deep-discharge conditions (cycle life); good power density; high recharge efficiency; good charge stability (resistant to thermal runaway); no addition of water (topping-up) during service life (maintenance-free); long service life; wide operating temperature; robust design; low cost per Wh; high volumetric energy density (Wh/l); low self-discharge; high gravimetric energy density (Wh kg^{-1}); may be stored and used in any position (orientation); resistant to shock and vibration; no need to be recharged directly after discharge and environmentally 'safe'. The most commonly used gelling agent, fumed silica, has many disadvantages such as, impurity of the local working environment, exclusively during paste-mixing, and professional hygiene and handling problems. It is also bulky to transport and has long gel times unless used at very high concentrations. There is, therefore, an increasing demand for an alternative gelling agent for sulfuric acid in the production of gelled-electrolyte (GEL) VRLA batteries. Silica sols can provide a solution to all of these problems, and moreover at a lower cost to the battery producer.

Keywords: *VRLA batteries, deep-discharge, gelled-electrolyte, Silica*

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Photoelectrochemical performance of g-C_3N_4/TiO_2 nanowires/nanotubes array photoanode with the optimized processing temperature of g-C_3N_4

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Abstract

TiO_2 nanowires/nanotubes arrays have been extensively investigated to build photoanode for photoelectrochemical (PEC) water splitting, due to their good stability, low cost, and nanostructure-derived unique properties but large band gap [1]. G-C_3N_4 as a new kind of polymer semiconductor with high thermal and chemical stability and surface area possesses appropriate bandgap (~2.7 eV) that can absorb visible light up to 450 nm. However, the physical and chemical properties of g-C_3N_4 depend on type of precursors and the processing temperature [2]. In this work, TiO_2 nanowires/nanotubes arrays were directly deposited on titanium foil via anodization method [3]. In addition, g-C_3N_4 were synthesized by thermal polycondensation of melamine at different temperatures (450, 550 and 650 ^{0}C) [2]. For sensitization of TiO_2 nanowires/nanotubes arrays, g-C_3N_4 samples coated on the TiO_2 nanowires/nanotubes arrays. Based on our results, the crystalline structure, nitrogen content, band gap and morphology of the g-C_3N_4 materials were varied with the increasing of temperature. Scanning electron microscopy (SEM) image of the g-C_3N_4 (550 ^{0}C)/ TiO_2 nanowires/nanotubes arrays (Fig. 1) shows presence of g-C_3N_4 g-C_3N_4 (550 ^{0}C) sheets on the TiO_2 nanowires/nanotubes arrays/Ti. Our results introduce the g-C_3N_4 obtained from thermal polycondensation of melamine, as promising photocatalytic materials for PEC water splitting application. Moreover, by using photoelectrochemical techniques, the optimal thermal condensation temperature for g-C_3N_4 in PEC water splitting was obtained.

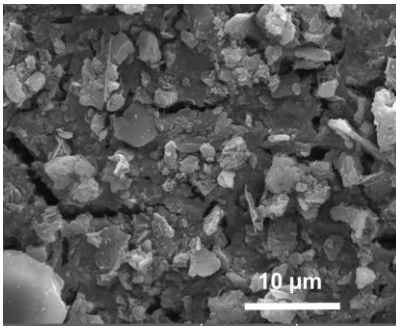

Fig. 1. SEM image of g-C_3N_4(550 ^{0}C)/ TiO_2 nanowires/nanotubes arrays.

Keywords: Photoelectrochemical, TiO_2 nanowires/nanotubes arrays, g-C_3N_4

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Photoresponse of graphene quantum dots (GQDs)/TiO_2 nanowires on FTO substrate in photoelectrochemical water splitting process

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Abstract

In recent years, world societies have focused on clean and renewable sources of energy. Hydrogen energy production from photoelectrochemical (PEC) water splitting under solar irradiation is a useful technique. In common, a main component of a PEC cell is a semiconductor material as a photoanode. Under illumination, photoelectron and photohole pairs are generated by semiconductor and caused hydrogen and oxygen production on cathode and anode. Titanium dioxide (TiO_2) is a n-type semiconductor with low cost, superior photocatalytic performance, long-term stability, and environmental compatibility but its photoactivity is limited in UV region of solar spectrum due to its wide band gap (3.2 eV). Visible light absorption of the TiO_2 can be improved by doping of metals and nonmetal elements, sensitizing with narrow band gap semiconductor, coupling with cocatalysts and so on [1]. Graphene quantum dots (GQDs) as a new graphene based materials with low dimensions (<100 nm), few-layer graphene sheets, high aqueous solubility and low cytotoxicity are utilized in energy conversion [2,3].

In this work, the TiO_2 nanowires and GQDs were synthesized by hydrothermal technique on FTO substrate and green electrochemical approach, respectively. The prepared TiO_2 nanowires on FTO were modified by the GQDs, using spin coating method. Physical and chemical properties of the GQDs/TiO_2 nanowires photoanode were investigated by SEM, XRD, UV-vis spectroscopy and FTIR analysis. The GQDs/TiO_2 nanowires electrode was utilized as photoanode in PEC cell and its photoresponse and PEC performance were compared with results from pure TiO_2 nanowires photoanode.

Based on our results, FESEM images confirmed the TiO_2 nanowires formation, with average length of 4 µm and diameter range of 100-250 nm (Fig. 1 (a)). After deposition of the GQDs, the GQDs covered the surface of the TiO_2 nanowires, uniformly, proving direct evidence for the successful fabrication of the GQD/TiO_2 nanowires photoelectrodes (Fig. 1(b)).

Photoelectrochemical properties of the TiO_2 nanowires and the GQDs/TiO_2 nanowires photoelectrodes were investigated in PEC cell with 0.1 M Na_2S solution as electrolyte under light illumination of 100 mW/cm^2. By using chronoamperometry technique (Fig. 2), the photocurrent density for the GQD/TiO_2 nanowires photoelectrode was measured at about 30 A/m^2, without any applied bias, 6 times larger than those of pure TiO_2 nanowires photoelectrode.

It was, thus, found that GQDs sensitized PEC cells greatly enhanced visible-light absorption due to favourable energy levels between the GQDs and TiO_2 that induce directional transport charge for efficient charge separation. Therefore, the GQD/TiO_2 nanowires provide a promising green photoelectrode for photoelectrochemical water splitting (H_2 and O_2 production) and other energy applications.

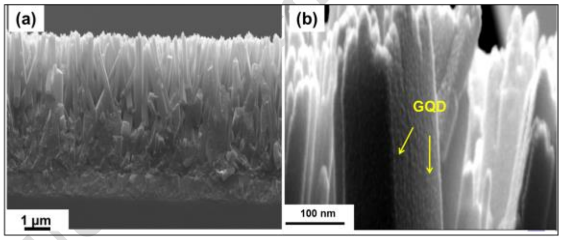

Fig. 1. (a) SEM image of (a) the TiO_2 nanowires and (b) the GQDs/TiO_2 nanowires photoelectrodes.

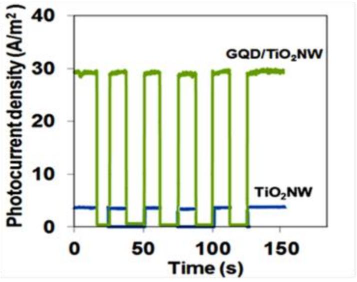

Fig. 2. Photoresponse of different photoanodes

Keywords: Photoelectrochemical, TiO_2 nanowires, Graphene quantum dot

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TiO_2 nanowire/nanotubes arrays on titanium substrate as a negative electrode for supercapacitor

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Abstract

Supercapacitors as storage devices have recently attended due to their high power density, long cycle life, fast charge-discharge rate. However, there is a limitation on the energy density of supercapacitors. According to the equation $E=1/2\ CV^2$ (where E, C and V are the energy density, the specific capacitance and the cell voltage) the energy density of supercapacitors can be enhanced by improving the specific capacitance and the cell voltage. Among these strategies, high cell voltage is more efficient and useful to improve the energy density (energy density is related to V^2 in the equation). Therefore, fabricating novel positive electrodes and negative electrodes with higher positive operating potential and lower negative operating potential, respectively, can be an efficient strategy to enhance the energy density of asymmetric supercapacitors [1, 2].

In this work, TiO_2 nanowires/nanotubes array electrode was synthesized on titanium (Ti) foil by anodization method. The Ti foil was anodized at 50 V over 2h in a two-electrode cell with an electrolyte, containing ethylene glycol, 0.5wt% NH_4F, 2.5wt% H_2O, a Ti foil as the anode, and another Ti foil as the cathode. The obtained TiO_2 nanowires/nanotubes array electrode was annealed at 550 ^{0}C for 1 h

Based on FESEM images, the nanowires formed on top of the nanotubes array. In some regions, the top of nanotubes is exposed. The nanotubes arrays with nanowires formed on their top improve surface area for effective interface of the TiO_2 nanowires/nanotubes array/Ti electrode and electrolyte. The average tube diameter of the TiO_2 nanotubes arrays was at about 100 nm (Fig. 1). The TiO_2 nanowires/nanotubes array/Ti electrode is used as the negative electrode for asymmetric

supercapacitor. Electrochemical measurements showed that the TiO_2 nanowires/nanotubes array structure is suitable for the electronic conduct and ionic transport. The TiO_2 nanowires/nanotubes array/Ti electrode as the negative electrode for supercapacitor at the ultra-negative potential region in 0.5 M Na_2SO_4 electrolyte, exhibited high capacitive performance and high rate-capacity. The CV curves at scan rate of 0.05 V/s and negative potential of -1, -1.2, -1.4 and -1.6 -0 V vs Ag/AgCl electrode for the TiO_2 nanowires/nanotubes array/Ti electrode indicated quasi-symmetric CV curves, only slight distortion from hydrogen at the potential of -1.6 V. These behaviors were resulted from the electrochemical stability of TiO_2 and inert for hydrogen evolution reaction.

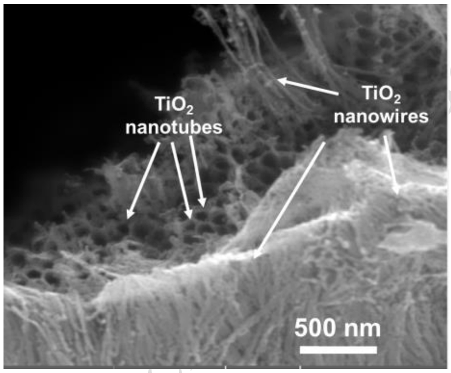

Fig. 1. FESEM image of the TiO_2 nanowires/nanotubes array/Ti electrode.

Keywords: TiO_2 nanowires/nanotubes array/Ti, negative electrode, supercapacitor

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Preparation of tungsten oxide nanoparticles modified graphenized pencil lead electrode: An efficient electrocatalyst for water splitting in alkaline medium

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Abstract

Developing efficient heterogeneous electrocatalysts for oxygen evolution reaction (OER) is a critical component for water splitting technology [1-3]. In this study tungsten oxide nanoparticles were electrodeposited on the surface of graphenized pencil lead electrode (GPLE) as a low cost and efficient electrocatalyst for the OER in alkaline media. The prepared tungsten oxide modified GPLE (WO_3/GPLE) was carefully characterized by scanning electron microscopy, energy-dispersive X-ray spectroscopy, electrochemical impedance spectroscopy and cyclic voltammetry techniques. The WO_3/GPLE exhibits excellent performance in electrocatalytic water oxidation in alkaline media due to synergistic effects arising from the GPLE and WO_3 nanoparticles. The developed electrocatalyst represents remarkably low OER overpotential of 1.38 V (vs. RHE) at the current density of 10 mA cm^{-2} and Tafel slope of 89 mV dec^{-1} in 1 M KOH solution. The WO_3/GPLE was highly stable and capable for maintaining catalytic activity for at least 5 h. Due to distinctive electrical conductivity, high mass transfer, and adequate active sites of GPLE, the electrocatalytic activity of the WO_3 nanoparticles were incredibly improved in WO_3/GPLE.

Keywords: Graphene, Pencil lead, Water splitting, WO_3 nanoparticles

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Methanol electro-oxidation on Pt/PGE modified by poly (aniline-co-p-phenylenediamine)-Ni nanocomposites

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Abstract

Direct methanol fuel cell has a significant advantage for powering portable applications due to its simple design, low operating temperature, and convenient fuel storage and supply. Methanol is also attractive low cost liquid fuel which is widely available, easy for handling, storage, and refueling. It has high energy density similar to gasoline. Pt catalysts for the methanol oxidation reaction have attracted a great deal of attention because they are key part of the anode in direct methanol fule cells (DMFCs) [1]. However, the low electrocatalytic activity and short-term stability of these catalysts in the methanol electrooxidation still prevent the widespread commercialization of DMFC. To develop cost effective electrodes, it has been shown that the dispersion of Pt in very minute quantities in the form of microparticles inside a polymer matrix lead to obtain modified electrodes which represent excellent electrocatalytic properties for the oxidation of methanol [2]. Such properties attribute to the increasing of active surface area by dispersion of the catalyst and also a lowering of Pt crystallites poisoning carbon monoxide [3].

In the present study, in order to achieve an inexpensive tolerable anode catalyst for direct methanol fuel cell applications, a nanocomposites of poly(aniline-co-*p*-phenylendiamine)-Ni and Pt nano-particles (PANI-co-*P*pda)@Ni/Pt), was prepared by in-situ emulsion polymerization. The synthesized nanocomposites was used to modify pencil graphite electrode (PGE) and the capability of the obtained modified electrode in methanol electrooxidation was investigated. The efficience of the modified electrode was studied by different electrochemical methods such as; cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and chronoamperometry and the results were compared with those obtained by the bare Pt/PGE. The electrode modifier was

characterized by FT-IR, X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM). FESEM images are indicated that (PANI-co-*P*pda)@Ni/Pt/PGE) make good jućtions between platinum particles and anchor the platinum particles and so reduce the Pt migration during methanol electrooxidation. The obtained results reveal that the introduction of nanocomposites within catalyst layer improved the catalytic activity of the Pt nanoparticles.

Keywords: Polymer based nanocomposite, Pencil graphite electrode, Electro oxidation of methanol

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Synthesis of MoS2 nanoflakes electrode for electrocatalytic hydrogen evolution

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INTRODUCTION

Engineering the morphology and characteristics of Transition metal dichalcogenides (TMDs) especially well-known MoS_2 is the essential challenge due to their unique properties and favorable applications[1-3]. This work is focused on enhancing the exposed edge sites and defects of MoS_2 for catalyzing Hydrogen Evolution Reaction (HER). The novelty of this procedure is the facile preparation of stable and efficient MoS_2 nanoflakes / FTO noble metal-free and non-toxic electrode directly and removing the need for the binder for hydrogen evolution.

EXPERIMENTAL STUDY

In brief, an adequate amount of Sodium Molybdate as Mo precursor and Thiourea as S precursor was added into 25 ml Di-Ionized water, then stirred and transferred together with FTO substrate pieces into the Teflon-lined autoclave and treated hydrothermally at temperature of 230˚ C for 20 h. Electrochemical measurements were carried out in presence of 0.5 Molar H_2SO_4 solution (pH=0).

RESULTS AND DISCUSSION

Raman spectroscopy is shown in fig. 5-a. The two main peaks at ~379 and ~404 cm^{-1} corresponding to in-plane E_{2g}^1 and out-of-plane A_{1g} vibration modes agree with the formation of pure hexagonal 2H- MoS_2 structure[4]. fig. 5-b shows the MoS_2 nanoflakes on the FTO substrate. As can be seen the MoS_2 nanoflakes are formed uniformly.

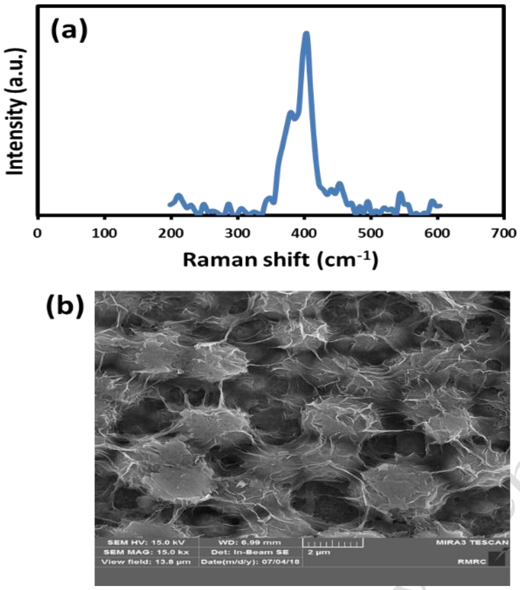

fig. 5. (a) Raman spectrum and (b) FESEM image of the binder free MoS_2 nanoflakes / FTO electrode.

Linear Sweep Voltammetry (LSV) and Electrochemical Impedance Spectroscopy (EIS) techniques were performed and the results are shown in fig. 6. According to LSV and EIS data, the obtained MoS_2 nanoflakes / FTO electrode demonstrates high HER activity with charge transfer resistance of 78 Ω that is an ideal elecrode for hydrogen evolution.

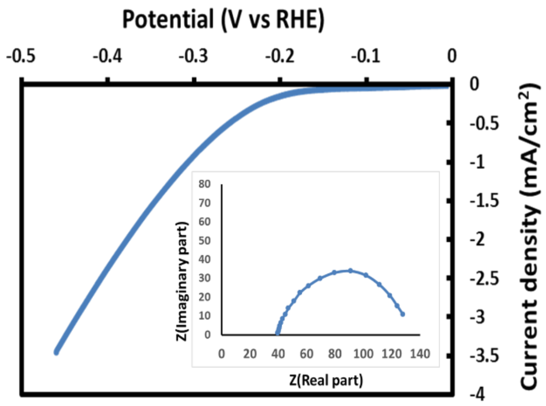

fig. 6. LSV curves and Nyquist plots of MoS_2 nanoflakes / FTO electrode.

CONCLUSION

In summary, we prepared an efficient, low cost, binder free and easily obtained MoS_2 nanoflakes / FTO counter electrode that offers remarkable advantageous over noble metal electrodes. It is suitable for large-scale production also it is a promising catalyst for various applications.

Keywords: Binder-free, edge sites, catalytic activity, Hydrogen evolution, MoS_2 nanoflakes

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Investigation of CuSO4.5H2O as a cathode electrode in sodium ion batteries

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Abstract

In large scale energy storage devices, sodium ion batteries due to desirable properties such as the abundance of sodium, low cost and safety over organic electrolytes are the suitable replacements for lithium ion batteries. We study the effect of copper sulfate on additional compounds for optimizing the battery in aqueous Environment [1]. Cobalt compound is sometimes a good choice for improving the properties of the positive electrode material. Cobalt raises the oxygen over potential increases the conductivity of the active material and reduces the electrode swelling during charge- discharge cycling [2,3].

In this work, we report a novel, high power SIB formed by coupling $CuSO_4.5H_2O$, $CoSO_4.7H_2O$ & Graphite as cathode with $MnSO_4.5H_2O$, $NiSO_4.6H_2O$ and $CoSO_4.7H_2O$ & Graphite as anode. Electrochemical properties were studied with cyclic voltammetry and chronopotentiometry techniques. After applying 100 cycles to the manufactured battery by using the CV technique, the battery could be discharged with 1.45 V in 7090 seconds and high efficiency of about 70.9%. Also the capacity of this battery resulted 856.08 mAh/g.

