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بسمه تعالی

پیش‌گفتار

یک پژوهشگر نباید انتظار داشته باشد همهٔ اطلاعات مورد نیاز خود را تنها از طریق تلاشهای فردی و ابتکارعملهای خویش به دست آورد.ارتباطات یکی از اجزای درونی فعالیتهای علمی روزمره است. چنین ارتباطاتی نقش مهمی را در علوم و فناوری ایفا می‌کنند. در زمانهای گذشته که تعداد دانشمندان و پژوهشگران اندک بود، بسیاری از ارتباطات در علوم بدون تلاشهای سازمان‌یافته و با تماسهای فردی و به صورت غیررسمی و سازمان‌نایافته صورت می‌گرفت. چنین شیوه‌ای اکنون دیگر کارایی ندارد و به سیستمهای سازمان‌یافته ارتباطی نیاز است.

انجمنهای علمی یکی از اجزای قابل توجه در علوم جدید و جوامع علمی هستند. سابقهٔ ظهور این انجمنها به قرن هفدهم میلادی برمی‌گردد. دو قرن هفدهم و هجدهم قرنهای انجمنهای علمی در جوامع غربی است. به دنبال تشکیل انجمنهای علمی در غرب، تأسیس دیگر انجمنهای علمی سرعت گرفت تا جایی که در سال ۱۷۹۰ شاهد حدود ۲۲۰ فرهنگستان علوم در سراسر جهان بوده‌ایم. در ایران امروز، بیش از ۲۰۰ انجمن علمی فعالیت می کنند. انجمنهای علمی به عنوان نوعی دانشکدهٔ نامرئی عمل می‌کنند و از این‌رو بسیار مفید هستند. در این انجمنها، دانشمندان می‌توانند با ملاقات یک‌دیگر اندیشه‌ها، نتایج آزمایش‌ها و اطلاعات خود را ردوبدل کنند. چنین کارکردی توسعهٔ بعدی علم را با تشویق مبادلهٔ اندیشه‌ها، گردآوردن همکاران و فعالیتهای تحقیقاتی را سرعت بخشیده است. ایجاد ارتباطات علمی میان دانشمندان، تدوین و هدایت اولویتهای تحقیقاتی در میان اعضای انجمن، ایجاد و اِعمال هنجارها و استانداردهای علمی، دفاع از منافع حرفه ای دانشمندان در جامعه و کنترل نسبی بر کاربرد نتایج تحقیقات علمی در جامعه از مهمترین دستاوردهای انجمن های علمی در سراسر جهان است.

بدین منظور انجمن الکتروشیمی ایران مفتخر است در جهت تقویت ارتباطات علمی، پنجمین سمینار الکتروشیمی ایران را با همکاری، دانشگاه تربیت مدرس، فرهیختگان الکتروشیمی و جوانان با دانش ایرانی برگزار کند. در اینجا لازم می دانم که از مشارکت صمیمانه و ثمر بخش همه دانش دوستان فرهیخته که در پیشبرد اهداف انجمن الکتروشیمی ایران از هیچ کوششی دریغ نکرده اند، سپاسگزاری نمایم. موفقیت و کامیابی انجمن الکترو شیمی ایران در برگزاری پنجمین سمینار الکتروشیمی ایران در ۱۷و ۱۸ اردیبهشت ماه ۱۳۸۸ در دانشگاه تربیت مدرس مرهون لطف و محبت بخش شیمی، مدیران محترم دانشگاه تربیت مدرس، اساتید و دانشجویان عزیزی است که همواره در این مسیر پشتیبان ما بوده‌اند .بی تردید، مسئولیت پذیری و علم دوستی شما، ارتباطات علمی در ایران عزیز را شکوفاتر خواهد کرد. از ایزد منان توفیق روز افزون شما را خواستارم.

حسین غریبی

دبیر پنجمین سمینار الکتروشیمی ایران

Analytical Electrochemistry
الکتروشیمی تجزیه

Conversion & Storage of Electrochemical Energy
تبدیل و ذخیره انرژي

Electrochemistry & Materials Science
الکتروشیمی و علم مواد

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Bioelectrochemistry
بیو الکتروشیمی

Analytical Electrochemistry
الکتروشیمی تجزیه

A Comparative Electrochemical Study of Commercial & Laboratory-Made DSA Electrodes

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ABSTRACT

Dimensionally stable anode (DSA) -type electrodes have been well succeeded nowadays due to their good electrocatalytic activity and stability for all common gas evolution reactions (O_2, Cl_2). These types of anodes usually consist of a Ti support coated by noble metal oxides and their mixture with titanium oxide. The use of mixed oxides can lead to synergetic effects improving the electrocatalytic or stability properties of the electrodes.