Keywords: Sodium battery, Aqueous environment, Electrolyte, Copper Sulfate

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A brief look at the theoretical studies on the storage of hydrogen gas in metal-organic frameworks

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Abstract

Metal-organic frameworks are periodic materials with crystalline lattices which are mainly formed by bonding metal ions with organic ligands[1]. The structural building blocks of MOFs can be combined to produce an almost unlimited number of materials. Each of these compounds naturally exhibits different properties in the absorption of various gases, including hydrogen. The problem is that synthesizing and evaluating the properties of all these compounds is time consuming and costly. For example, in 2012 Wilmer et al managed to identify 137953 hypothetical MOFs through computations and using only 102 building blocks[2]. This huge number of compounds shows that the use of computational tools rather than experimental work is more logical for high-throughput screening. However, the use of conventional simulation techniques in this area, such as Molecular dynamics (MD), Grand canonical Monte Carlo (GCMC) and Density functional theory (DFT), somewhat reduced the complexity of this massive amount of materials, but these methods do not appear to be fast enough to find ideal structural constituents and conventions. Therefore, in addition to the simulation methods used for phenomenology, in recent years the modeling of the gas absorption process in the MOFs has also been considered. Methods such as Quantitative structure- property relationships are proposed to predict the absorption of various gases such as methane, nitrogen, carbon dioxide and hydrogen based on the structure of the MOFs. Eventually, these models will be able to predict the amount of hydrogen uptake at high accuracy in the shortest time, as well as the rules and procedures for designing higher-efficiency MOFs[3].

Keywords: Metal-organic frameworks, Hydrogen uptake, Simulation, Quantitative structure-property relationships

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Electrochemical storage of hydrogen with the coating of mercury alloys

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Abstract

Energy storage is a way to help bring life and progress to the next generation. Fossil fuels are not renewable and eco-friendly; therefore the researchers focus on renewable energies.

The electrochemical storage of hydrogen as a green fuel can solve numerous problems, such as high cost and unsaifty.

Recently, researchers have done numerous research on electrochemical hydrogen storage by different metals but still acceptable results are not available for mercury metal [1-3].

In the present study, a comparison was made between the ability of hydrogen electrochemical storage in nickel and mercury in the different situations.

The electrochemical studies were done by cyclic voltammetry (CV) and chronopotentiometry (CE) techniques.

Based on the results, in the current of -0.5,-1 and -2 mA, and at the same charging times,
the hydrogen storage efficiency in mercury is higher than nickel.

Keywords: Electrochemical techniques, Hydrogen storage, Mercury, Nickel

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Molten-salt chemical exfoliation process for preparing Si layered structure as anode for lithium-ion batteries

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Introduction

Lithium ion batteries are becoming a key-enabling technology for electric vehicles and hybrid electric vehicles[1].Silicon (Si)-based compounds, such as $SiLi_{4.4}$, are among the possible alternatives and have shown high capacity values as anode materials (4200 mA h g−1). One drawback associated with Si-based materials is structural decomposition in conjunction with volume expansion during charge/discharge cyclin .Furthermore, Si-based materials having different structures and compositions have also been investigated as a means of preventing this structural damage[2].

Methods

In a typical procedure, 1 g of CaSi2 was mixed with 10 g of $AlCl_3$ at a weight ratio of 1/10. The mixed reactants were loaded in a stainless-steel autoclave (volume 20 mL). The above procedure was conducted in a glove box filled with N_2. Then, the autoclave was sealed immediately and heated in an electric stove at a heating ramp rate of 10 °C.min−1 and maintained at 195 °C for 10 h. After cooling to room temperature naturally, the precipitate was collected and washed with 0.1 M hydrochloric acid, distilled water, and ethanol. Finally, the product was dried in vacuum at 50 °C for 10 h for further characterization[3].

Results and discussion

In this work, a molten-salt chemical exfoliation methodology is developed for producing freestanding si layered by a deintercalation reaction between layer-structured $CaSi_2$ and excess $AlCl_3$ at 195 °C. $AlCl_3$ promotes the exfoliation process not only by participating in the chemical reaction $3CaSi_2 + 5AlCl_3 = 3CaAlCl_5 + 2Al + 6Si$, extracting Ca^{2+} and generating layer-structured Si,but also by providing a nonpolar non-oxygen liquid medium for exfoliation of layer-structured Si.

The morphology and structure of these samples were characterized by IDFix report analysis and scanning electron microscopy.The morphology and microstructure of the asprepared samples were investigated by SEM, as shown in Fig 1.IDFix report analysis (fig 2) illustrates that Ca ions were extracted from the $CaSi_2$, the generated $CaCl_2$ can be dissolved in the excess molten $AlCl_3$, leaving layer-structured bulk Si. Then, the layerstructured Si particles are exfoliated in the liquid medium of molten AlCl3. After the byproducts and excess salts were removed by washing,a mesoporous Si nanosheet powder was obtained.

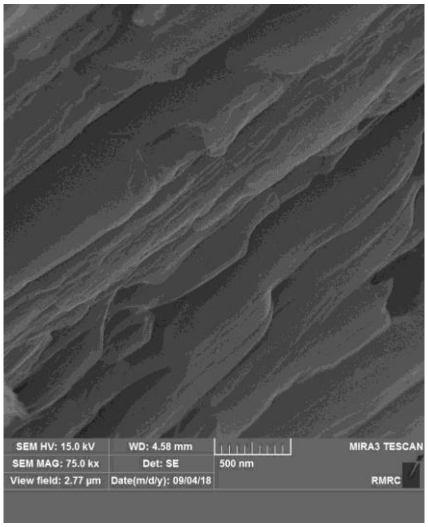

Figure 1 SEM images of final sample

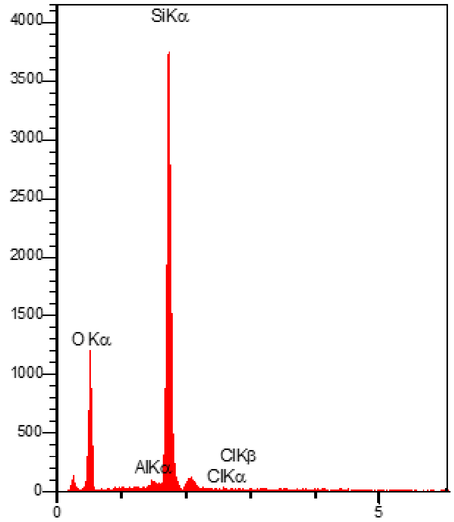

Figure 2 IDFix report analysis of final sample

Conclusion

We used exfoliation process for fabrication silicon layered structure by reaction of layer-structured $CaSi_2$ in molten $AlCl_3$ at 195 °C (Note that gram-scale synthesis of Si layered structure was realized in this work, and the proposed method is simple and easy to scale up). Also This unique framework is beneficial for buffering the volume variation and for fast ionic diffusion.

Keywords Keywords: lithium ion batteries – chemical exfoliation process - Si layered structure

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Chemical Synthesis of Pt and Pt-ZrO2 Nanoparticles on Graphite oxide (GO) and Multi Wall Carbon Nanotubes (MWCNT) used as an anode electro catalyst in DMFC

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Abstract

Graphene Nano sheet, is one the critical topics in materials science, which has been extensively studied due to the thermal, mechanical, and chemical properties arising from their strictly 2D structure, also because of the potential technical applications [3ref]. Particularly, these remarkable characteristics enable it to be a promising candidate as a new 2D support to load metal nanoparticles (NPs) for application in fuel cells [2ref]. A high-efficiency energy production without contamination is a major challenge in technology which can be resolved by using the electrochemical conversion of fuel cells [2ref].

In this research, we tried to figure out this challenge by using *Methanol*, because *methanol* shows a lower ratio of *H/C* due to lack of *C-C* bindings. In addition, it can be deformed at lower temperature in comparison with other organic material [ref]. our anode electro catalyst is designed by chemical synthesis of platinum electrocutes and platinum-zirconium oxide in 4:1 ratio on *Graphit oxide*(GO) and multi-wall carbon nanotubes (MWCNT). Furthermore, *NaBH4* used as a reducing agent to provide the anodic electro catalysts in direct *methanol* fuel cells. To investigate the structural properties, morphology and, electrochemical we characterized our electro-catalysts by X-ray diffraction (XRD), transmission electron microscopy (TEM), and cyclic voltammeter (CV) methods. Our results indicate that the *PtZrO2 /GO* electro catalyst shows significantly higher flow rate in high initial potentials to compare with what it is reported in the literature.

Keywords: Platinum, Electrocatalyst, Methanol Oxidation, Graphene nanosheet

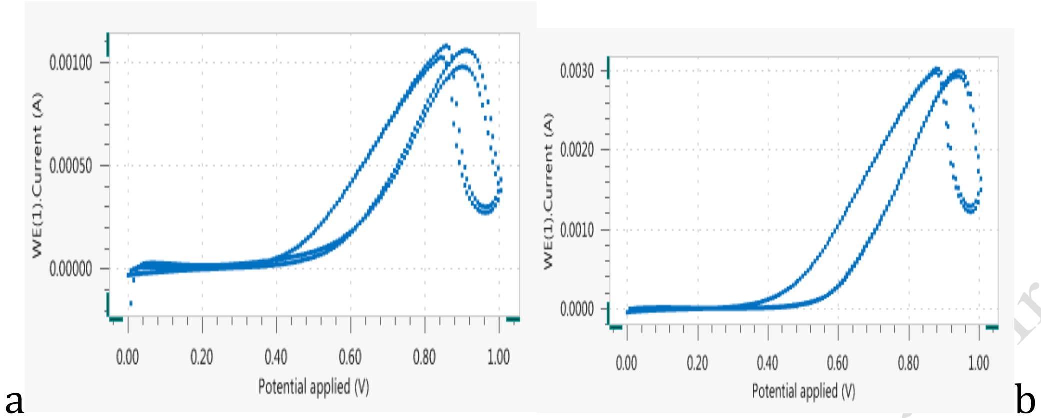

Fig.1.CVs of Pt-ZrO2/MWCNT (a), Pt-ZrO2/GO (b) in 0.1M CH3OH and 0.2M H2SO4

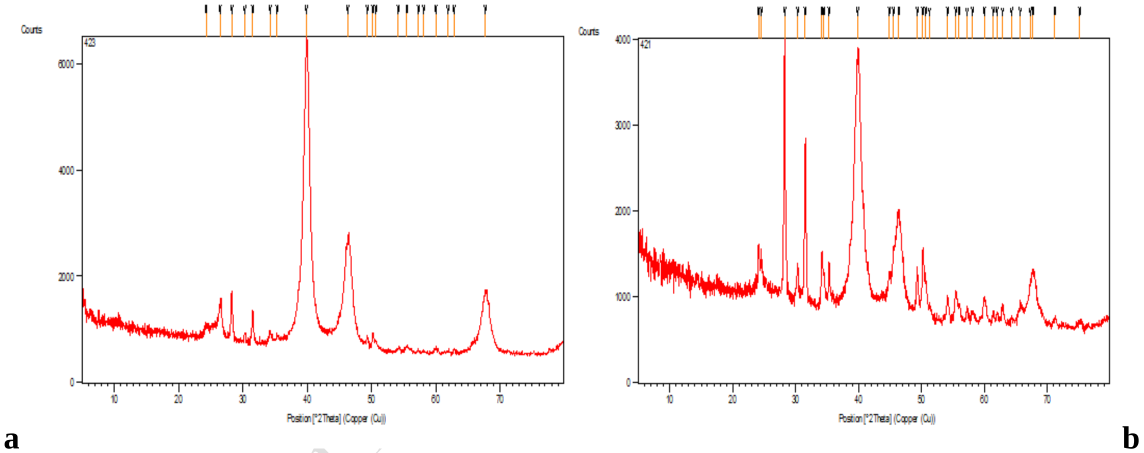

Fig.2.XRD of Pt-ZrO2/GO (a), Pt-ZrO2/MWCNT (b).

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Electrocatalytic Activity Investigation of Alloyed $PtZrO_2/C$ and $PtZrO_2/SWCNT$ Nanoparticels as an anode electro catalyst in DMFC

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Abstract

Direct methanol fuel cell (DMFC) is a promising power source of technology, but it has not been successfully commercialized yet due to the high cost and low kinetic oxidation. Platinum-based electrocatalysts have been extensively developed as efficient catalysts for both the anode and cathode in DMFC [3 ref]. To improve the electrocatalytic activity for methanol oxidation, other platinum-supporting materials have been studied as electrode catalyst component of low-temperature fuel cells [2ref]. Platinum (Pt) is commonly used as the catalyst because of its high electro-catalytic activity [1ref]. Carbon nanotubes are suggested as an ideal anode electrocatalyst supporting material for the practical application of direct methanol fuel cells [ref].

In this study, we reported the electrocatalytic activity of alloyed *PtZrO2/V and PtZrO2/SWCNT* nanoparticels. A simple approach is planned for a deposition of platinum (pt) nanoparticles onto surfaces of Single-wall carbon nanotube and Vulcan carbon by using NaBH4 as a reducing agent in direct methanol fuel cells. The structural properties and morphologies of all nanocatalysts are fully characterized by using techniques such as transmission electron microscopy (TEM), X-ray diffraction (XRD), and cyclic voltammetry (CV). Cyclic voltammetry and chronoamperometry measurements indicated that a ratio of *PtZrO2/SWCNT* (4:1) is an optimum ratio to obtain the best electrocatalytic activity on CNTs-supported alloyed nanoparticles for methanol oxidation reaction.

Keywords: Direct methanol fuel cell, Pt-based catalyst Electrocatalysis, Carbon nanotube

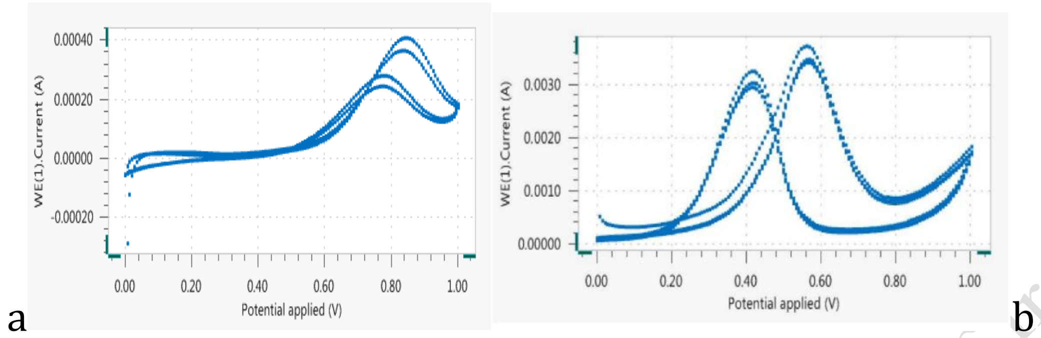

Fig.1.CVs of Pt-ZrO2/V (a), Pt-ZrO2/SWCNT in 0.1M CH3OH and 0.2M H2SO4

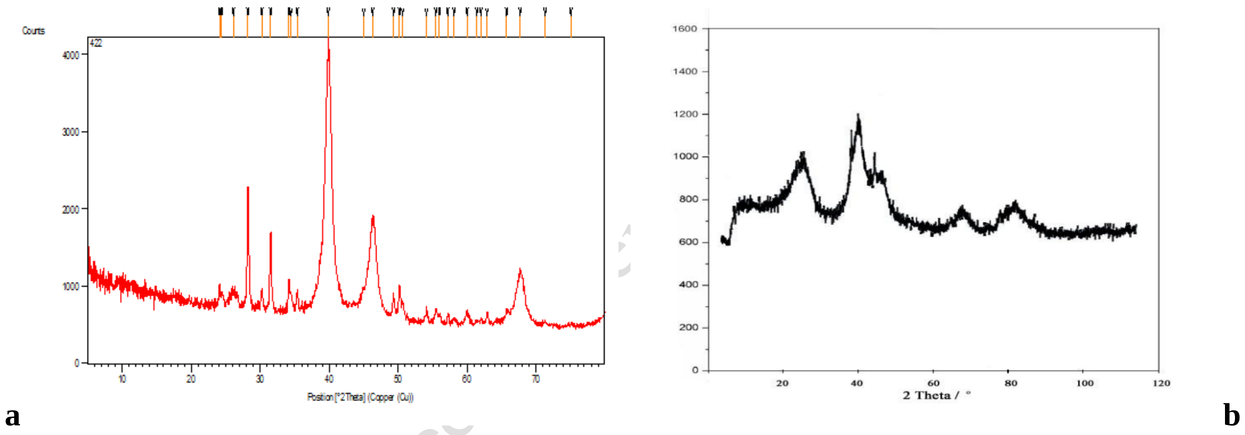

Fig.2. XRD of Pt-ZrO2/V (a), Pt–ZrO2/SWCNTs (b).

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Review on $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) as a Promise 5V-class Cathode Material for Li-ion Batteries

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Abstract

With respect to the shortcoming the unrenewable energy sources in recent years, Li-ion batteries as a high energy, high voltage, high specific capacity, and long cycle life energy storage device had attracted the customer's attention. Towards the better electrochemical performance, a high capacity anode, a high energy and high rate cathode, and a wide-potential electrolyte are required. Until now, numerous anode materials such as traditional graphite, Sn, Al, Ge, LTO as a safe electrode, and Si with 4200 mAh/g theoretical specific capacity were introduced. Nevertheless, cathode electrode as a Li-ion source plays a critical role in the supplying energy. Recently, various high capacity or high voltage cathode materials including layered oxides, phosphates, sulfates, borates, and silicates were developed to access up to 5V operating voltage and 400 mAh/g specific capacity. One of the promise 5V-class cathode materials is $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) with the discharge voltage of 4.7-4.8 V vs. Li^+/Li and 147 mAh/g theoretical capacity. LNMO is categorized into the spinel structures with oxygen vacancies. There is two crystal symmetry for synthetic LNMO including $Fd\bar{3}m$ and $P4_332$, corresponding to disordered and ordered Ni/Mn location in octahedral sites, respectively. The Jahn-Teller distortions for oxygen deficiency cause to the formation of M^{3+} during delithiation and improvement electrochemical behavior. So, the Mn^{3+}/Mn^{4+} redox couple presents a voltage plateau at around 4V during charge/discharge process. The stability of the Mn^{3+}/Mn^{4+} plateau during several cycles is depended to $Fd\bar{3}m$ disorders in the crystal structure. Moreover, two plateau at around 4.6 and 4.8 V is related to Ni^{2+}/Ni^{3+} and Ni^{3+}/Ni^{4+} redox couples [1]. In order to prevent a dissolution of Mn-ion into the electrolyte solution due to higher difference electronegativity of Mn-O bond than Ni-O bond and increase the cycle

life, charge-barrier dopants and surface modification are two important solution, which is mostly reported.

In 2017, Giulio Gabrielli had synthesized $LiNi_{0.5}Mn_{1.5}O_4$ modified by $LiNbO_3$ with 97 and 90 mAh/g specific capacity at 5C-rate before and after modification [2]. Sheng Li has investigated the effect of Na_2CO_3 and $NaHCO_3$ as a precipitating agent on the electrochemical performance of LNMO. LMNO hollow spheres synthesized by Na_2CO_3 were shown 128, 121 and 120 mAh/g at 0.1, 5 and 10C, respectively with >80% retention after 100 cycles. Furthermore, the energy densities of as high as about 600 Wh Kg^{-1} and 520 Wh Kg^{-1} were obtained at the rates of 0.1 and 5C, respectively, as for power density from 59.7 to 2000 W Kg^{-1} with the increase of current density from 0.1 to 5C [3]. In addition, Metal-doping into the $L_{1-x-y}(NiMn)_x M_y O_4$ with y=0.1-0.2 was frequently reported [1, 4, 5]. Recently, the scientists could synthesize modified-LNMO with 135 mAh/g specific capacity at 1C, which can remain to 105 mAh/g at 30C discharge rate after 1200 cycle.

Keywords: Cathode, High Voltage, LNMO, Li-ion Battery.

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Investigation of catalytic behavior of palladium nanoparticles supported by carbon nanodots as an electrocatalyst for methanol oxidation

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Abstract

Noble metal (Pd) electrocatalysts supported on carbon quantum dots (CQD) are used for methanol oxidation in alkaline media. The results show that noble metal electrocatalysts supported on carbon nano dots give better performance than that without any carbonic nanomaterials. Because CQDs by their unique properties provide high active surface area and caused to increases the electronic conductivity. The results show a synergistic effect by the interaction between Pd and carbon nanodots. The Pd supported on carbon quantum dots in this paper possesses excellent electrocatalytic properties and may be of great potential in direct alcohol fuel cells.

This nanocomposite fabricated by facile one step electrochemical method. Electrocatalytic behavior of mentioned catalyst was studied by different electrochemical technique such as cyclic voltammetry and linear sweep voltammetry. The effect of electrolyte temperature also was investigated by linear sweep voltammetry and results show that, increases of temperature has an incremental effect on oxidation of methanol, so that at high temperatures, the required activation energy for starting the reaction became lower than low temperature.

Keywords: *Nobel metal, Carbon quantum dots, methanol oxidation, synergistic effect*.

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Electrochemically Reduced Graphene Oxide Deposited on Nickel-Nickel Oxide Foam for Supercapacitor Applications: Toward High Specific Capacitance

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Abstract:

Electrochemical supercapacitors are known as the next-generation energy storage device due to their high capacitive capacities, high cycle stability and fast recharging. Types of supercapacitors include electrical double-layer capacitors (EDLCs) and pseudocapacitors. Various types of materials include transition metal oxides and conductive polymers as applications. Several studies have been conducted to the surface area of electro-active materials to create a high specific capacitance. Also, the use of high conductivity materials such as carbon nanotubes and graphene can also increase the conductivity of metal oxide electrodes. Meanwhile, graphene is an excellent choice for the growth of metal oxides due to its high conductivity, electrochemical stability, high surface and excellent mechanical properties. This paper introduced a new two-step method for generating a highly nanoporous nickel and nickel oxide (Ni-NiO) foam/Electrochemically reduced graphene oxide (ERGO) electrode with an exceptional specific capacitance for supercapacitor applications. This method first involved a drop cast of graphene oxide on Ni-NiO foam, and in the next step, graphene oxide was reduced in a constant current method at a current density of -0.6 mA cm^{-2} to -20 mA cm^{-2} in a 1 M KOH electrolyte. The Raman spectra for GO and ERGO at a density of -1.2, -3.0, -5.0 and -10 mA cm^{-2} were shown in Fig. 1(a). The I_D/I_G intensity ratio was 0.89, 0.93, 0.95, 1.0 and 1.11, respectively. As a result, the major oxygen functional groups which were intercalated into the interlayer spacing of graphite was eliminated. The XPS spectrum for GO

sheets and Ni-NiO-foam/ERGO composite at a current density of -10 mA cm^{-2} showed a significant decrease in the oxygen-containing functional groups, especially peak C (epoxy)/C-OH. These results indicated that functional groups have been significantly eliminated (Fig. 1(b,c)). According to the galvanostatic charge-discharge (GCD) curve for the Ni-NiO foam/electrochemically reduced graphene oxide, a specific capacitance of 1995 F g^{-1} was obtained at a current density of 1 A g^{-1} (Fig. 1(d,e)). Also, after 6000 cycles at a current density of 20 A g^{-1}, 95.1% of the initial specific capacitance was maintained (Fig. 1(f)).

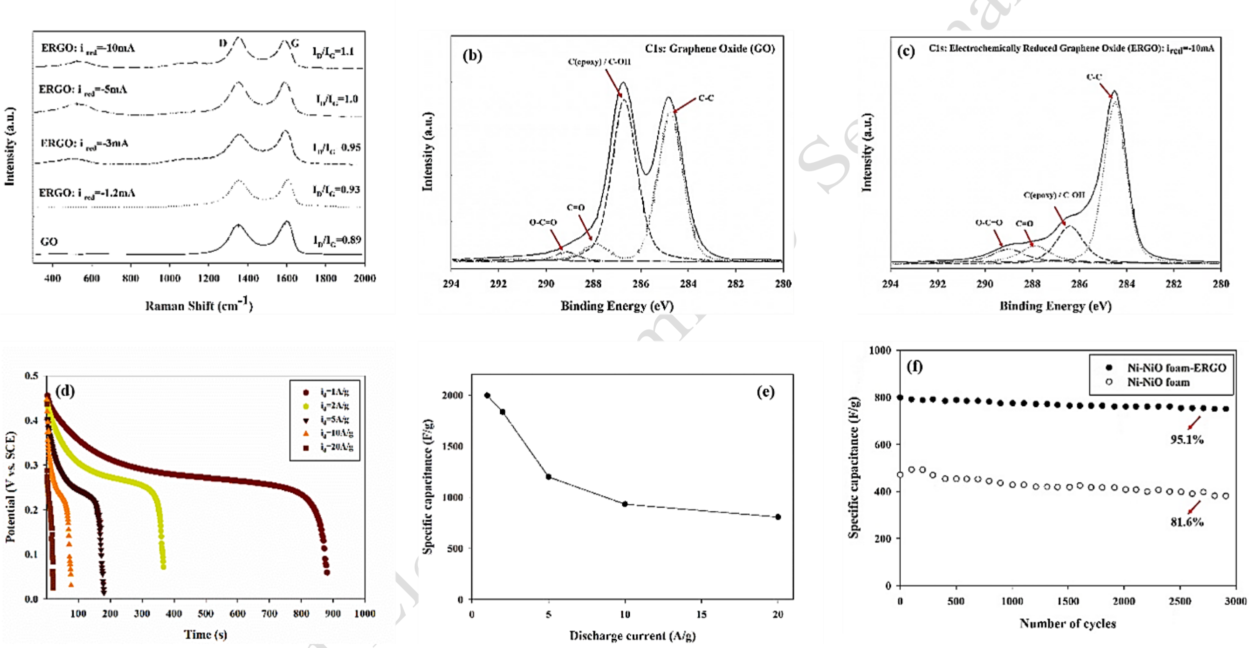

Fig. 1: The Raman spectra of GO and ERGO under the different constant reduction currents (b,c) The XPS survey spectra of GO and ERGOs, (d, e) The GCD and average specific capacitance at the various discharge current densities for Ni-NiO foam/ERGO reduced,and (f) the cyclic stability of electrodes at a current density of 20 A g^{-1}

Keywords: *ERGO, Ni-NiO foam, Supercapacitor, Electrochemical reduction, Constant current*

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Mechanisms for electrochemical performance enhancement by the salt type electrolyte additive, Vinyltriethoxysilane, in high-voltage lithium-ion batteries

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Abstract

Lithium-ion batteries (LIBs) have attracted attention due to their potential to facilitate the rapid development of mobile electronic devices, electronic vehicles and energy storage. However, the high flammability of carbonate-based electrolytes has long been one of the most important obstacles for the further applications of these types of batteries. To develop safer advanced batteries, herein we use an environmentally-friendly additive, vinyltriethoxysilane (VTES), to suppress the flammability of a carbonatebased electrolyte. VTES was found to not only reduce the flammability of the electrolyte, but also enhance the thermal stability of both the electrolyte and the LiCoO2 cathode by forming a stable surface layer. In order to gain insight into the reaction process of the electrolyte with VTES, we used density functional theory to elucidate their formation mechanism. The results indicate that the vinylsilyl radical tends to preferably react with the oxygen atoms of solvent molecules to form more stable compounds. These results show that VTES is a promising additive to improve the safety of LIBs.

Keywords: Lithium Ion batteries, Vinyltriethoxysilan, Electrolyte Additive, energy storage

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Li_2MnSiO_4/C/Graphene composite as a high performance cathode material for li-ion batteries

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Abstract

Among different cathode materials, the lithium orthosilicates, Li_2MSiO_4, have unique properties, such as high theoretical capacity of (>300 $mAhg^{-1}$), plausible extraction of more than one Li^+ ion per formula unit and high thermal stability through strong Si-O bonding[1]. Among the silicate groups, Li_2MnSiO_4 are more attractive than other counterparts because they are more cost effective and environmentally benign .in addition, Li_2MnSiO_4 provides a high cell voltage due to the possible oxidation of the Mn^{3+}/Mn^{4+} couple [1-4].

Li_2MnSiO_4/C samples were prepared by a citric acid assisted sol–gel method. Graphene oxide prepared by a modified Hummer's method [5,6]. For the preparation of working electrodes, 90 wt% Li_2MnSiO_4/C/Graphene-carbon black composites (20% carbon contents) and 10 wt% polyvinylidene fluoride binder were mixed with N-methyl-2-pyrrolidinone. Synthesized materials were characterized by X-ray diffraction (XRD) techniques and we finally have synthesized carbon coated LMS/C-Graphene composite by sol-gel method associated with citric acid, TEOS and Lithium and manganese acetate. Besides providing carbon wiring, GAL aids the gelling process, reduces particle agglomeration during annealing and promotes phase purity.

The LMS/(C/RGO) shows an improved electronic conductivity due to the conductive network formed by reduced graphene oxide nanosheets and amorphous carbon in particles. Electrochemical characterizations results indicate high increased reversible capacity of 301 $mAhg^{-1}$ with a high initial columbic efficiency, and a high discharge capacity at current rate of 0.5 C. that's double value Compared with LMS/C – carbon black composite, the LMS/(C/RGO) electrode exhibits

higher capacity and better cycling stability. The first charge and discharge capacities of Li_2MnSiO_4/C-graphene composite are 455.1 mAhg^{-1} and 300.7 mAhg^{-1}, respectively, which indicates an initial columbic efficiency of 66.1%. The Li_2MnSiO_4/C-carbon black composite electrode exhibits similar charge capacity (433.6 mAhg^{-1}) with that of the Li_2MnSiO_4/C -graphene composite electrode. However, its initial discharge capacity (237.1 mAhg^{-1}) and columbic efficiency (54.7%) were much lower than those of the Li_2MnSiO_4/C - graphene composite. The improved performance can be contributed to the, reduced crystal size, good particle dispersion, and the improved conductive network between LMS particles.

Keywords: Graphene, Nanocomposite, Li ion batteries, Cathode Materials, Polyonions

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Theoretical investigation of voltage-time behavior of Li_2FeSiO_4 as a lithium ion batteries cathode material

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Abstract

Three important challenges in cathode materials of lithium-ion batteries are the energy density, cost, and safety. Orthosilicate base cathodes provide safety considerations due to their high chemical and thermal stability and the presence of non-toxic elements, especially in Li_2FeSiO_4 and Li_2MnSiO_4 compounds. However, the other two challenges, those are, the cost and energy density, are the limiting factors for these cathodes. The purpose of this study is to attempt to better understand the mechanisms governing the electrochemical behavior of orthosilicate-based cathode material in order to provide solutions for improving the energy density of the battery. The cathode material used in this study was $Pmn2_1$ polymorph from Li_2FeSiO_4, synthesized by sol-gel nitrate method[1-3]. Voltage-time (voltage-capacity) behavior obtained from synthesized samples of Li_2FeSiO_4 cathode was investigated and theoretically analyzed. The relationship between voltage-time behavior and related factors, such as particle size, rate and reaction energy, was presented. The proposed relationship in this study was evaluated using theoretical calculations and experimental data and confirmed in the assumed boundary. Based on theoretical studies and evaluation of the results obtained in this study and similar studies, it was suggested that reducing the size of the grain and the appropriate additive can improve the properties of Orthosilicate-based cathodes of lithium-ion batteries. As a result, the slope of the voltage-time (so voltage-capacity) curve is linearly related to radical of applied current rate.

Calculations in this work were performed using the full-potential linear augmented plane wave (FP-LAPW) method as implemented in the WIEN2K code within the framework of density

functional theory (DFT). The calculations were carried out in two different assumed categories of RMTs (atomic radial). In one of the categories, the RMT belonging to Fe, Li, O, and Si atoms is 1.75, 1.60, 1.42 and 1.42 a.u. It was name $R_{Fe} = 1.75$. In the other hand, the RMT of Fe, Li, O, and Si atoms are 2.00, 1.97, 1.42 and 1.42 a.u., respectively (name $R_{Fe} = 2.0$). The integrals were calculated on the Brillouin region with k-pionts of 4 × 5 × 5 of the Monkhorst-Pack (MP) network for the $Pmn2_1$ structure [4-6]. The calculations were performed as ferromagnetic (FM) using LSDA, PBE-GGA, LDA + U and GGA + U methods.

Keywords: Li ion batteries, Cathode Materials, Density Function Theory, Polyonions

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Corrosion

Synthesis of anodic TiO_2-nanotubes in organic electrolyte and influence of voltage on corrosion properties of TiO_2-NT

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Abstract:

One dimensional nanostructures with their unique properties find their application in a variety of devices such as sensor, solar cell, batteries, etc. nanostructure titanium dioxide such as nanotube, nanofibers and nanowires has high surface to volume ratio compared to conventional microstructures[1]. Moreover TiO_2-NTs are known to be chemically stable[2]. There are several synthesis methods for the TiO_2 nanotubes growing such as seeded growth, hydrothermal process, sol-gel and electrochemical anodization[3], which among them anodization is one of the most common. Anodization was used for the first time to growth alumina (Al_2O_3) nanostructures by Masuda et al, and the Zwilling et al reported formation of the TiO_2 nanoporous on Ti metal sheet by anodization in electrolyte containing HF. Anodization is a simple, low cost, an effective with a great degree of control on growth parameters (potential, PH, time, the chemistry of electrolyte solution)[4].

The present work reports on the effect of voltage on morphology and corrosion properties of self-organized TiO_2 nanotube layers formed by anodization of Ti. The anodization process was performed at room temperature by electrolyze cell consist of the Ti substrate as anode and Pt as cathode, in electrolyte solution consist of ethylene- glycol, 0.5%wt NH4F and DI water 2.5 %wt. anodization process were performed at 20,30,40 V for 2h, using a constant voltage(DC) source. In order to enhance the crystal structure, they annealed at 450 C^0 for 2h in air (heating rate: 5 C^0/min). morphology and chemical composition of the coating were evaluated by field emission scanning

electron microscope (FESEM) and X-ray diffraction (XRD). Electrochemical corrosion behavior of the TiO_2-NTs was determined by electrochemical impedance spectroscopy (EIS). Fig 1 Show FESEM images of TiO2-NT prepared by anodization in different voltage. When the potential is increased, rate of chemical dissolution and oxidation increase resulting in nanotube growth. Fig2 show XRD pattern for TiO_2-NT after and before annealed at 450 C^0. We showed that annealing TiO_2-NT under oxidizing condition result in the formation of anatase crystal structure in the 450C^0. The EIS result are shown in Figure3,a and the equivalent circuits used for fitting the TiO_2-NT samples are illustrate in Fig 4. the coating which was formed in the 20 V had the highest corrosion resistance because this sample had lowest porosity, diameter and surface area.

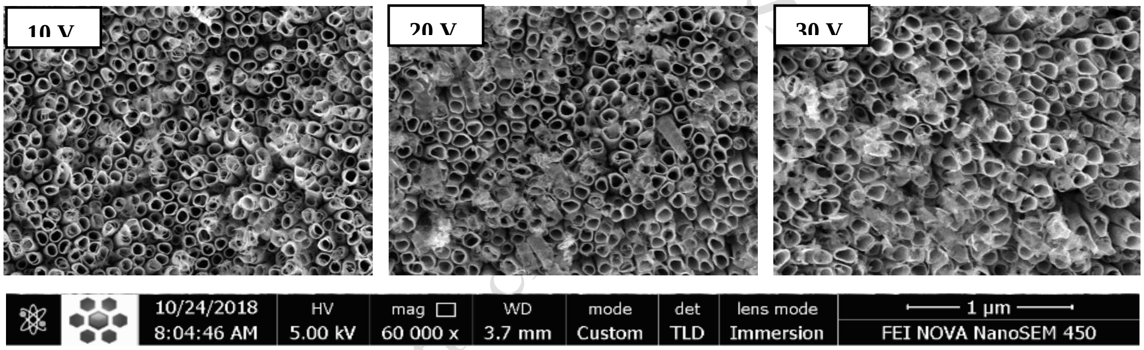
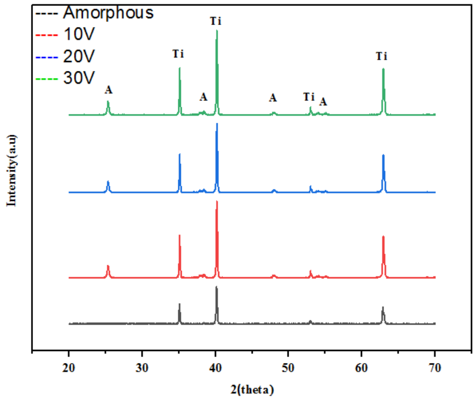


Fig.1. FESEM top images of the nanotube layer grown with different voltage.



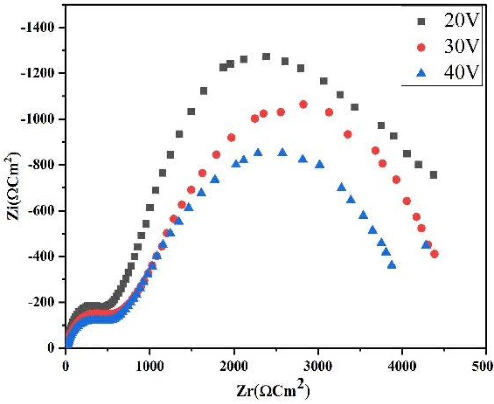


Fig.2. XRD patterns of nanotubes layers grown At 10,20,30 V before and after annealed at 450 C^o .

Fig. 3. Impedance spectra (Nyquist) of the generations of TiO_2-NTs performed at different voltage.

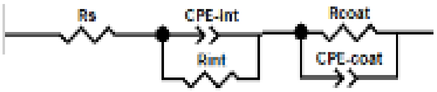


Fig.4. Equivalent circuit employed to fit the impedance data for TiO_2-NTs

Keywords: Anodizing, Ti, Nanotubes, EIS, Corrosion.

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Preparation and study of anti-corrosion metal coatings based on self-healing properties of polymer composites

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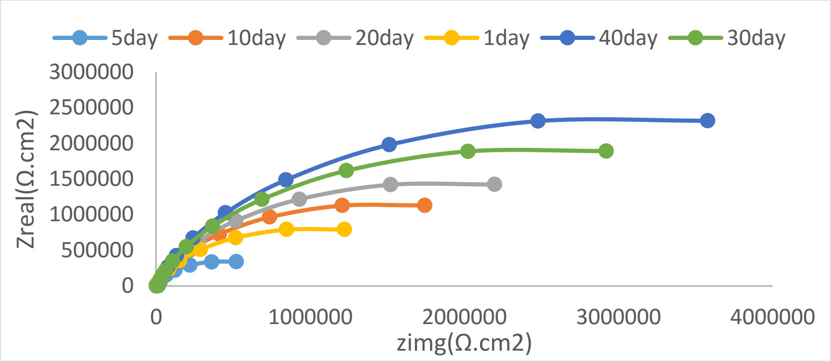
Abstract

One of the ways to prevent corrosion is to use paints as an anti-corrosion coating [1,2]. Another way of preventing corrosion is to use a variety of organic inhibitors. Permanent use of anti-corrosive materials is not economically feasible and has environmental damaging effects [3]. The main goal of this study is to make polymer coatings with a self-healing property that can repair themselves after mechanical destruction and prevent oxidation of the metal surface. EIS and Tafel polarization results are indicating an increase in the corrosion resistance. This polymeric coating acts as a corrosion inhibitor carrier system [4]. This polymer coating with its gradual release of corrosion inhibitor in the surrounding media reduces the amount of corrosion inhibitor consumption. micellar polymerization has been used to polymerize the monomer and 2% of the corrosion inhibitor has been loaded in the polymer network. According to the XRD result , peak which is located at 2θ =19 to 20°, it is related to the polymer structure network amorphous structure. When the coated metal is in contact with a electrolyte solution, the penetration of oxygen into the surface of the metal leads to the metal oxidation of Fe^{2+} ion and the reduction of the polymer to the neutral state. polymer reduction leads to the release of corrosion inhibitor in the environment, which, through the formation of a protective layer. The results of the EIS show that the resistance after 5 days is in an initial loss due to the penetration of corrosive agents, which, due to the release of corrosion inhibitor, increases again after 10 days.