In this work, many electrodes by different nominal compositions of electrocatalycally active oxides were prepared by thermal decomposition of iridium, ruthenium, tin and titanium chloride solutions in different mole ratios or calcining temperature, and their electrochemical properties of these anodes (as chlorine anode) were compared with commercial DSA. Electrochemical characterization of the samples was performed by cyclic voltammetry, polarization measurement and electrochemical impedance spectroscopy (EIS). All the measurements were carried out in an electrochemical cell with a Pt counter electrode, an Ag/AgCl reference electrode and the electrolyte 0.5 M NaCl, pH 2, at room temperature. Based on cyclic voltammograms, anodes with composition of $Ru_{30}Ti_{70}O_2/Ti$ and $Ir_{20}Ru_{30}Ti_{50}O_2/Ti$ have the same shape and effective surface area in comparison with commercial type, and polarization curves in NaCl solution were used for the evaluation of the electrocatalytic effects. The value of the Tafel slope for $Ru_{30}Ti_{70}O_2/Ti$ is more close to commercial one and higher slightly currents of chlorine evolution reaction for $Ru_{30}Ti_{70}O_2/Ti$ electrode shows that it is more active for chlorine evolution reaction. Finally the impedance results in chlorine evolution reaction indicated that the electrocatalytic activity of RuO_2 material decreases with increase of calcining temperature and stability of them increased with IrO_2 content.

Keywords:*Dimensionally stable anode; Cyclic voltammetry;Electrochemical impedance spectroscopy*

Voltammetric determination of hydroxylamine at the surface of TiO_2 nanoparticles modified carbon paste electrode

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Abstract

There is today an increasing demand for the analysis of numerous chemical compounds. The electroanalytical methods have several advantages over other analytical systems. Among those are the simplicity, the rapidity and the low cost of the operations. In many cases, however, chemicals of analytical interest show a slow heterogeneous electron transfer with the electrode surface and it is necessary to find materials with specific electrocatalytic properties. In a certain number of cases, metallic nanoparticles were found to have higher catalytic properties in comparison with the corresponding bulk material. However, the construction of a large number of nanoparticles-based electrodes for the screening of various nanomaterials as electrocatalysts is a time consuming process.

Hydroxylamine is recognized as a mutagenic substance, moderately toxic and harmful to human, animals and plants. It has also been identified as an intermediate in synthesis of pharmaceutical and drug substances. Therefore quantitative determination of hydroxylamine is very important in biochemistry and industrial processes. Many methods have been developed for the determination of hydroxylamine because of its toxicity, biological function and broad industrial utilization.

In the present work, the electro-oxidation of hydroxylamine has been studied by quinizarine-TiO_2 nanoparticles modified carbon paste electrode of using cyclic voltammetry, chronoamperometry and differential pulse voltammetry. This modified electrode exhibited potent and persistent electron mediating behavior towards hydroxylamine with activation overpotential. The obtained catalytic peak current, was linearly dependent on the hydroxylamine concentrations. The diffusion coefficient (D), and the kinetic parameters such as electron transfer coefficient, (α) and heterogeneous rate constant, (k') for hydroxylamine were also determined using electrochemical approaches.

Keywords: *Hydroxylamine, Nanoparticles, Voltammetry*

Zeolite-modified Carbon Paste Electrode as a Selective Voltammetric Sensor for Detection of Tryptophan in Pharmaceutical Preparations

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Abstract

Several synthetic zeolites such as mazzite, mordenite, zeolite L, zeolite beta and MCM-41 were tested as electrode modifiers in voltammetric determination of tryptophan (Trp). The effect of the composition of carbon paste electrode on its voltammetric profiles were evaluated in basic solution with 1.0×10^{-4} M Trp. It was found that addition of zeolite beta to the carbon paste would generate the peak current of Trp because of its catalytic effect on redox process. The pH strongly affects the peak potential of Trp. The best analytical response was obtained at pH 13.0. The effect of potential scan rate between 25 and 500 mVs^{-1} on the peak potential and peak current of tryptophan was investigated. The correlation of the peak current against $v^{1/2}$ (v is the scan rate) is linear (r = 0.9989) which is attributed to a diffusion-controlled process. The anodic peak currents were proportional to Trp concentrations in the range of $5.0 \times 10^{-7} – 5.0 \times 10^{-3}$ M under the optimized experimental conditions. The detection limit was 1.0×10^{-7} M. The influence of several species especially other amino acids were tested. From our results, it is concluded that the method is relatively selective for determination of Trp. The proposed method was applied to the determination of Trp in pharmaceuticals formulations successfully.