Keywords: *Corrosion Inhibitor, Self-Healing, Polymer Composite, Electrochemical Impedance Spectrometry.*

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Synthesis nanoparticle for treating crude oil

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Abstract

The formation of harmful water in oil (w/o) emulsion is related to surface active materials in crude oil (such as resin, clay, and asphaltene). The w/o emulsion causes corrosion in pipes and pumps in the oil industrials [1]. Several studies showed that nanoparticles have high capacity for dehydration of crude oil [1.2]. In this work we used TiO_2 nanoparticle for dehydration of the oil. TiO_2 nanoparticle was prepared with sol-gel method according to reported procedure by Tahir[3]. Briefly titanium butoxide was solved in alcohol. Then acetic acid which was dissolved in alcohol, was added dropwise to the solution. The solution was stirred at room temperature for 1 day. Next the resulting solution was dried in oven. Finally, the samples were calcined in 500°C. The result of FT-IR spectra shows the Ti-O bond appeared as broad signal about 450 cm^{-1} [4]. The XRD spectra of the titania nanoparticle indicates that TiO_2 was synthesized successfully. Moreover this spectra reveals anatase phase of nanoparticle was formed [3].

Keywords: *TiO_2 nanoparticle, sol-gel method, crude oil*

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Electrochemical and DFT study on corrosion inhibition of aluminum by imidazolium type ionic liquid

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Abstract

Organic compounds, especially those containing polar functions with oxygen, nitrogen and/or sulfur in a conjugated system, have been frequently reported to inhibit the corrosion of metals in aggressive environments. In recent decade investigations, ionic liquids (ILs) have been pro-posed as green inhibitors to control corrosion of different metallic substrates exposed to corrosive media, particularly acid solutions. Utilizing ILs is one of the goals of green chemistry because of their tempting properties such as negligible vapor pressure, large liquids range, high thermal stability, high ionic conductivity and large electrochemical window [1-3].

In the present work, different imidazolium type ionic liquid was synthesized and their inhibiting action on the corrosion of stainless aluminum in HCl was investigated by means of potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). The results of the investigation show that the newly synthesized compounds show excellent inhibition efficiencies against the corrosion of Al in acidic solution. The adsorption of ionic liquid ions onto the Al surface followed the Langmuir adsorption model. Electronic properties such as highest occupied molecular orbital (HOMO) energy, lowest unoccupied molecular orbital (LUMO) energy and frontier molecular orbital coefficients for inhibitors have been calculated.

Keywords: inhibitor, Al, ionic liquid inhibitor, EIS, quantum chemical calculations.

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An investigation on KOH concentration effect on morphology, phase composition and corrosion behavior of nanocomposite coatings on Ti_6Al_4V via plasma electrolytic oxidation

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Abstract

Titanium and its alloys are used in a wide range of industries such as biomedical, aerospace and marine fields. In such applications, Ti components are often in tribological contact with different metals and media under stationary or dynamic loading [1]. These contact loads can cause damage of the thin native oxide film which passivates the titanium surface, and titanium with a strongly negative standard electrode potential, undergoes intensive interactions with other materials and/or media [2]. These interactions can generate various adverse effects on titanium components, such as high friction, galvanic and crevice corrosion as well as corrosion embrittlement [3]. Therefore, different surface treatment processes have been developed in order to enhance the tribological behavior of this group of alloys. Plasma electrolytic oxidation (PEO) is a relatively new surface engineering process to apply ceramic-like coatings on light alloys such as titanium, magnesium, aluminum and zirconium in order to improve the corrosion and wear resistance properties of the substrate [4]. PEO is based on conventional anodic oxidation in aqueous electrolyte solutions, but operated above the breakdown voltage, which results in the formation of plasma micro-discharge events [5]. In the present work, Ti6Al4V substrates were used as the anodes. Four electrolyte systems with the same concentration of sodium aluminate ($NaAlO_2$) (10 g/L) and different concentrations of potassium hydroxide (KOH) (0, 2, 4 and 6 g/L), were prepared. PEO test was conducted in constant voltage mode with the voltage of 400 V. Frequency, duty cycle and process time were set to be 1000 Hz, 40% and 10 min, respectively. Morphology and chemical composition

of the coatings were evaluated by field emission scanning electron microscope (FESEM) and X-ray diffraction (XRD). Electrochemical corrosion behavior of the coatings was determined by electrochemical impedance spectroscopy (EIS). The XRD patterns of the coated samples are shown in Figure 1 (a). All the coatings consisted of Al_2TiO_5 and Al_2O_3 phases as well as strong Ti peaks from the substrate and by increasing the concentration of KOH, oxide peaks were intensified. FESEM graphs of all the coatings showed a porous structure which is a characteristic of PEO coatings. The EIS results are shown in Figure 1 (b, c and d) and the equivalent circuits used for fitting the PEO-coated samples and the bare specimen are illustrated in Figure 1, e and f. The coating which was formed in the electrolyte with 4 g/L of KOH had the highest corrosion resistance which was 51 times higher than that of the substrate.

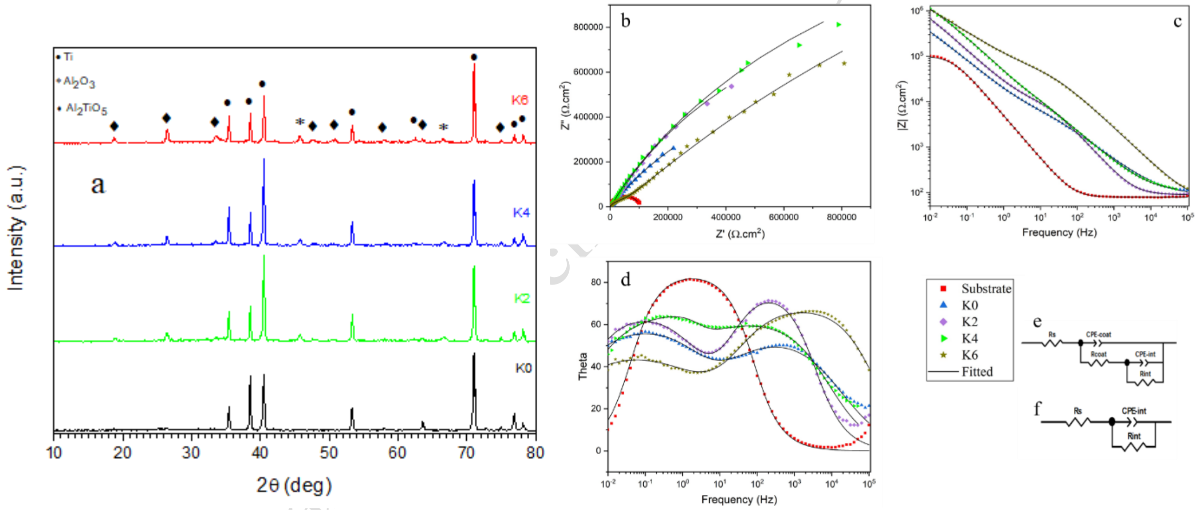

Fig 1: a) The XRD patterns of the coatings formed in different electrolytes, b) Nyquist plot, c) Bode plot, d) Phase angle plot, e) Equivalent circuit for the coated samples and f) Equivalent circuit for the untreated specimen.

Keywords: Ti6Al4V, Plasma electrolytic oxidation, KOH concentration, Corrosion resistance.

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Fabrication of zirconia tetragonal phase by plasma electrolytic oxidation on Zircaloy-4 alloy and its electrochemical corrosion behavior

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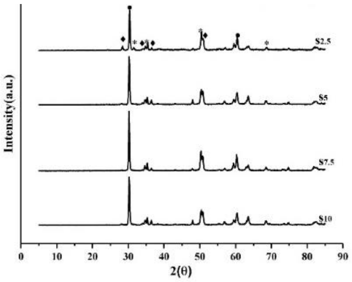
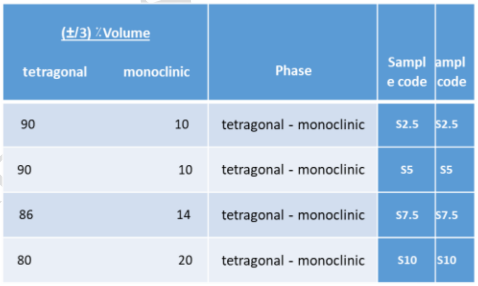
Abstract:

Zirconium has suitable characteristics for the fabrication of the fuel cladding tubes and coolant channel materials in water-cooled power reactors, such as low neutron absorption coefficient, high flexural strength, good corrosion resistance and high temperature mechanical properties.

The native oxide film (zirconia) formed on the surface of zirconium and its alloys provides an effective 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. However it has been known that the native film may be destroyed in LiOH environment [1, 2]. A technique for surface treatment of zirconium and its alloys is plasma electrolyte oxidation (PEO) which enables the production of a uniform, hard and dense coating results in improvement of corrosion and wear resistance [3]. In this paper, zirconium oxide coating was produced on Zircaloy-4 alloy using plasma electrolytic oxidation (PEO). Sodium silicate and sodium aluminate based electrolytes were selected in PEO process and the effects of the concentration of sodium aluminate (2.5, 5, 7.5, and 10 g/L) on the phase structure and the corrosion behavior of the formed coatings was studied. The phase structure of coatings was investigated by x-ray diffraction (XRD). Corrosion properties of the Zr-1%Nb alloys were assessed by electrochemical impedance spectroscopy (EIS) test in 1 M LiOH solution at 293 K in order to evaluate the corrosion behavior. EIS test was carried out at a frequency range of 1mHz to 100 kHz at the open circuit potential and the perturbation amplitude

was 10 mV. Fig.1 shows XRD pattern of the PEO coatings formed in different electrolytes. Sodium aluminate leads to inhibition of formation of low-temperature monoclinic Zirconia phase in PEO coatings. By increasing the concentration of $NaAlO_2$ to up to 10g/L the content of t-ZrO_2 phase increases (Fig.1 and table1). After the addition of 10 g/L Sodium aluminate (s10) in the electrolyte %20 tetragonal zirconia was formed on the surface. The improvement in corrosion properties mainly depends on the phase composition of the produced coatings. The corrosion resistance values of coatings are in the decreasing order of Zr > s2.5 > s5 > s7.5 > s10 (Fig.2). The addition of $NaAlO_2$ into the electrolyte decreased the pore density of the produced coatings as well as increasing the corrosion resistance. So the electrolyte of 10g/L $NaAlO_2$ (S10) had more compact/uniform structure in comparison with the other coatings.





(±/3) ٪Volume		Phase	Sampl e code	ampl code
tetragonal	monoclinic			
90	10	tetragonal - monoclinic	S2.5	S2.5
90	10	tetragonal - monoclinic	S5	S5
86	14	tetragonal - monoclinic	S7.5	S7.5
80	20	tetragonal - monoclinic	S10	S10

Fig. 1.XRD pattern for the coating formed in Zircaloy-4 in different $NaAlO_2$ concentration.

Table1. Phase composition and volume % of phase of the monoclinic and tetragonal phases in the coatings.

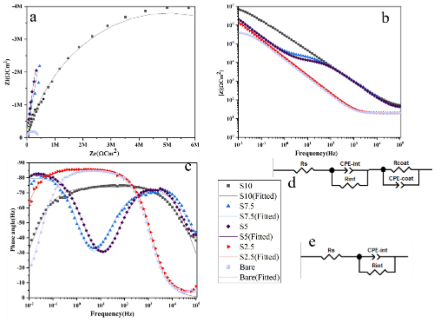


Fig. 2. Electrochemical impedance behaviour of Al-PEO coated Zircaloy-4 specimens. (a) Nyquist (b and c) Bode plots (d) Equivalent circuit employed to fit the impedance data for coating and (e) uncoated

Keywords: Zircaloy-4, electrochemical impedance spectroscopy, plasma electrolytic oxidation, sodium aluminate.

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Ni-P-TiO_2-ZrO_2 anti-corrosion coating on AISI 316 steel; Part I: effect of bath temperature

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Abstract

Austenitic stainless steels have been extensively used in various industrial areas such as chemical equipment, nuclear fusion equipment, and marine application, due to its excellent machinability, weld-ability, and non-magnetic property [1-3]. However, these kinds of alloys are very susceptible to pitting corrosion in chloride-containing environments. In particular, marine atmospheric environments have posed a great threat to the application of 316 SS due to the deposition of high chloride containing airborne sea salts on the metal surface [4]. In the present work electroplating method is used to preparation of Ni-P-TiO_2-ZrO_2 coating on AISI 316 stainless steel alloy in order to protection of substrate against corrosion in NaCl 3.5 %. For the direct current (DC) electrodeposition process, a one-compartment cell was used. Platinum foil was used as the anode and it was placed in the same compartment as the working electrode. Ammonia hydroxide or 20 vol% H_2SO_4 was used to adjust the electrolyte pH. Bath electroplating with composition of $NiSO_4$ 240 g/L + $NiCl_2$ 35g/L + $H_2NaO_2P.H_2O$ 25g/L + ZrO_2 20 g/L + H_3BO_3 30 g/L + $C_7H_5NO_3S$ 1g/L at pH 4 and current density of 40 $mA.cm^{-2}$ was used to electrodeposition of Ni-P-TiO_2-ZrO_2 coating. In order to investigate the corrosion behavior, an AutoLab Model 302N potentiostat was used for the corrosion studies. Measurements were carried out in a three electrode cell assembly containing a 3.5% Sodium chloride solution. A platinum foil and a saturated calomel electrode (SCE) were used as the counter and reference electrode, respectively.

The NOVA software was used to plot the polarization diagrams. In order to investigate the effect of TiO_2 concentration on microstructure and corrosion behavior of coating, different amounts of TiO_2 (10, 20 and 30 g/L) were inserted to the bath electrolyte. Figure 1 shows the polarization curves of coated 316 steel in NaCl 3.5 % in different amounts of TiO_2. Table 1 shows the result of polarization. Data obtained from potentiodynamic polarization tests shows that the coated specimen at TiO_2=30g/L had the highest polarization resistance (Rp= 12.3030MΩ) relative to other coatings.

Keywords: Corrosion, Polarization, Ni-P-TiO_2-ZrO_2, Electrodeposition, AISI 316 stainless steel.

Table 1: Electrochemical parameters for Ni-P-TiO_2-ZrO_2 coated AISI 316 steel in NaCl 3.5 %

TiO_2	10	20	30
I(nA/cm^2)	620.540	479.060	0.453
E(mV)	-229.370	-262.500	-283.960
R_P	22.7110KΩ	17.2500KΩ	12.3030MΩ
Rate(mm/year)	0.0072106	0.0055666	0.00000526

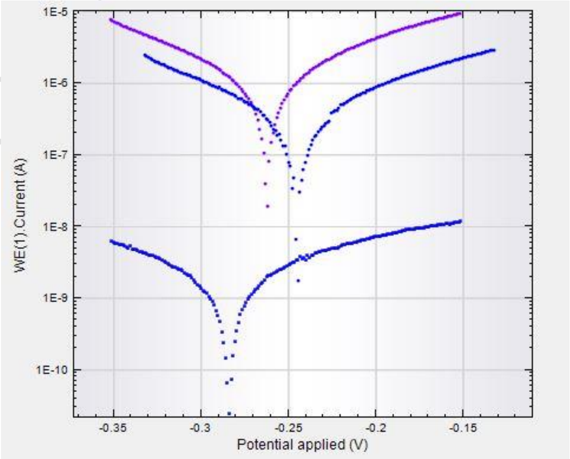

Figure 1: Polarization curves measured for coated 316 SS in 3.5 wt. % NaCl under different TiO_2 amounts.

(a) 10g/L ● (b) 20 g/L● (c) 30 g/●

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Effective factors in cavitation and corrosion in the industry and the ways to prevent and control it

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Abstract

When the pressure in the fluid decreases to a surface to below saturated vapour, it creates hollow holes in the fluid causing this cavitation or cavitation phenomenon. These bubbles, after passing through the short path to a region with a higher pressure It reaches and explodes, generates noise and creates shock waves and strikes the boundary between the fluid and the structure and after a short time it causes erosion and corrosion on the solid border.

Cavitation and corrosion is one of the most important problems affecting the life of equipment and operation.

The factors affecting the cavitation phenomenon are: special physical conditions-geometric factors and ......

In order to prevent damage caused by this type of cavitation, the following solutions are suggested, including lowering the temperature and increasing the liquid level. In this paper, we have tried to introduce the various types of cavitation in the industry and identification methods and mechanisms for their creation, and provide suitable solutions to prevent these corrosion.

Keywords:Cavitation, Bubbles, Cavitation Phenomenon,Corrosion.

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Corrosion in the oil, gas and petrochemical industry and its preventive methods

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Abstract

Corrosion is one of the major problems facing the oil, gas and petrochemical industry, which is costly to deal with. Corrosion is effective on the life of the equipment, its exploitation, the return on capital, the quality of the products manufactured, and so on. The industry can include condensate wells, sweet oil wells, sour oil wells, offshore platforms (drilling), transportation and maintenance, refining operations, and others that recognizing these environments and the corrosion rate of these environments can help to control corrosion In the equipment.

The higher temperatures and pressures usually cause more severe corrosion conditions. Corrosion control agents include: material selection ,Change in corrosive condition or corrosive material , Change in environmental conditions such as temperature, pressure and ... , Design changes , Use of corrosion inhibitors , Use of protective coatings , Use of cathodic protection and use of anode protection.

In this paper, it has been tried to introduce the types of corrosion in the oil, gas and petrochemical industry, identification methods and mechanisms for their creation, and provide appropriate solutions to prevent these corrosion.

Keywords: Corrosion , Corrosive Condition ,Industry Problem , protection ,Coating

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Evaluation of Polymer Nano Pigments Performance as Corrosion Inhibitor

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Introduction

Conducting polymers gained much attention during the past two decades because of their environmentally friendly behavior as well as their unusual corrosion inhibiting action for metals. Among these conducting polymers, polyaniline is considered to be one of the best anticorrosive materials not only because of its unique redox tunability, environmental stability and simple acid–base doping–dedoping process, but also because passivation of oxide layer between metal and coating is induced by PANI, which protects the metal from further corrosive attack.[1]

It should be noted that obtaining a long corrosion protection using organic coatings without reinforcing it by other inhibiting materials seems impossible. Nanopigments doped with inhibitive species like Zn, Ni, Co and Mn has been considered as route for obtaining inhibitive performance. These nanopigments release inhibitive species like Co^{2+}, Mn^{2+} and Ni^{2+} cations in the scratched area and protect it from corrosion through precipitating a passive film on the bare metal surface.[2]

Purpose of the research

The gole of this research is synthesized and characterization a anticorrosive nanopigment based on cobalt ferrite nanopigment and polyaniline - $CoFe_2O_4$ composite. The corrosion inhibition properties of the nanopigment was examined in the extract form in3.5 wt.% NaCl solution

Results & Discussion

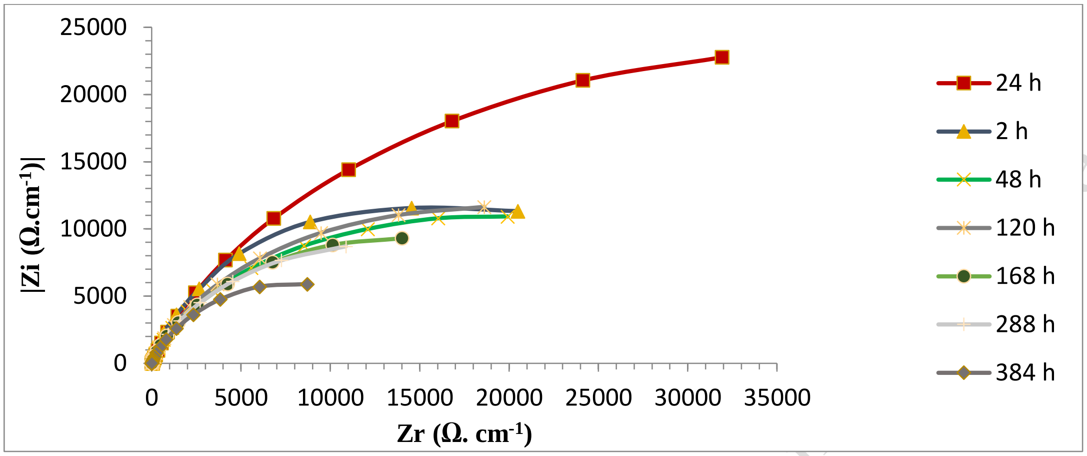

Fig.1.Nyquist diagram of the steel sample with $CoFe^2O^4$ nanopigmentg extract during the time

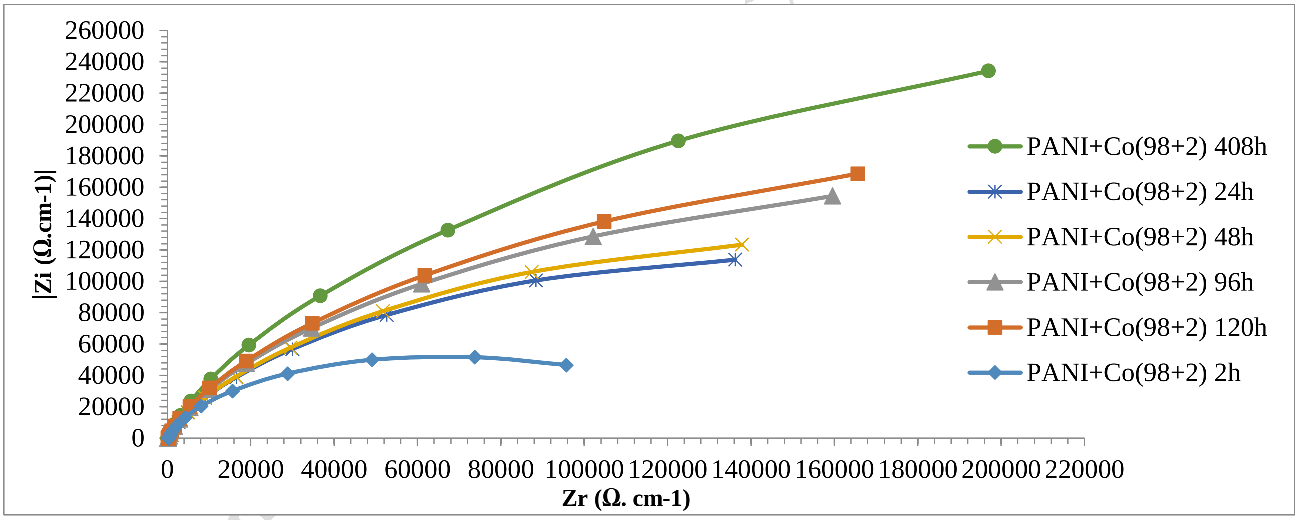

Fig.2.Nyquist diagram of the steel sample with $CoFe^2O^4$ - Polyaniline nanopigmentg extract during the time

The results showed that use of conducting polymer-oxide nanocomposites coatings can either act as a physical barrier toward corrosive environment or as inhibitory pigments to reduction of the corrosion rate.

Conclusion

The effect of cobalt ferrite nanoparticle on the corrosion protection properties of the epoxy coating was studied on mild steel substrates. Results showed that $CoFe^2O^4$ nanoparticle reduce the porosity of the coating matrix and inhibit the ions and water penetration into the coating and subsequent electrochemical reactions at the coating/metal interface, leading to improved barrier performance of polyaniline polymer coating.

Keywords: *corrosion, conducting polymer, epoxy coating, inhibitor pigment*

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Ni-P-TiO_2-ZrO_2 anti-corrosion coating on AISI 316 steel; Part II: effect of TiO_2 concentration

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Abstract

Austenitic stainless steels have been extensively used in various industrial areas such as chemical equipment, nuclear fusion equipment, and marine application, due to its excellent machinability, weld-ability, and non-magnetic property [1-3]. However, these kinds of alloys are very susceptible to pitting corrosion in chloride-containing environments. In particular, marine atmospheric environments have posed a great threat to the application of 316 SS due to the deposition of high chloride containing airborne sea salts on the metal surface [4]. In the present work electroplating method is used to preparation of Ni-P-TiO_2-ZrO_2 coating on AISI 316 stainless steel alloy in order to protection of substrate against corrosion in NaCl 3.5 %. For the direct current (DC) electrodeposition process, a one-compartment cell was used. Platinum foil was used as the anode and it was placed in the same compartment as the working electrode. Ammonia hydroxide or 20 vol% H_2SO_4 was used to adjust the electrolyte pH. Bath electroplating with composition of $NiSO_4$ 240 g/L + $NiCl_2$ 35g/L + $H_2NaO_2P.H_2O$ 25g/L + ZrO_2 20 g/L + H_3BO_3 30 g/L + $C_7H_5NO_3S$ 1g/L at pH 4 and current density of 40 $mA.cm^{-2}$ was used to electrodeposition of Ni-P-TiO_2-ZrO_2 coating. In order to investigate the corrosion behavior, an AutoLab Model 302N potentiostat was used for the corrosion studies. Measurements were carried out in a three electrode cell assembly containing a 3.5% Sodium chloride solution. A platinum foil and a saturated calomel electrode (SCE) were used as the counter and reference electrode, respectively.

The NOVA software was used to plot the polarization diagrams. In order to investigate the effect of TiO_2 concentration on microstructure and corrosion behavior of coating, different amounts of TiO_2 (10, 20 and 30 g/L) were inserted to the bath electrolyte. Figure 1 shows the polarization

curves of coated 316 steel in NaCl 3.5 % in different amounts of TiO_2. Table 1 shows the result of polarization. Data obtained from potentiodynamic polarization tests shows that the coated specimen at TiO_2=30g/L had the highest polarization resistance (Rp= 12.3030MΩ) relative to other coatings.

Keywords: Corrosion, Polarization, Ni-P-TiO_2-ZrO_2, Electrodeposition, AISI 316 stainless steel.

Table 1: Electrochemical parameters for Ni-P-TiO_2-ZrO_2 coated AISI 316 steel in NaCl 3.5 %

TiO_2	10	20	30
I(nA/cm^2)	620.540	479.060	0.453
E(mV)	-229.370	-262.500	-283.960
R_P	22.7110KΩ	17.2500KΩ	12.3030MΩ
Rate(mm/year)	0.0072106	0.0055666	0.00000526

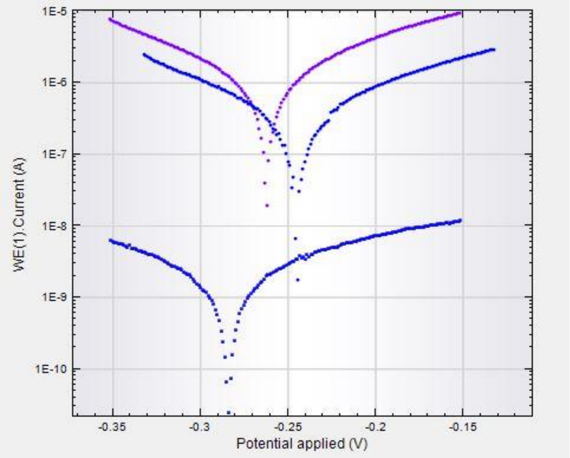

Figure 1: Polarization curves measured for coated 316 SS in 3.5 wt. % NaCl under different TiO_2 amounts.

(a) 10g/L ● (b) 20 g/L● (c) 30 g/●

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Corrosion Resistance of Electroless Ni-P Coating from chloride bath on Brass Alloy

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Abstract

Nickel- phosphorus coating was plated on brass substrate from chloride bath by electroless process. The corrosion behavior of plated substrate was studied by potentiodynamic polarization (DC) method in 3.5 wt% of NaCl solution. The results show that corrosion current density of coated sample obtained 0.68 µA/cm^2 compared to uncoated substrate 5.76 µA/cm^2. Moreover, the chemical composition of plated sample was characterized by the energy dispersive X-ray spectroscopy (EDS).

Keywords: Brass Alloy, Electroless Ni-P Coating, Corrosion Resistance, DC.

Introduction

The autocatalytic or chemical reduction of aqueous metal ions coated to a base substrate without passage of external current is referred to as electroless plating[1]. Electroless nickel–phosphorus (Ni–P) coating is widely used in different industries because of its high hardness, excellent corrosion and wear resistances [2]. The corrosion process of brass often involves a mechanism of dezincification in which Zn is selectively dissolved. Brasses containing only a few percent of zinc may crack under load if the stresses are high and the environment is sufficiently corrosive. Dezincificaiton and stress corrosion cracking are major limiting factors for the use of brass in numerous applications[3-4]. These phenomena can be prevented by applying high-corrosion resistance coatings such as electroless Ni-P coating.

Experimental

Brass samples with composition of (29.6% Zn, 0.03% Pb, 0.01% Sn, 0.011% P, 0.005% Fe, 0.005% Ni, 0.005% Si, 0.001% Al, 0.002% Ag, 0.01% Co and Cu %remaining) obtained from Spectrochemical Analysis were plated in electroless Ni–P bath. The substrate surfaces were polished by using 1000 and 1200-grade SiC papers. First, the specimens have cleaned in alkaline solution containing NaOH 40 $^{gr}/_{lit}$ at 65°C for 10 min and second, activated in nitric acid solution 300 $^{gr}/_{lit}$ for 1 min[5]. After each step, the samples were washed with distilled water. The aqueous solution for electroless deposition was prepared from nickel chloride 20 $^{gr}/_{lit}$, sodium hypophosphite 24 $^{gr}/_{lit}$, succinic anhydride 10 $^{gr}/_{lit}$, sodium chloride 10 $^{gr}/_{lit}$ and thiourea 2 ppm. The pH of bath was 4.6 and brass samples were plated for 45 min at temperature of 92°C.

Results and discussion

The corrosion behavior of Ni–P composite coating was studied using potentiodynamic polarization, were conducted by sweeping the potential at a scan rate of 1 mVs^{-1} in the range of ±400 mv versus open circuit potential in 3.5 wt% NaCl solution and the results were analyzed via Tafel extrapolation theory. The electrochemical results shows in figure1 and table 1. According to the results, the polarization resistance of electroless Ni-P coating increased by five times compare to the bare sample. This can be attributed to the high protective properties of electroless Ni-P coatings that corrosion current density have decreased 88% and corrosion rate have decreased significantly. The results of the EDX test showed that Ni-P composite coating has 11.5 wt% phosphorous and 88.5 wt% nickel. It was determined that the electroless Ni-P coating, is in the range of high-phosphorous Ni-P coatings. Coatings with a phosphorus content of more than 11% (amorphous structure) have a coherent and heterogeneous structure[6].

Table 1. Corrosion parameters of electroless Ni–P composite coatings and substrate in 3.5% NaCl solution.

Specimens	E_{corr}(mV)	i_{corr} (μA.cm^{-2})	R_P (KΩ.cm^2)	CR (mpy) × 10^{-3}
Ni–P coating	-385.68	0.68	21.140	0.008
Substrate	-250.800	5.76	4.16	66

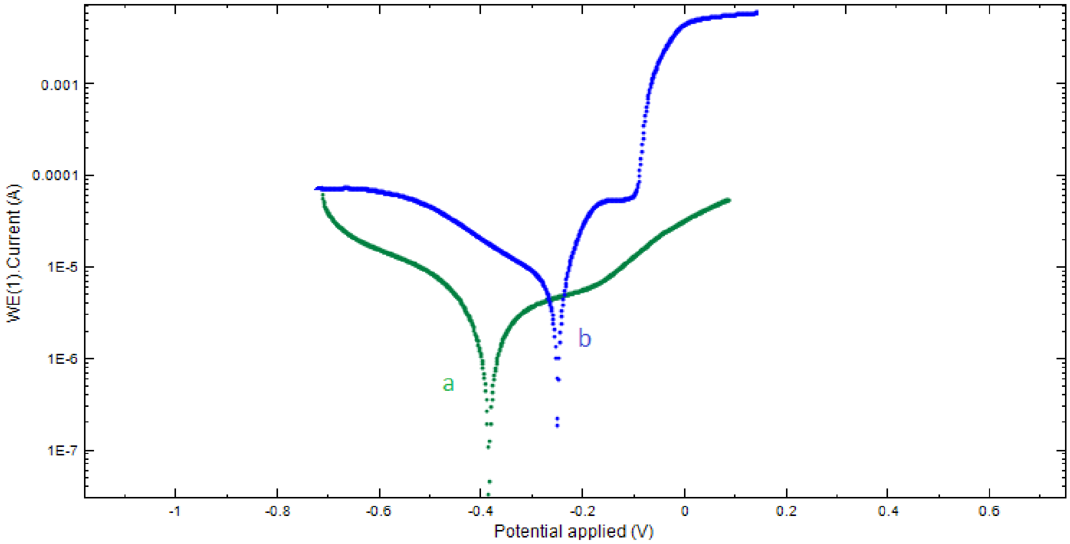

Figure 1. Potentiodynamic polarization curves of samples in 3.5 wt% NaCl solution (a) electroless Ni–P composite coating, (b) bare sample.

Conclusion

By applying electroless Ni-P coating on brass alloy, a high phosphorous coating with corrosion resistance up to 5 times better than bare sample was obtained.

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Evaluation of ultrasound wave frequency effects on the electroless Ni-P-nanoAlumina coating by electrochemical impedance spectroscopy (EIS) method

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Abstract

Electroless nickel deposition was discovered in 1946 by Brenner and Riddell [1]. These coatings are produced by the catalytic reduction of nickel ions using sodium hypophosphite as a reducing agent [2]. The nickel–phosphorous (Ni–P) deposits obtained from electroless plating which is an autocatalytic process are widely used in different industries for their unique combination of properties such as wear resistance, corrosion resistance, and higher hardness [3]. In the present project, electroless nickel phosphorous coatings in the presence of nanoparticles were studied by using ultrasound waves on mild steel. In this regard, Ni-P composite coatings containing alumina nanoparticles prepared with sonoelectroless autocatalytic method using an ultrasound probe. On the other hand, the wavelength effects of the ultrasound waves on the properties of the coatings is studied. Corrosion performance of the coatings was examined by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). The surface morphology and composition of the composite coatings were characterized by scanning electron microscopiy (SEM), energy-dispersive X-ray spectroscopy (EDX) measurements and X-ray diffraction (XRD) analysis. The tribological properties of the surface have been investigated. Results show that by increasing the ultrasound wave frequency up to certain amount, the corrosion resistance of coating increases. There is an specific optimum ultrasound wave frequency for coats.

Keywords: Nano Composite Coating; Corrosion; Sono Electroless; Ultasound Wave Frequency

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Physical-Electrochemistry

Dispersing of SiC particles using surfactant for the application in camposite coating

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Abstract

From the earliest development of a composite solid, the goals for composite development have been to achieve a combination of properties not achievable by any of the materials acting alone.[1]Deposition of electrochemical composite coatings (ECC) is not a newly developed technique , but has been in continuous development since the 1970s.[2]One of them is nickel coatings that are used in the range of mechanical (preventing wear) and chemical (protecting against corrosion) to electrical and magnetic (storing electronic data in magnetic media).[3]These coatings, which can be produced via combined electrodeposition and electrophoretic deposition have demonstrated enhancements in tribological, physical, chemical, and electrochemical properties. A wide range of particles are available including (a) solid lubricant materials e.g. PTFE, graphite, MoS2, (b) hard oxide, nitride or carbide particles e.g. SiC, TiO2, SiO2, Si3N4, WC and (c) metallic particles, e.g. Al, Cr.[4]

SiC has a high resistance to abrasion due to its high toughness, chemical resistance to corrosion and its high stability at high temperatures (melting temperature is about 2730 ° C) and because of its covalent bonding properties.[4]

Due to their high wear resistance and the low cost of ceramic powder, Ni–SiC composites have been investigated to the greatest extent and successfully commercialised for the protection of friction parts.[5] In this study, the sliding wear corrosion behaviour of a pure nickel and nano-structured SiC–nickel composite coatings were studied. Both measurements of electrochemical

corrosion and wear corrosion show a better resistance of nancomposite coating compared with pure nickel coating.[2]

The addition of metal cationic accelerants and organic surfactants in an electrolytic bath improved the amount and the distribution of co-deposited particles.[1] It was confirmed that suitable surfactants could not only improve the stability of a suspension by increasing the wettability and the surface charge of suspended particles but also enhance the electrostatic adsorption of suspended particles on a cathode surface by increasing their positive charge .[5] Addition of the surfactants into electrolyte changes the polarization potentials at the cathode and alters the grain size, rate of grain growth, smoothness and adhesion of the coating. The most common application of surfactant in electroplating is to reduce the surface tension of the bath to produce smaller hydrogen bubbles, thus preventing pitting. Hence, it also helps in improving the current efficiency of the electrodeposition. The most common surfactants used in the electrodeposition bath are sodium dodecyl sulfate (SDS), cetyltrimethylammonium bromide (CTAB) and sodium lauryl sulfate (SLS) .[4,5]

Keywords: dispersion ;SiC ; surfactant ; Composite coatings

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Synthesis and electrochemical investigation of polysulfone-based anion exchange membrane applied in capacitive deionization water treatment cell

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Abstract

In this work, various anion exchange membranes were prepared based on polysulfone and functionalized by trimethylamine and N,N,N,N-tetramethyl-1,6-hexanediamine using chloromethylation and amination steps. Also, electrochemical properties of the synthesized membranes were investigated and compared in terms of electrical area resistance, transport number, and nitrate ion conductivity. Finally, the performance of optimum membrane was tested in an electrochemical cell for CDI process.

Keywords: electrochemical water treatment, Capacitive deionization, Anion exchange membrane.