Keywords: *Tryptophan, Voltammetric sensor, Zeolite-modified carbon paste electrode, Inorganic modifiers, Zeolite beta****.***

Determination of ultra trace amounts of copper in food samples by highly sensitive adsorptive stripping voltammetric method

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Abstract

Copper is an essential trace element in the biological systems and in the living organisms where it serves as a cofactor in at least 30 important enzymes. Copper is also is an important bioelement that is present in animals, plants and micro organism. It is both vital and toxic to many biological systems, depending on the level of concentration. Their maximum tolerated concentrations have been fixed by legislation: 50 μ g/ L for copper (II). The concentration of copper in various samples is low, so developing sensitive and selective methods for determination of copper in food and biological samples are required. A number of techniques for copper determination have been reported, including spectrophotometry, atomic absorption spectroscopy, inductively coupled plasma, cloud point extraction, kinetic method, flow injection analysis, derivative potentiometric stripping analysis and microdialysis sampling. Usually, the detection limit of these methods are reported not to be good, some others has a little linear dynamic range .Adsorptive stripping voltammetry (ASP) is a useful method to determine the trace levels of copper since its combines excellent sensitivity, selectivity, accuracy and precision with low cost of instrumentation. This technique is based on adsorptive accumulation of a complex of the element with an added specific ligand on a hanging mercury drop electrode followed by electrochemical reduction of either the element or the ligand in the complex. In this work a highly sensitive and selective procedure is presented for voltammetric determination of copper in food, blood and water samples. The procedure involves an adsorptive accumulation of copper thiosemicarbazide complex on a hanging mercury drop electrode, followed by a stripping voltammetric measurement of reduction current of adsorped complex at -0.65V (vs. Ag/AgCl). The optimum conditions for the analysis of copper include pH 9.7 (Britton-Robinson Buffer), 2.5×10^{-6} M thiosemicarbazide, an accumulation potential of -0.05V (vs. Ag/AgCl), an accumulation time of 60s and scan rate of 80mV/s.The peak current is proportional to the concentration of copper over the range 0.01-90.00 ng/ml with a detection limit of 0.007 ng/ml. Most of foreign species do not interfere with determination. The proposed method was directly applied for the determination of copper in food, blood and water samples without any separation steps.

Study of electrochemical behaviour some novel shiff-base manganese (III) complex covalently linked on 3-aminopropyl triethoxy silane functionalized SiO_2-Al_2O_3 at a surface of carbon nanotube paste electrode

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Abstract

In this work, Synthesis and electrochemical behaviour of Mn(III)-Schiff base complexes covalently linked on 3-aminopropyl triethoxy silane functionalized SiO_2-Al_2O_3 was stdied at a surface of carbon nanotube paste electrode. Cyclic voltammogram result shows that some of this complexes in natural condithion (pH-7.00) oxidize better than the other complexes. These results shown good agreement with organic oxidation raction in present these catalysts. In addition, impedance spectroscopy and chronoamperometry used for determination of kinetic and thermodynamic parameters in aqueous solution.

Keyword *Shiff-base, Voltammetry, manganese (III) complex, Impedanse, spectroscopy*