Introduction

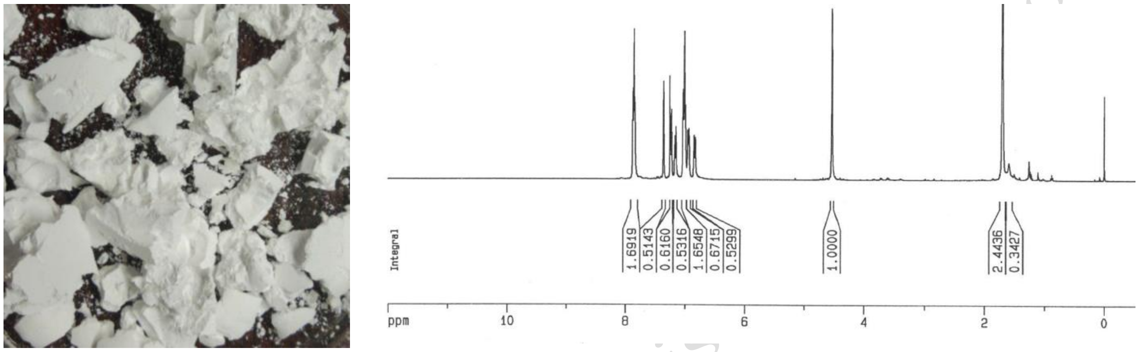
Low energy consumption, modest operational cost, and high efficiency have attracted the attention of researchers towards electrochemical desalination technologies. Because of operation at potentials of 1.0 up to 2.0 V and lack of electrolysis reactions, the capacitive deionization (CDI) process is known as an energy-efficient desalination technology in water and wastewater treatment industry. This process has higher efficiency and lower operational cost compared to electrodialysis process. Recently a significant modification to the process is proposed by addition of ion exchange membranes (AEMs) to the respective electrodes which are used in the CDI modules [1]. This modification results in higher charge and current efficiencies and the enable selective removal of water pollutant ions. Regarding the importance of synthesis and modification of CDI membranes, a novel anion exchange membrane was prepared in this work for application in capacitive deionization process.

AEMs with different morphologies have been prepared by changing the polymers chemistry, cationic groups, and functionalization methods. Homogeneous AEMs can be prepared by different approaches depending on the preparation method and used precursors [2]. Among different polymers and cationic groups, polysulfone (PSF) and ammonium species can be considered as good candidates for AEM preparation. PSF is a high-performance engineering thermoplastic polymer which is highly soluble in a wide range of polar solvents and exhibits good thermal, mechanical and chemical stabilities in a variety of pH values. Quaternary ammonium (QA) groups are the most common functional groups used in AEM fabrication due to preparation simplicity and high performance in ionic exchange measurements. The amination moieties may be monoamines i.e. trimethylamine (TMA) and triethylamine (TEA) or diamines such as N,N,N',N'-tetramethyl-1,6-hexanediamine (TMHDA), N,N,N',N'-tetramethyl-1,4-butanediamine (TMBDA). Using diamines in AEM structure can be a good strategy to maintain ionic conductivity, mechanical and chemical properties in the reasonable levels. Among different diamines, TMHDA with long alkyl chain can be more appropriate. This diamine provides functionalizing and crosslinking processes in a single step. The length of alkyl group has a significant effect on membrane conductivity, chemical stability, and selectivity toward less hydrated ions [3].

In this work, various anion exchange membranes were prepared based on polysulfone and functionalized by trimethylamine and N,N,N,N-tetramethyl-1,6-hexanediamine using chloromethylation and amination steps. Also, electrochemical properties of the synthesized membranes were investigated and compared in terms of electrical area resistance, transport number, and nitrate ion conductivity.

Experimental

To perform a safe synthesis, in this study chloromethylation step was carried out based on a route reported by Iravaninia et al. work [4]. 5.0 g of PSF was dissolved in 250.0 ml of chloroform. After that, the solution was transferred to a three-necked flask equipped with a magnetic stirrer and reflux condenser. When the temperature of the mixture raised to 55 °C, 3.38 g of paraformaldehyde and 12.3 g of chlorotrimethylsilane were added to the solution. Finally, $SnCl_4$ as the reaction catalyst was added dropwise to the solution. This reaction was carried out for 24 hr. The obtained solution from chloromethylation reaction was precipitated in ethanol and vacuum filtrated to collect solid particles of CMPSF. The obtained CMPSF was dried in a vacuum oven at 50 °C for a day. The purification step with ethanol was performed several times to ensure highly pure CMPSF was synthesized. The obtained CMPSF (a) and the related HNMR spectra (b) are shown in Fig. 1.



(a) (b)

Fig. 2- (a) Chloromethylated polysulfone powder, (b) CMPSF HNMR spectra

The amination step started with dissolving 2.0 g of CMPSF powder in 20 ml of NMP solvent. After that TMHDA and TMA were added to the mixture in an appropriate molar ratio to make different AEMs. Amination reaction was carried out at 70 °C for 24 hr. When the reaction completed, the solution was degassed and was casted on a glass plate and was dried in 70 °C oven to remove the solvent. To ensure that all the solvent has been evaporated, the AEM film was vacuum dried at 80 °C for 12 hr. During the alkalization step, the AEM films in chloride form were soaked in 1 M KNO_3 solution for 24 hr at room temperature. The KNO_3 solution was refreshed several times throughout this period to ensure exchange of all chloride ions with hydroxide ones. Subsequently, the AEM films were washed and immersed in deionized water for 24 hr to remove residual KNO_3. Finally, the AEMs with an average thickness of 200 µm were obtained.

Results and discussion

The prepared membranes exhibited through plane ionic conductivity of 2-8 mS/cm at 25 °C. The ion exchange capacities and anion transport numbers were within the range of 1.6-2.1 mmol/g, 0.95-0.98 for nitrate and chloride, respectively. Furthermore, the membranes showed acceptable water uptake and swelling ratio at 25 °C. Based on the experiments, it can be inferred that suitable proportions of amination and crosslinking agents, could lead to the membranes with well-balanced performance between ion transport and stability. Finally, the performance of optimum membrane was tested in an electrochemical cell for CDI process as depicted schematically in Fig. 2. Regarding the improved electrochemical and physicochemical properties, these anion exchange membranes are proposed as a good candidate for membrane capacitive deionization cells.

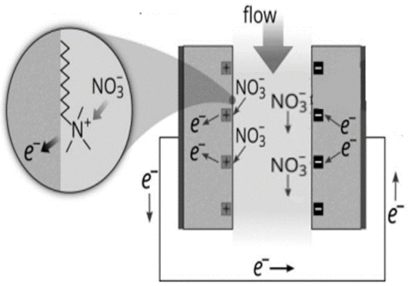


Fig. 2. Schematic of Electrochemical cell of CDI process.

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Preparation and electrochemical assessment of polysulfone-based cation exchange membrane for fuel cell application

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Abstract

Proton exchange membranes are a key component of a fuel cell and have a significant effect on the electrochemical performance of fuel cells so achieving a proton exchange membrane with appropriate electrochemical properties such as proton conductivity, electrical area resistance while maintaining suitable physiochemical properties such as water uptake. So in this study, the sulfonated polysulfone membrane was performed using chlorosulfonic acid at 50 ° C for 4 hours for application in the proton exchange membrane fuel cell. The electrochemical-physiochemical properties of the synthesized ion-exchange polymer were investigated. The degree of sulfonation of 54% was determined using the H1 NMR and titration method from ion exchange capacity (IEC) formula, and proton conductivity of and 51 mS cm-1 was examined from impedance spectroscopy analysis. Also, the water uptake (WU) of 27% was obtained. The result of experiments showed that synthesized polysulfone has a reasonable performance in full cell applications.

Keywords: PolySulfone, Fuel cells, Proton exchange membrane, Sulfonation degree.

Introduction

According to environmental problems that have recently affected the world, the use of fuel cells is more and more serious. Among the fuel cells, Proton exchange membrane fuel cells (PEMFCs) have attracted more attention to researchers due to its high proton conductivity, mechanical, thermal and chemical stability. As a new technology, Proton exchange membrane fuel cells are a good option for replacing fossil fuels because of high efficiency and low or even zero emissions [1]. Proton exchange membranes are a key component of a PEMFC and have significant effect on electrochemical performance of fuel cells so achieving a proton exchange membrane with appropriate electrochemical properties such as proton conductivity, electrical area resistance while maintain suitable physiochemical properties such as water uptake. Polysulfone is one of the polymers used in proton membranes and has been commercialized [2]. The degree of sulfonation is a significant parameter to attain a proton exchange polymer with optimum electrochemical-physiochemical properties. A typical sulfonation reaction of polysufone is presented in Fig. 1.

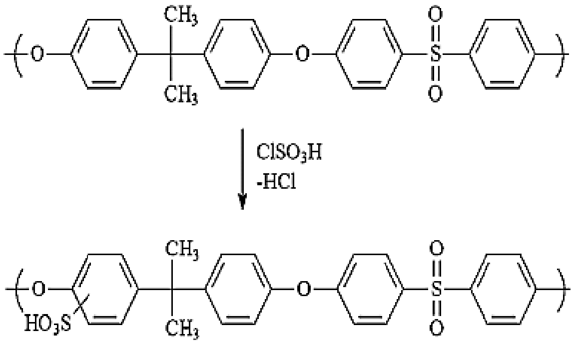

Fig. 1. Sulfonation reaction of Polysulfone [3]

Experimental

Polysulfone polymer was prepared by a Sulfonation reaction using chlorosulfonic acid at a specific temperature. Before the reaction, polysulfonated polymers was dried in a vacuum oven at 100 ° C for 12 hours. Polysulfone sulfonation reaction was performed in a three-neck flask with magnetic stirring under nitrogen atmosphere. Polymer granules were stirred in a three-neck flask with 50 ml of dichloroethane for 1 hour at ambient temperature then was placed at 50 ° C followed by addition of 6 ml of chlorosulfonic acid diluted with 10 ml of dichloromethane. This reaction is carried out for 4 hours. Then the solution was washed with deionized water to reach a neutral pH. The extruded powder was first dried at 80 ° C for 12 hours in an oven and finally was vacuum dried at 80 ° C for 12 hours. The photograph of sulfonated powder of polysulfone is shown in Fig. 2.

Fig 2. photograph of sulfonated powder of polysulfone.

Sulfonated polysulfone membrane for use in proton-exchange fuel cells was casted from the solution of respective ionomer onto a glass plate for 30 hours in a conventional oven dry at 80 ° C. The casted membrane sheet with the thickness of 110 µm is shown in Fig. 3.

Fig 3. Prepared sulfonated polysulfone membrane with thickness of 110 µm.

Ion exchange capacity (IEC) using titration method and nuclear magnetic resonance spectrometry (H-NMR) were used to calculate the sulfonation degree of the sulfonated powder of polysulfone and the bare polysulfone membrane.

Results and discussion

According to Fig. 4, sulfonation degree (DS) of 54% was examined for synthesized ion-exchange polymer after 4 hours which is in consistence with the DS obtained from IEC calculation. The relation of DS and IEC is indicated in the Eq. (1):

$$DS\,(\%) = \frac{(0.442 \times M_{NaOH} \times V_{NaOH})}{W - 0.08 \times M_{NaOH} \times V_{NaOH}} \times 100 \qquad (1)$$

Where M_{NaOH}, V_{NaOH} and W, are concentration standard solution (mol/L), amount of volume used to neutralize (mL) and weight of sample (g) respectively. The water uptake (WU) and proton conductivity of synthesized polymer were estimated 27% and 51 mS cm^{-1}. The result of experiments showed that synthesized polysulfone has a reasonable performance in full cell applications.

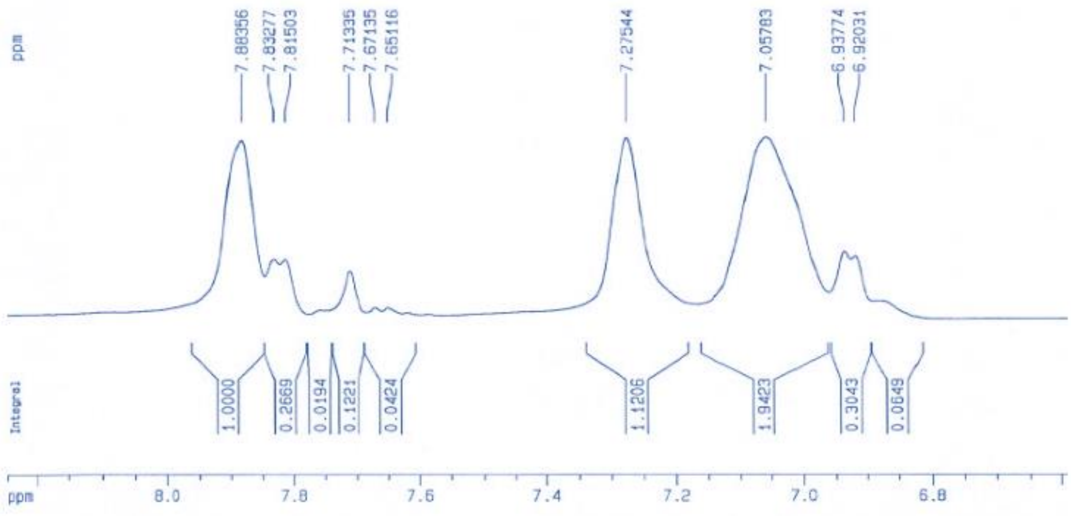

Fig. 4. H^1 NMR spectra of sulfonated polysulfone.

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Investigation of Nano Composite TiO_2 Nanotube/rGO as Anode Materials for Li 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. Metal oxide nanostructures with high surface area are attractive for photocatalysis, dye-sensitized solar cell and lithium ion battery applications and have been investigated intensively in recent years. 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 used an affective and facile electrochemical method to improve the properties of Titanium nano arrays (TNAs) in order to achieve high capacity and significant conductivity. Titanate nanotubes were employed as a substrate and then carbon materials were coated onto their surface via electrostatic interaction [2]. In this method, we increased the conductivity and also reduced the destruction of TNAs in the calation/intercalation Li+ ion by creating a carbon coating. These excellent performances are attributed to the unique structure of the composite material. First, the empty space inside the nanotubes and the thin tube walls are beneficial for the diffusion of Li ions. Second, the closely coated Carbon materials frame can support faster electron transfer to a TiO2 electrode [3,4].

Keywords: electrochemical synthesis; Morphology; Characterization; storage; nanostructure

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A new simple theoretical-experimental approach to estimate surface charge of surfactant-covered CNTs

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Abstract

The power of binary mixtures of dodecyl trimethyl ammonium bromide and sodium dodecyl sulfate surfactants for dispersion of multi-wall carbon nanotubes (MWCNTs) in aqueous media was investigated. Stable dispersions were obtained at lower total surfactant concentration as compared to their concentration when used alone, indicative a synergistic effect in these catanionic mixtures. The dispersion of carbon nanotubes was characterized using UV-Vis spectroscopy and Zeta potential measurement. In this study, for the first time we introduce a new simple approach to estimate surface charge of surfactant-covered CNTs in a combined theoretical-experimental way. To do so, we have utilized the well-known Poisson-Boltzmann equation and thermo gravimetric analysis (TGA) results. According to the Poisson equation, calculation of electric potential needs charge density, a parameter which in this work has been estimated using thermo gravimetric analysis results. The TGA-based estimated potentials are in good agreement with experimental results. Ultimately, using the surface charge results, we have calculated interaction energy between two parallel tubes. Calculated results clearly show that the dispersions could be stable, which has been confirmed experimentally too by using zeta potential measurements.

Keywords: Carbon nanotubes, surfactant, synergism, dialysis tubing, Poisson – Boltzmann equation.

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Developing non platinum group metal electrocatalyst for oxygen reduction reaction derived from metal-organic-frameworks precursors

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Abstract

Pt-based materials are the state-of-the-art catalysts in full cells [1]. However, the scarce reserve, high cost, poor durability, and low poison resistance significantly prohibit their large-scale commercial application [2]. Hence, great efforts have been made to develop low cost, highly active, and high-performance non-precious metal catalysts (NPMCs) for the oxygen reduction reaction (ORR), including alloys [3], metal oxides [4], and heteroatom-doped carbons [5]. Among them, transition-metal–nitrogen–carbons (TM-N-C, TM = Mn, Fe, Co, Ni, etc.) have been considered as promising candidates because of their low cost, comparable catalytic activity and durability [6]. Such electrocatalyst can be obtained from different precursors, but one of attractive materials which have been used recently are metal–organic frameworks (MOFs) precursors. Some unique features that distinguish MOFs from other materials include well-defined crystal structure, large and adjustable surface area, ultrahigh porosity, and variety in the synthetic chemistry [7, 8]. One of the extensive applications of MOFs are in catalysis field, but they still suffer from difficulties including poor conductivity and facile collapse during solvent extraction. To overcome these obstacles, MOFs can be used as a precursor to synthesize MOF-related nanomaterials by carbonization of MOFs at high temperatures in inert atmosphere that the result of this action is produce microporous carbon materials with high surface area which increases active sites and benefits mass transfer [9, 10]. In other words, compared with the traditional precursors to synthesis of NPMCs, MOFs are particularly suitable for electrochemical applications. Because in this

material, there is an inherent coordination between metals, heteroatoms and carbon into one framework that eliminating tedious extra-treatment synthesis steps for heteroatom-doping, and there is homogeneous dispersion of metal-heteroatom doping throughout framework which can serve as active sites and increase ORR performance. One of the effective strategies to lead up promising ORR performance is synthesis approach deviation to encapsulated metal/inorganic NPs in the graphitic carbon shells, such as carbon nanotubes (CNTs). In this way, a charge transfer from the metal NPs cluster to the carbon nanotubes takes places and this modification is expected to decrease the local work function and increase the chemical reactivity of the functionalized region of the CNTs exterior. It has been demonstrated that in such electrocatalyst derived from MOF, catalytic activity and their stability can be improved especially in harsh acidic medium.

Keywords: *Fuel cell, Carbon-doped with heteroatom, Cathode, MOF, Transition metal.*

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Electrochemistry-Industry

Investigation and optimization of effective parameters on electropolish process of stainless steel used in cryogenic reservoirs

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Abstract

The effect of electropolish process on the roughness and glossiness of stainless steel 316 used in cryogenic storage dewars is investigated here. A mixture of phosphoric and sulfuric acid (with 4:6, 5:5, and 6:4 volume ratios), 10% water, and 2% glycerin is prepared and subjected to electropolish process with electric current density of 0.05-0.3 A/cm^2, temperature of 50-70 °C, and time of 2-30 minutes. Atomic force microscopy (AFM) is implemented for surface coating analysis. Results indicate that when the volume ratio of phosphoric and sulfuric acid is 4:6, the electric current density is 0.2 A/cm^2, the temperature is 55 °C, and the time is 7 minutes, the electropolish process has the best outcome on the surface quality.

Keywords: electropolish process, stainless steel, glossiness, roughness, cryogenic, copper electrolysis

Introduction

Electropolish process is widely used as a surface treatment method. Making a shiny surface for decorative purposes, sterilization of health and medical instruments, deflashing, increasing corrosion resistance, and preparing a surface for plating are among the vast applications of electropolishing [1-2]. Electropolishing is an electrochemical process in which the desired sample acts as the anode. When a cathode and an electrolyte is conjugated to the anode, an electric current is established and selective separation of metal ions occurs from the surface of the sample. A bipolar layer of the electrolyte is accumulated on the surface of the metal sample as a result of implementing an electric voltage. This layer is thicker over the protruding parts and thinner over the recesses, leading to higher and lower electrical resistance, respectively. Therefore, in the electrochemical process, sharp points of the metal sample will turn into metal ions mush faster and metal removal from these areas will be higher. A smooth and shiny surface will be reached eventually [3].

Specific Aims

1. On an elecropolished surface, bacteria can not easily live and proliferate. Thus, electropolishing is a suitable method to build medical equipment [4].
2. In cryogenic industry, storage is one of the most challenging steps. Due to the very low temperature of the cryogenic fluid, minimizing heat transfer between the fluid and the surrounding is of great importance. Electropolished surfaces provide the possibility of achieving ultra-high vacuum condition to reduce heat transfer.
3. In copper electrolysis industries, copper purification to the highest level is the main goal. Lower roughness and less pollution on the desired surface result in higher adhesion of copper to the sample.

Materials and Methods

A 2 cm×3 cm sheet of stainless steel 316 with the thickness of 2 mm was used in this study. The sheet was rinsed in room temperature with acetone and ethanol for 10 minutes each. It was then washed with nitric acid, chloric acid, and water with volume ratio of 5:1:7 in 30-40 °C for 10 minutes to remove soot from the surface. Finally, the sheet was placed in distilled water for 1 minute. Electropolishing solution was prepared by mixing phosphoric acid, sulfuric acid, water, and glycerin with the chosen volumetric proportions. The stainless steel sheet was subjected to the electropolish process to find the optimum values of the parameters.

Results and Discussion

Experiments were performed under various operational conditions. Analyzing the results by AFM has shown that the surface quality is at its best when the volume ratio of phosphoric and sulfuric acid is 4:6, the electric current density is 0.2 A/cm^2, the temperature is 55 °C, and the time is 7 minutes.

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Electrochemistry-Synthesis

Yttrium Aluminum Garnet Thin Film: Electrochemical Synthesis and Characterization

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Abstract

A novel method based on the cathodic electrochemical synthesis was developed for the preparation of thin film yttrium aluminum garnet (YAG) from ethanol and water medium. First, hydroxide precursor was deposited from the mixture of YCl3 and AlCl3 solutions. To obtain final YAG product, the deposited hydroxide was heat treated at 1100°C for 4 h in dry air atmosphere. Mechanism of oxide formation during calcination was investigated by thermogravimetric analysis (DSC-TGA). Furthermore a mechanism of hydroxide precursor formation during cathodic deposition was proposed based on the possible cathodic reaction. The formation of crystalline YAG nanopowder was confirmed by Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), and scanning electron microscopy (SEM). The results revealed that cathodic electrodeposition followed by heat-treatment can be recognized a facile for preparation of thin film YAG compounds.

Keywords: Yttrium aluminum garnet; Electrochemical synthesis; Cathodic deposition

Preparation and Characterization of YAG:Ce Nanophosphor by Cathodic Electrodeposition Method

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Abstract

YAG:Ce nanophosphor was synthesized by a novel method, based on the cathodic electrodeposition from the mixture of bath chloride dissolved in water/ethanol 1:3 solution. First, hydroxide precursors cathodically grown on the steel substrates then, heat treated the hydroxide powder at 1100 °C for 4 h in dry air atmosphere. The obtained oxide product was confirmed by X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), and scanning electron microscopy (SEM). Broad emission band in the range 500-700 nm was observed in photoluminescence (PL) spectrum of the crystalline YAG:Ce nanophosphor with the maximum intensity at 528 nm. These results revealed that cathodic electrodeposition followed by heat-treatment is a unique method for preparation of YAG:Ce nanophosphor compound.

Keywords: Cathodic electrodeposition; Crystalline; Preparation; YAG:Ce nanophosphor

Synthesis and Characterization of YAG Nanostructure

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Abstract

Pure nanostructures of yttrium aluminum garnet (YAG) was prepared based on the cathodic electrodeposition method from the mixture of YCl_3 and $AlCl_3$ dissolved in water/ethanol solution. At first, hydroxide precursors cathodically grown on the steel substrates then, heat treated the hydroxide powders at 850 °C for 4 h in dry air atmosphere. The formation of crystalline YAG nano powder was confirmed by X-ray diffraction (XRD), thermogravimetric analysis (DSC-TGA), scanning electron microscopy (SEM) and Fourier transformed infrared spectroscopy (FT-IR). The results of the SEM showed that applied current density and bath temperature have the prominent effect on the morphology and particle size of the products. The results revealed that cathodic electrodeposition followed by heat-treatment can be used as a facile method for preparation of YAG nanostructures with different morphology.

Keywords: Cathodic electrodeposition; Hydroxide; Nanostructure; Yttrium aluminum garnet

Electrochemical Preparation of Manganese Hexacyanoferrate/Carbon Nanotubes Composite Film on Graphite Substrate via a Two-Step Method

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Abstract

As the intermediate energy storage devices between conventional batteries and dielectric capacitors, supercapacitors have attracted significant attention because of its advantages, such as high power density, fast charging/discharging, long cycle life and superior reversibility, etc. Nowadays, exploiting an electrode material with excellent electrochemical properties and high conductivity is very important for the development of supercapacitors. Prussian blue (PB), namely iron hexacyanoferrate with FCC crystal structure, is an important kind of mixed-valence compoundsand considered as one of the oldest synthetic coordination compounds. Manganese hexacyanoferrate (MnHCF) has attracted attention in some field due to the abundant raw materials, unique tunnel structure, low cost and higher specific area, etc.

Herein, MnHCF was electrochemically deposited on CNTs-coated graphite via a pulse galvanostatic electrodeposition technique at 100 μA cm^{-2} with both on-time and off-time equal to 0.5 s, to prepare MnHCF/CNT composite electrode. The CNTs-coated graphite was prepared by electrophoretic deposition (EPD) of functionalized CNTs onto the graphite substrate from ethanolic suspension (50 ml) containing 12.5 mg of functionalized CNTs, 50.0 mg of $Al(NO_3)_3 \cdot 6H_2O$ as the charging agent and 1.0 mg of polyvinylpyrrolidone (PVP, 25000 g/mol) as the stabilizing agent. EPD was performed by applying a constant voltage of 30 V between graphite working electrode and 316 L stainless steel counter electrode spaced 10 mm apart for 30 min. After

EPD, MnHCF was electrodeposited from the solution containing 2 mM $K_3Fe(CN)_6$, 2 mM $MnSO_4.H_2O$ and 0.5 M KCl.

The crystal structure of the composite film was characterized by XRD (Fig. 1). The diffraction peaks located at 17.5°, 24.8°, 35.5°, 39.5° and 44° were assigned to planes (200), (220), (400), (420) and (422) of the face-centered cubic MnHCF, respectively (JCPDS Card no.04-0850).

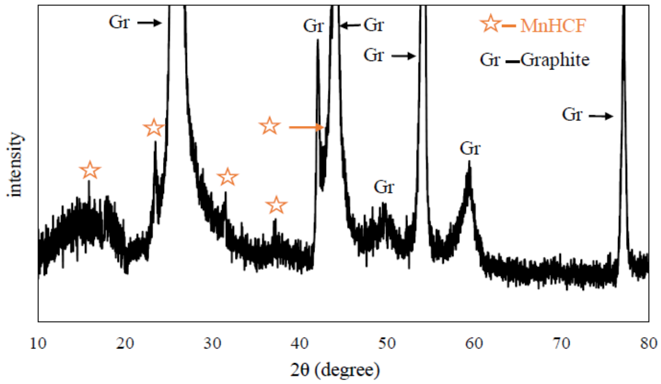

Fig. 1. XRD patterns of the MnHCF/CNT composite film.

FESM images related to the obtained CNTs film and MnHCF-coated CNTs film are shown in Fig. 2 (a,b) and (c,d), respectively. As indicated, a uniform structure with an open nanoporous network and without any crack is obtained for CNTs film. Also, it can be seen that MnHCF nanoparticles were homogeneously distributed and coated on the CNTs matrix, to form a porous hybrid nanostructure.

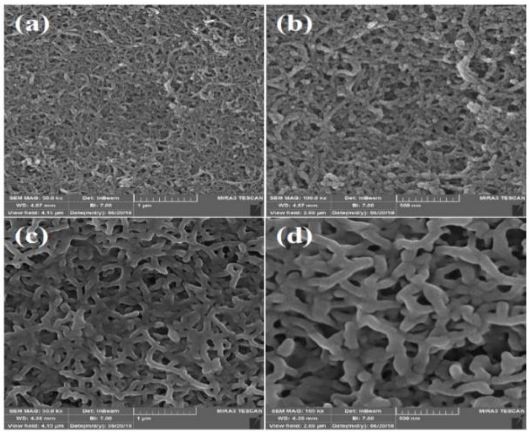

Fig. 2. SEM images of CNT (a,b) before and (c,d) after coating MnHCF.

Keywords: Electrochemical deposition, Manganese Hexacyanoferrate, CNTs, Composite film.

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Synthesis of Nano_Oxide manganese by Electrochemical Deposition Methods

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Abstract

The electrochemical synthesis of nanoparticles of manganese dioxide is of high value both nutritionally and in terms of application in the industry parameter such as temperature, pH and current density on its structure were investigated using XRD and FT-IR techniques. This test at 3 current densities, the best sediment was obtained at 2 mA / cm^2.

Keyword: Manganese Nanoparticles, Electrochemical Synthesis, pH, Temperature, Current Density

Introduction

Nanotechnology is one of the most important topics in today's world which is rapidly expanding in all fields of science and technology. One of the widely simplest nanostructures used in industry is metal-oxides nanoparticles, and the optimization of nano-sized metal oxides are processing in most nanotechnology research due to their special and different properties compared to the bulk state. Among these oxides metals, transition metals and among them manganese, iron, copper, etc., are highly valuable in terms of nutritional requirement and industrial application. One of the best methods for synthesis of such nano-oxides is the electrochemical deposition method and cathodic deposition is one of the subsets of this method [1].

Methods

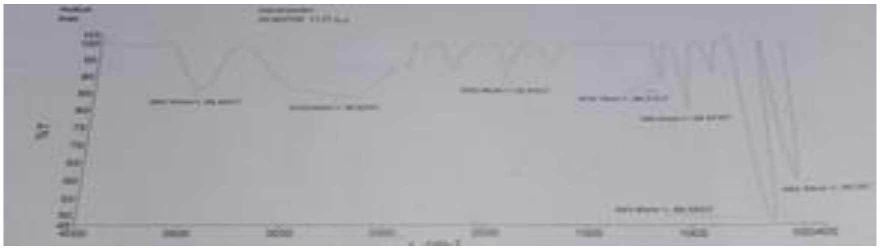
A cathodic electrochemical deposition method (with open electrochemical production at the cathode surface) was used to synthesize the manganese dioxide nanoparticles. For this purpose, aqueous solution of manganese nitrate salt obtained from Merck (Germany) with purity of 98.5% was selected as electrolyte in the process of deposition with the concentration of 0.005 M. The process of depositing of manganese nitrate solutions on both sides of the cathode of steel sheet (with a profile of 313 L cm-1 at 5 cm in 0.5 mm) was performed under the current density of 2 mA/cm2 and the temperature of 25 °C and galvanostatic state. Subsequently, the cathode substrates with deposited hydroxide product on it were removed from the electrolyte and dried in room temperature 25 ° C for 48 hours, subsequently, following the hydroxide deposition was collected from the cathode surface. Finally, X-ray diffraction device and infrared spectrometer were used to determine the properties of manganese dioxide nanoparticles.

Results and discussion

The mechanism for deposit formation is that the occurrence of reduction reactions leads to the increase in pH near the electrode surface and increase the concentration of OH- leads to deposit the metal ions as $Mn(OH)_2$ on the surface of the electrode.

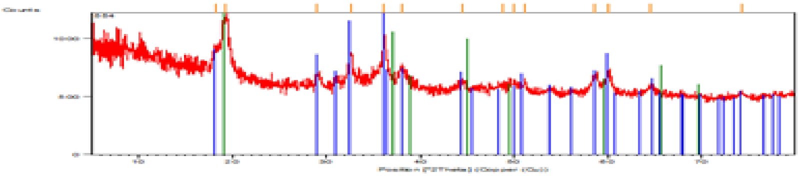
Study of Fourier transform infrared spectrum

As observed, there are several absorbance bands in 3456, 2735, 1859, 1070, 949, 623, 449 cm-1. The band 3457 cm-1 is related to the tensile vibrations of the O-H group. The peak of 2735cm-1 is related to the tensile vibrations of the RCHO C-H group. The peaks of 1859, 1070 and 949 cm-1 are related to the O-H bending vibrations. Peaks of 623 and 493 cm-1 are related to Mn-O vibrations in MnO6 octahedral[2].



The study of X-ray spectra XRD

In order to determine the obtained deposited structure, the XRD spectrum was investigated. The results showed that freshly deposit obtained has sharp peaks of crystalline structure of hydroxide and low amount of manganese oxide which is the because of low amounts of oxidative form of instable manganese hydroxide and its transformation into the oxide form[3].



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A combination of silicon pores and cracks fabricated via photo-assisted electrochemical etching

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Abstract:

The modifying surface of silicon is one of the ways that improve the conversion efficiency of silicon-based device. The photoelectrochemical etching of n-type silicon (100) surface was performed using ($HF:C_2H_6O:H_2O_2$) solution with a constant current density of 40 mA cm^{-2}. The morphology of the porous silicon was obtained using a Field-Emission Scanning Electron Microscope (FE-SEM). Influence of time on etched wafers was studied.

Keywords: porous silicon, photoelectrochemical Etching, light trapping

Introduction

Porous silicon (PSi) has represented lower reflectance and large effective area that is a widely used in various applications[1]. Here, by increasing surface roughness, the incident light is trapped inside the pores of substrate. Generally, the physical properties of PSi layer depend on the shape, diameter of pores and uniformity the thickness of the formed PSi layer. Although, the control of pore morphology of silicon is obtained by controlling the Some parameters like etching time, applied current density, voltage and concentration solution that these have main role in modifying porosification[2-3]. In this study, the porous film was investigated at different time. we report the effect of etching time on the porosity of silicon substrate.

Experimental

The n-type silicon wafer was used as the substrate which had (100) orientation. The silicon surface was chemically cleaned using a conventional RCA method [4]. The etching process was performed in a teflon cell containing a mixture of ($HF:C_2H_6O:H_2O_2$= 2:1:1) etching solution by using Pt wire as the cathode and silicon substrate as the anode.

Result and discussion

Fig. 3 shows the FE-SEM images of the PSi samples prepared at different etching times. The porosity within the network PSi layer, can be evaluated by gravimetric measurements according to Eq. 1. where M_1 and M_2 are the weight of the sample before and after etching, respectively and M_3 is the weight after removing the PSi layer in corrosive solution (3% KOH) [5]. The results shown that the structure of the samples were homogeneous that uniform distributed in surface and nano pore diameters ranging was 0.1µm to 0.3µm. The porosity of obtained n-type porous silicon at different etching time 25, 30, and 35 min are 23.42%, 31.79%, and 36. 67%, respectively.

$$P\,(\%) = \frac{M_1 - M_2}{M_1 - M_3} \qquad \text{Eq. 1}$$

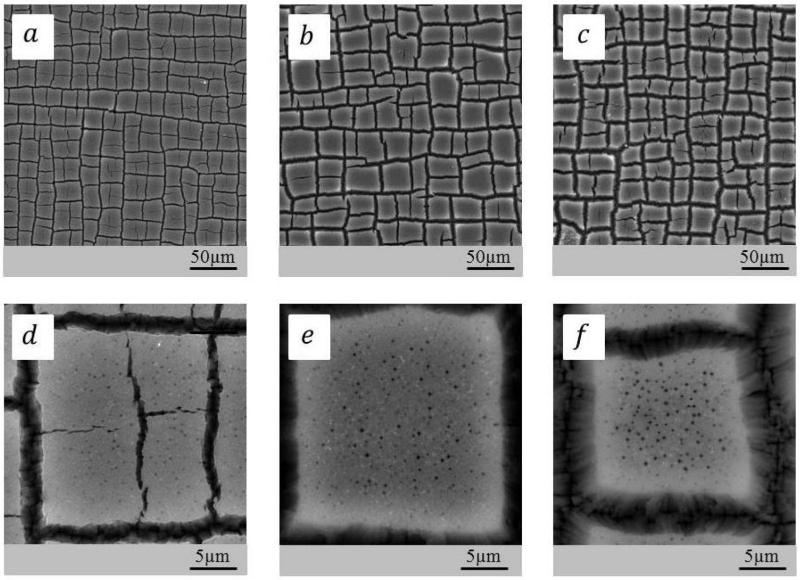

Fig 3. FE-SEM micrographs of the porous silicon which were etched with different time (a,d)25, (b,e)30, and (c,f)35

Conclusions

The Porous Silicon substrates were fabricated by photoelectrochemical etching . In this report, formation of porous silicon structures was optimized by controlling etching time.

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Electrochemical oxidation of acetaminophen in the presence of Methyl-Meldrum's acid: Experimental and Theoretical Studies

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Abstract

Acetaminophen (1,4-acetamidophenol) is a popular medicine, and electrochemical behavior of it has been studied in aqueous and non-aqueous solvents [1]. The electrochemical oxidation of acetaminophen in the presence of different nucleophiles has been investigated [2, 3]. In this work electrochemical oxidation of acetaminophen in the presence of Methyl-Meldrum's acid (MMA) has been studied both experimentally and theoretically. The experimental results were obtained using cyclic voltammetry and controlled-potential coulometry, and also the computational data was obtained by the use of density functional theory (DFT). The theoretical results were calculated at (B3LYP) level of theory and 6-311G(p,d) basis set. Acetaminophen oxidized to its *p*-benzoquinoneimine (**1ox**) via two-electron, two-proton process, and the produced **1ox** is unstable and reacts with MMA as a nucleophile. According to the voltammetry and coulometry study and by the use of the computational data, a mechanism was presented for the electrochemical oxidation of acetaminophen in the presence of Methyl-Meldrum's acid (MMA). Also using computational study, a mechanism was estimated for the electrochemical oxidation of 1,2-acetamidophenol in the presence of Methyl-Meldrum's acid (MMA).

Keywords: Electrochemical oxidation, Cyclic voltammetry, Acetaminophen, 1,2-Acetamidophenol.

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Thermodynamic study of electrochemical oxidation of some p-dihydroxybenzenes in the presence of p-toluenesulfinic acid

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Abstract

In this investigation, electrochemical oxidation of some *p*-dihydroxybenzenes (**1**-**3**) in the presence of *p*-toluenesulfinic acid as a nucleophile was studied experimentally and theoretically. The experimental results were obtained using cyclic voltammetry and controlled-potential coulometry (CPC), and the computational data was obtained by the use of density functional theory (B3LYP level of theory and 6-311G(p,d) basis set). The CPC was performed in an aqueous solution containing Methylhydroquinone (**1**) and *p*-toluenesulfinic acid (**2**), and monitoring of the electrolysis progress was performed by the use of the cyclic voltammetry. The coulometry was terminated after consumption of about two electrons per molecule of **1** and **1a** is produced as a final product. Also, the electrochemical oxidation of **1** in the presence of **2** was studied theoretically. Firstly the effect of the substituents on the oxidation potential of the studied species (**1-3**) was investigated using computational study. It was found that species with larger ΔG_{tot} value have more positive oxidation potential [1, 2]. Secondly calculated ΔG_{tot} of the electrochemical oxidation of **1a** indicates that because ΔG_{tot} of the product (**1a**) is more than starting molecule (**1**), mechanism of the electrolysis is *EC* and produced **1a** is not electroactive in the CPC [3].

Keywords: Electrochemical oxidation, Cyclic voltammetry, Methylhydroquinone, ΔG_{tot}.

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Glucose biosensor based on porous silicon

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Abstract

The various field of biosensors can be most organized according to the physical process by the device translates the adsorption of material into a measureable signal. Biosensors can have a variety of biomedical, industry, and military applications. The major application is in blood glucose sensing because of its market potential. Electrical Biosensors Based on Nanostructured Porous Silicon has been developed due to favor of silicon porous structure into immobilization of glucose[1-3].