الکترود Sr^{2+} گزین با زمان پاسخ سریع تهیه شده به روش سل-ژل

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چکیده

الکترود Sr^{2+} گزین با یونوفورخنثای ۶-(۴-نیترو فنیل)-۲-فنیل-۴ و ۴-دی پروپیل -۳و ۵ –دیازا- بی سیکلو[۰و۱و۳] هگز -۲ –ان(NPDBH) به روش سل-ژل ساخته شد محاسبات تئوری تمایل این یونوفور را نسبت به Sr^{2+} در مقایسه با تعدادی کاتیون دیگر به خوبی اثبات می کند.اثر ترکیب ممبران ،اثر pH و حضور یونهای مزاحم مورد بررسی قرارگرفت . این الکترود به یون Sr^{2+} در محدوده غلظتی از ۱/۰*۱۰$^{-۱}$ تا ۸/۰*۱۰$^{-۷}$ مولار با شیب ۰/۴ ± ۲۹/۱ میلی ولت پاسخ می دهد. این الکترود زمان پاسخ بسیار کوتاه برابر با ۱۱ ثانیه داشته و در محدوده pH از ۳ تا ۱۰ پاسخ خوبی می دهد و حد تشخیص آن برابر ۷/۵*۱۰$^{-۸}$ مولار است. الکترود پایداری دمایی خوبی دارد اما در دماهای بالای ۶۰^{oc} منجر به انحراف در پاسخ آن میشود. این الکترود برای اندازه گیری Sr^{2+} در ادرار انسان و نمونه های استخوان بطور موفقیت آمیز بکار رفت.

واژهای کلیدی : *الکترود Sr^{2+} گزین، کالبدهای آلی-معدنی سل -ژل، حامل های خنثی، پتانسیومتری.*

الکترود یون گزین برای تعیین برخی از داروهای مقاوم کننده مانند دی بوکائین

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چکیده

مخلوط دارویی مقاوم کننده(MDR) می تواند به طور گسترده ساختار شیمیایی و فعالیت بیولوژیکی داروهای ضد سرطان را تغییر دهد. بهترین فرم مطالعه شده از داروهای مقاوم کننده در پزشکی و زیست شناسی پلی گلایکوپروتئین است. بر طبق نظر معمول موجود پلی گلایکوپروتئن ها عوامل سیتوتوکسیک را به طور فعال به خارج سلول منتقل می کند و غلظت درون سلولی داروهای ضد سرطان را کاهش داده و از این طریق عمل می کند. در این کار پلیمر پلی وینیل کلراید با چندین نرم کننده متفاوت با ترکیب درصد مختلف برای اندازه گیری داروهای مقاوم کننده به کار رفت. غشا PVC-لیگاند ۱-نفتیل اتیلن دای آمین دی کلراید با نسبت ۱به ۲ با ۷ درصد وزنی نرم کننده دای اکتیل فتالات ۶/۹ به عنوان بهترین غشا انتخاب شد. با این غشا داروهای دی بوکائین، دای فنیل هیدرامین، ایمیپرامین و کلروپرومازین در ناحیه خطی $۱۰^{-۱}$ ۱/۰ تا ۱/۰ × $۱۰^{-۶}$ با تکرارپذیری و تکثیرپذیری خوب و شیب منحنی کالیبراسیون ۵۸/۵ بدست آمد. حد تشخیص روش برای دی بوکائین در pH بهینه ۲/۲تا۷/۴ و زمان پاسخ گویی یک ثانیه ۶/۹ × $۱۰^{-۷}$mol/L بدست آمد. از این غشا برای تعیین چند دارو در نمونه های دارویی استفاده شد.

واژه‌های کلیدی: مخلوط دارویی مقاوم کننده، اندازه گیری، غشا یون گزین

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Modified Electrode with Cobalt Ions Dispersed into Poly (N-methylaniline); Application in Electrocatalytic Oxidation of Hydrogen Peroxide

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Abstract

Hydrogen peroxide is the product of the reactions catalyzed by a large number of oxidases. Detection of hydrogen peroxide which is a byproduct in an enzymatic reaction is important in the field of biosensor fabrication. Many methods such as titrimetry, spectrophotometry and chemiluminesence have been developed for this purpose. Electrochemical methods have been proved to be an inexpensive and effective way for hydrogen peroxide determination. In this work, conducting and stable poly (N-methylaniline) (PNMA) film was prepared by using the repeated potential cycling technique in aqueous solution containing (N-methylaniline), sulfuric acid and sodium dodecyl sulfate (SDS) at the surface of carbon paste electrode (CPE). The transition metal ions of Co(II) were incorporated to the polymer by immersion of the modified electrode in 0.1 M cobalt chloride solution. The modified electrode showed well defined and stable redox couples in alkaline aqueous solution. Also, the modified electrode showed excellent electrocatalytic activity for oxidation of hydrogen peroxide. This modified electrode has many advantages such as simple preparation procedure, good reproducibility and high catalytic activity toward the hydrogen peroxide oxidation.

Keywords: *Hydrogen peroxide, N-methylaniline***,** *Electrocatalytic Oxidation, sodium dodecyl sulfate*

Copper Supported Platinum Nanoporous Deposited on Gold Substrate for Electrocatalysis of Methanol Oxidation

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Abstract

In this work, we report application of highly porous copper nanoparticle as a support to loading platinum by galvanic replacement method to make nanoporous platinum structure and investigation of its catalytic ability for methanol oxidation reaction. We applied simple but very effective method for deposition of highly porous copper nanoparticles. This technique involves electrochemical deposition accompanying hydrogen evolution, which has been deliberately suppressed in typical electro-deposition processes to produce dense metallic components. In this process, hydrogen bubbles function as a dynamic template for metal deposition, resulting highly porous structure. This graded structure is ideally suited as a support to loading noble metal catalysts due to its high surface area and excellent electrical conductivity. We found that effective surface area, stability of platinum film and its catalytic ability depend on thickness and potential applied for deposition of copper nanoparticle used as a support. This new approach can be consider as a effective method for extra fine platinum loading lead to design efficient Pt base catalysts with lower cost.

Keywords: *Copper nanoparticle, Platinum nanoparticle, Methanol oxidation, Electrocatalysis.*

Determination of strychnine in *strychnos nux vomica* plant by Nanogold-modified carbon paste electrode

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Abstract

A gold nanoparticles modified carbon paste electrode (nanoAu-CPE) has been used for the determination of Strychnin in strychnos nux vomica plant by cyclic voltammetry, differential pulse voltammetry (DPV) and chronoamperometric methods. *Strychnos nux-vomica* L. (Loganiaceae), widely used in traditional medicine, is grown extensively in southern Asian countries. The dried seeds of this plant have been claimed to improve blood circulation and relieve rheumatic pain.The electro-oxidation and detection of strychnine has been studied using EG&G. the results revealed that the modified electrode show an electrocatalytic activity toward the anodic oxidation of strychnin by a marked enhancement in the current response in buffered solution at pH of 8. The linear analytical curve was observed in the 1.80×10^{-6} to 7.0×10^{-4} $molL^{-1}$ range with correlation coefficient of 0.997. The method was then successfully applied to the determination of strychnin in plant. The detection limit of this simple method is 6.3×10^{-8} M which was lower than other similar work. In brief the use of carbon paste electrode has the advantages of diversity of paste modification and the convenience in manipulation and the method show good sensitivity and selectivity.

Keywords: *Gold nanoparticles modified CP electrode; strycnnine; Differential pulse voltammetry; Drug formulation; Urine*

Electrochemical Hydride Generation of cadmium and Determination by Electrothermal Atomic Absorption Spectrometry

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Abstract

Electrochemical and chemical hydride generation systems for determination of cadmium(II) by atomic absorption spectrometry with in situ trapping in graphite tube atomizer are described. A batch electrolytic cell with a Sn-Pb alloy cathode was used to generate cadmium(II) hydride. The cell body was made from polymethylmethacrylate. Anodic and cathodic chambers were separated by an ion exchange membrane. The cathode was placed in the cathodic chamber parallel to the membrane and the platinum anode. Tungsten used as the permanent chemical modifier to treat the graphite tube atomizer in electrochemical hydride generation method. The optimized constant current and catholyte concentration, both for electrolysis were determined. The effect of some ions on the electrothermal atomic absorption signal of electrochemical generated hydride of cadmium(II), were evaluated as interfering ions. Chemical hydride generation of cadmium(II) was done to let a comparison of electrochemical and chemical hydride generation of this element. The graphite tube temperature program of the electrochemical method was applied for the chemical approach with changes. Tungsten was used as the chemical modifier for the chemical hydride generation, too. The analytical figures of merit of mentioned procedures were evaluated. For the electrochemical hydride generation of Cd(II), the calibration curve was linear over the range of 0.5-5 pg ml^{-1} with a detection limit of 0.05 pg ml^{-1} determined by dividing 3S_b by the slope of the calibration curve and R.S.D=5.5% (n=3) for 3pg ml^{-1} of cadmium solution. The accuracy of electrochemical method was evaluated by the analysis of two spiked water samples. The sensitivity of the electrochemical method, based on the calibration curve slope, was0.1198 ml pg^{-1} . For the chemical hydride generation, the calibration curve was linear over the range of 0.5-6 pg ml^{-1} with a detection limit of 0.291 pg ml^{-1} (3S_b / m) and R.S.D=10.4% (n=3) for 3pg ml^{-1} of cadmium(II) solution. The sensitivity of the chemical method, based on the calibration curve slope, was 0.0103 ml pg^{-1}. Electrochemical hydride generation of cadmium(II), in comparison with the chemical one, had lower detection limit and higher sensitivity. Electrochemical method was used to determine Cd(II) in water samples by standard addition technique.