Experimental

The PS layers were synthesized by photoelectrochemical etching of silicon wafer in a HF-based bath at room temperature under the illumination of a 100W tungsten lamp placed 20 cm above the samples. The electrochemical cell was a Teflon container 10 mm in diameter and 25 mm in height. The solution contained a mixture of hydrofluoric acid (40%), ethanol (95%) and with the volume ratio of 1:4. The silicon substrate was used as an anode electrode, and the cathode was an inert metal (Pt) wire. The etching current density was fixed at 40 mA/cm2 at etching time of 20, 25, 30 minutes.

Result and Discussion

SEM images of Silicon porous structure are shown in figure 1-a and 1-b. according to figure 1-c, the pours diameters are in the range of 800 to 1800 nanometer.Typical current-voltage (I-V) characteristics acquired immediately after the immobilization of glucose on the surface of nanoPS are shown in Figure 1-c. The different curves were recorded for several concentrations of glucose in distilled water, ranging from 0 µg/mL to 1,000 µg/mL. It is understood that increasing glucose concentration results in lower current for a given voltage. the horizontal distance between the curves is smaller for increasing glucose concentration, indicating that the devices are approaching the saturation limit.

Conclusion

In smarry it is achived that silicon porous structure is favor into immobilization of glucose. It is demonstrated that increasing glucose concentration results in lower current for a given voltage.

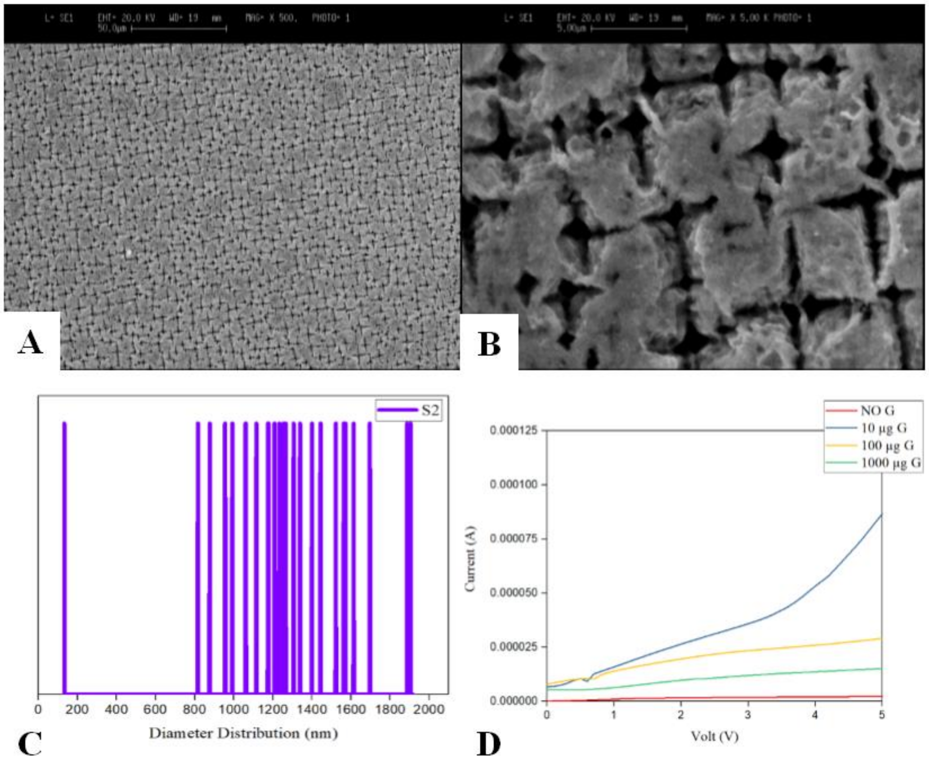

Figure 3-a SEM images of porous silicon structure in 50 micrometer, 4-b SEM images of porous silicon structure in 5 micrometer, c diameter distribution of Psi and d typical IV curve

Keywords : biosensor , porous silicon , photoelectrochemical etching

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Electrodeposition of nickel cobaltite oxide semiconductor thin film: Photocathode fabrication

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Abstract

Nowadays, the matter of energy and fuel supplying via sustainable approaches, using renewable sources has gained a global importance. In this regard, the utilization of solar energy and fabrication of semiconducting photoelectrodes play a crucial role; using this strategy, sunlight is directly converted to electricity or the energy is stored as fuel (chemical bond) [1]. Herein, with applying an appropriate aqueous electrolyte containing Co (II) and Ni (II) nitrate, a green film of Layered Double Hydroxide (LDH) was cathodically electrodeposited on fluorine-doped tin oxide (FTO) glass and copper substrates, and the film was then converted to a black porous nickel cobaltite oxide ($NiCo_2O_4$; NCO) by annealing in the ambient atmosphere [2]:

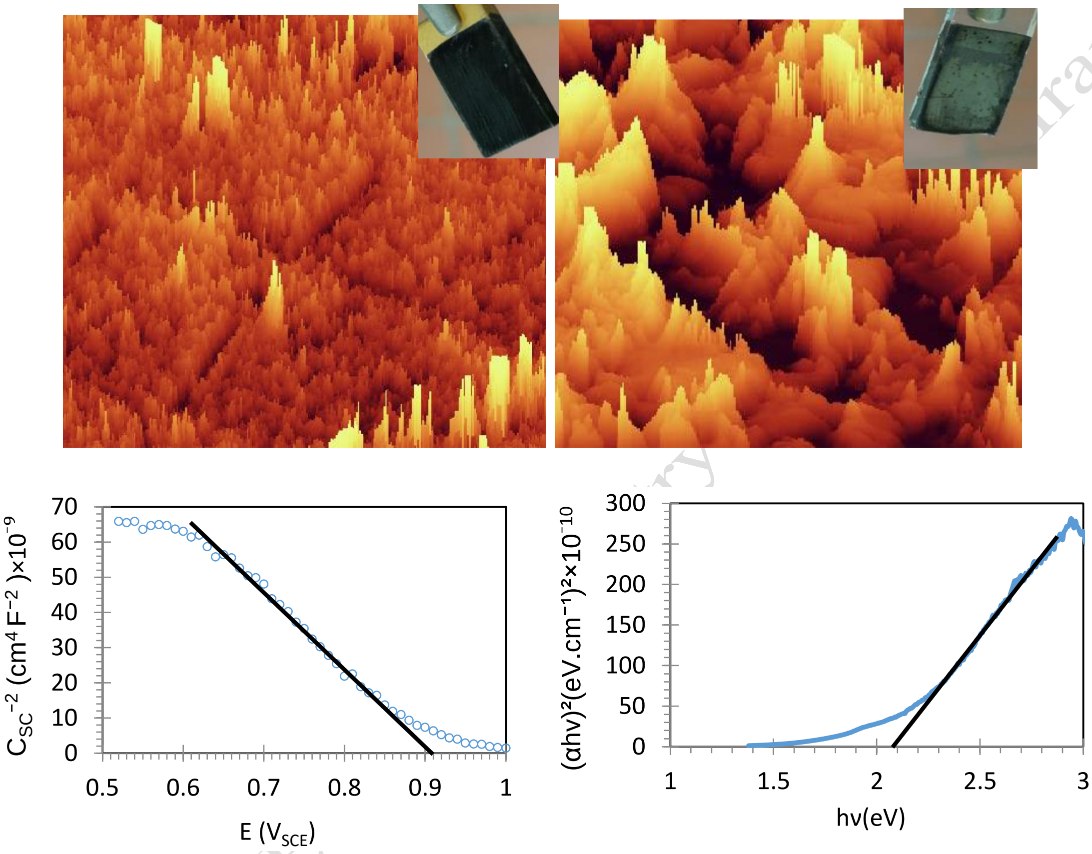
$$NO_3^- + 7H_2O + 8e^- \rightarrow NH_4^+ + 10\,OH^- \quad (1)$$

$$M^{2+} + 2OH^- \rightarrow M(OH)_2\,; M = Ni, Co \quad (2)$$

$$Ni(OH)_2 + 2Co(OH)_2 + \frac{1}{2}O_2 \xrightarrow{473\text{ K}} NiCo_2O_4 + 3H_2O \quad (3)$$

Mott-Schottky analyses revealed a p-type conductivity for the fabricated electrodes (*majority* charge *carriers: hole, flat-band potential:* $0.9V_{SCE}$ at pH=6.2). Furthermore, due to strong absorption in a broad spectral region ($E_g = 2.1$ eV; Tauc's plot), it was suggested that the Schottky junction NCO/Cu electrode fabricated here, could be employed as an affordable/potential photoelectrode for effective harnessing of photons and application in cathodic reactions [3].

Keywords: *Semiconductor thin-film, Cathodic electrodeposition, Photoelectrochemistry, $NiCo_2O_4$*



AFM micrographs (5×5 µm), digital photographs, Mott-Schottky diagram and Tauc's plot of the electrodeposited $NiCo_2O_4$ semiconducting thin film

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Effects of etching time on the morphology of n -type porous silicon structure

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Abstract:

The photoelectrochemical etching of n-type silicon (100) surface was performed using HF / Ethanol solution with an optimum constant current density of 25 mA/cm^2. Etching times of 15, 25 and 35 min were applied. The optimal etching time is 25 min for creating porous silicon layers based on silicon n-type (100). Average diameter for the porous silicon layer based on silicon n-type (100) were 1.9µm , 2.1µm and 2.6 µm at15, 25 and 35 min, respectively .

Keywords: porous Silicon, photoelectrochemical Etching, etching time

Introduction

Porous silicon has suitable properties for enhancing the optical and electrical silicon-based device such as photodetector that is due to a wide band gap, rang of the absorption spectrum and elevated ratio of surface to volume [1-2]. The photoelectrochemical etching is an attractive technique for fabricating n-type porous silicon. In this work, we report the effect of etching time on the uniformity and diameter of the stare-like pore in the silicon substrate.

Experimental

The n-type silicon wafer was used as the substrate which had (100) orientation. The substrates were successively dipped in 1:1:5 (by volume) of NH_4OH:H_2O_2:H_2O for 10 min, 1:50 of HF:H_2O for 20 s, and then in 1:1:6 of HCl: H_2O_2: H_2O for another 10 min[3]. The samples were then washed with deionized water and dried under an ambient nitrogen flow. The photochemical solution was a mixture of HF, and Ethanol with the volume ratio of 1:4.

Result and discussion

Fig. 3 shows the FE-SEM micrographs of porous silicon that prepared at different etching times (15, 25 and 35 min). Table 1 summarizes the size of the stare-like pore, which increases with increasing the etching time.

Table 1 the average size of pore at different time

Etching time (min)	Diameter (µm)
15	1.9
25	2.1
35	2.6

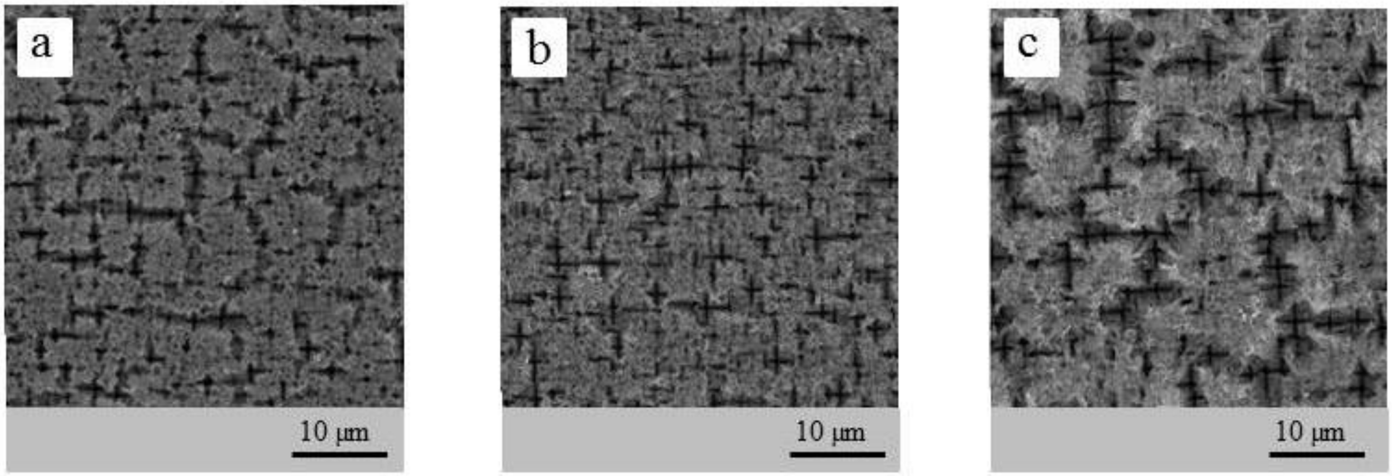

Figure 3.FE-SEM micrographs of porous silicon at different time (a)15 min(b)25 min(c)35min

Conclusions

In the this work, we have successfully fabricated the PS by using photoelectrochemical etching methods .

The optimal conditions for etching (100) silicon surfaces was determined.

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Modifying Porous Silicon with surfactant for Optoelectronic Applications: the Influence of triton on the pore characteristics

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Abstract:

The electrochemical etching of p-type silicon (100) surface was performed using HF / Triton solution. The presence of surfactant in etching solution cause to increase pore diameter and as well as effect in the distribution range of porosity. The morphology of porous silicon (PS) were obtained using a Field-Emission Scanning Electron Microscope (FE-SEM).

Keywords: porous Silicon, electrochemical Etching, surfactant,

Introduction

The most common technique for fabricating porous silicon (PS) is electrochemical etching of a silicon wafer in a hydrofluoric acid (HF) based electrolyte solution. In general, the pore morphology of PS layer depends on different parameters like dopant type, etching time, applied current density and composition of the electrolyte solution (HF concentration and use of surfactant or organic solvent) [1-2]. In this paper, we report the effect of the composition of etching electrolyte. The results showed that the structure of the PS layer prepared in HF solutions containing Tritons was homogeneous and pore diameters range increased.

Materials and Method

A high-doped p-type silicon (100) wafer was used as a substrate. The silicon surface was chemically cleaned using a conventional RCA method [3]. The porous structure was formed on the silicon substrate by using the electrochemical etching method with a constant current density of 10 mA cm^{-2} at room temperature using the Pt wire and Si wafer as cathode and anode, respectively. The electrochemical etching process was carried out in a Teflon cell containing a mixture of HF:Triton (1:4) and few drops of Trinron.

Results and discussion

Figure 1 shows the porous structure of etched Si wafers at different time 20, 25, 30 and 35 min respectively. In these figures, small porous are visible and the whole surface is not covered by the same pore. Moreover, Figure 2 shows that applying Triton will improve the pore size and uniformity of the PS layer. The properties of different samples with and without Triton are summarized in Table 1.

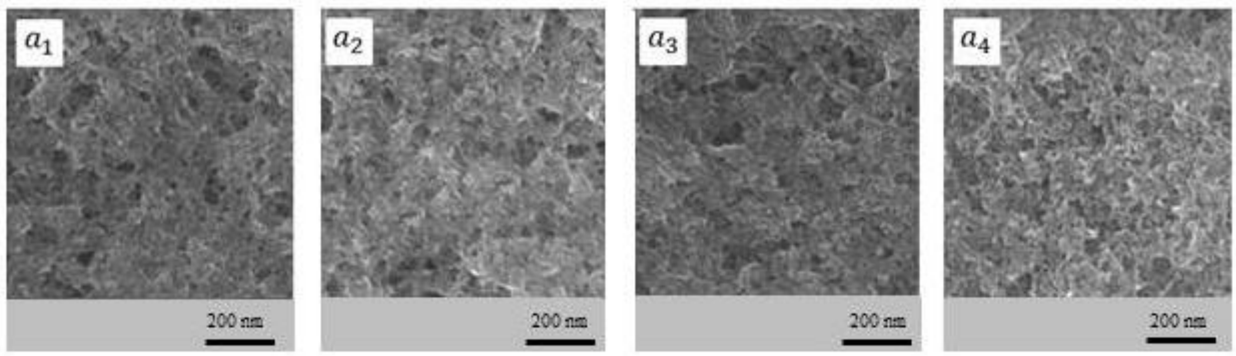

Fig 1. FE-SEM micrographs of porous silicon without Triton which were etched with a different time a_1 (20 min), a_2 (25 min), a_3 (30 min), and a_4 (35 min).

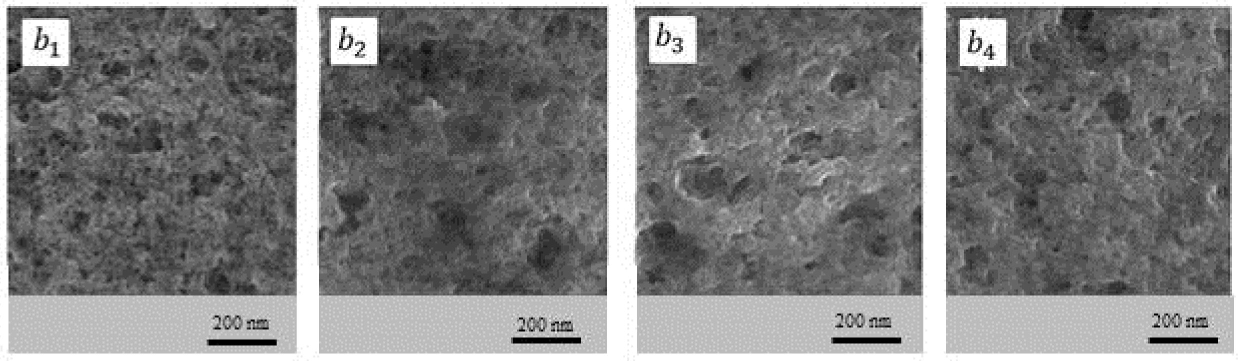

Fig 2. FE-SEM micrographs of porous silicon with Triton which was etched with different time b_1 (20 min), b_2 (25 min), b_3 (30 min), b_4 (35 min).

Table 1 the properties of various sample with and without Triton

Time (Min)	**20**	**25**	**30**	**35**
Sample with Triton	a_1	a_2	a_3	a_4
Diameter (nm)	19.3	27.4	30	34
Sample without Triton	b_1	b_2	b_3	b_4
Diameter (nm)	29.2	40.3	48.7	51.6

Conclusions

In this work, we have successfully fabricated the PS by using electrochemical method in HF-based etchant solution containing Triton. The porous silicon with high uniformity can perform high antireflection properties. Therefore, it can promise potential applications in high efficiency, silicon-based devices.

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Computational Electrochemistry

Mathematical modeling of oxygen crossover in lithium-oxygen battery

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Abstract

Lithium-air battery attracted great attention because of their high energy density. Energy density of Lithium-oxygen batteries is more than ten times greater than energy density of lithium-ion battery that is currently used in electric vehicles. In spite of high energy density of lithium-oxygen batteries, there are several challenges that need to be overcome for developing of these batteries. Herein we investigate oxygen crossover in lithium-oxygen battery that is one of the main challenges in these batteries. We developed a mathematical model based on Newman porous electrode method to investigate effect of oxygen crossover on the cycling behavior of lithium-oxygen battery. Effect of diffusion coefficient and oxygen solubility on the performance of the battery are investigated. The results show that with decrease of diffusion coefficient and oxygen solubility on the electrolyte cycling performance of the battery is enhanced. But these two parameters have negative impact on full discharge of the battery. In other words, these two parameters decrease the specific capacity of the battery. Our study shows the importance of these two parameters in the performance of the battery. Furthermore, consideration of these two contract effect (enhancing in cycling and diminishing in full discharge) is greatly suggested.

Keywords: Lithium-oxygen battery, Oxygen crossover, Mathematical modeling, Lithium superoxide

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