Keywords: *Hydride Generation, cadmium,Tin Alloy*

Synthesis of nano-structured gold by pulsed chronoamperometric method and its application in the electrochemical determination of metronidazole

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Abstract

The surface of conventional gold electrodes was simply transformed to nanostructures by means of pulsed techniques, and it was characterized by scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray differaction (XRD), and electrochemical methods. The usual method for the fabrication and preparation of gold nanoparticles on the electrodes is electrodeposition or chemical methods. But, this proposed method, which is based on the continuous pulses on the gold electrodes, doesn’t need to any expensive reagents in the formation step. The nanostructured gold electrode can prepared in the relatively low period times and it enhances significantly electron transfer kinetics. For optimization of this modified electrode, by an electrochemical probe, different parameters such as pulse time, pulse height, pulse number, and relaxation time were optimized to obtain higher current signal and reversibility. This new system was used for the determination of metronidazole drug in the pharmaceutical and biological samples with satisfactory results.

Keywords : *Pulsed chronoamperometry, Nanostructure, Gold, Metronidazole*

Amperometric Detection of Adefovir Dipivoxil at a Preheated Glassy Carbon Electrode Modified with Multiwall Carbon Nanotubes and a Ni-Schiff Base Complex

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Abstract

Adefovir dipivoxil is indicated for the treatment of chronic hepatitis B in adults with compensated and decompensated liver disease with evidence of active viral replication, and either evidence of histologically active disease or elevation in serum aminotransferases. In this work, a highly sensitive and fast responding amperometric sensor for the determination of adefovir dipivoxil is described. The multiwall carbon nanotubes (MWCNTs) were first immobilized on a preheated glassy carbon electrode (5 min at 50 °C) by gently rubbing of electrode surface on a filter paper supporting the carbon nanotubes. Then, the MWCNTs-GC modified electrode was dipped into 1 ml acetonitrile solution containing 2 mg of the Ni-complex. The modified electrode was dried for 20 min at room temperature and rinsed with distilled water before use. The results indicated that prepared carbon Ni-complex-MWCNTs-GC modified electrode exhibited efficient electrocatalytic oxidation of the drug with relatively high sensitivity. Under the optimized conditions, the amperometric calibration plot found to be linear in the concentration range 0.7-3000 µM with a detection limit ($S/N = 3$) of 0.3 µM and sensitivity of 12154 nA/µM. The amperometric response is extremely stable, with no loss in sensitivity over a continual 25 min operation stability, and long life. Finally, the ability of the modified electrode was evaluated by its application to the determination of adefovir dipivoxil in real samples.

Keywords: *Glassy carbon modified electrode, Adefovir dipivoxil, Multiwall carbon nanotubes, Ni complex, Amperometry*

Conversion & Storage of Electrochemical Energy
تبدیل و ذخیره انرژی

Optimization of the Amount of Nafion in MWCNT/Nafion Composite as a Pt Support in GDE of PEMFC.

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Abstract

In this work, the effect of multi-wall carbon nanotubes (MWCNT) composite with Nafion as a Pt support on oxygen reduction reaction (ORR) was studied. We utilized different percentages of Nafion in the composite with MWCNT with 0.5 mg.cm^{-2} Pt loading in the catalyst layer. The performance of the electrodes in ORR was studied by linear sweep voltametery (LSV), electrochemical impedance spectroscopy (EIS), chronoamperometery, X-ray diffraction (XRD), transmission electron microscopy (TEM), and scanning electron microscope (SEM) techniques. In addition, we compared the results from MWCNT as a Pt support with the composite as a Pt support. Our results indicate that when the composite was used as a Pt support, the performance of electrodes increased rather than MWCNT as a Pt support.

Keywords: *Catalyst Layer; Gas Diffusion Electrode; Multi-wall Carbon Nanotube; Nafion; Oxygen Reduction Reaction; Proton Exchange Membrane Fuel Cell*

Investigation of Methanol Electro-oxidation on Modified Pt/C by Electrochemical impedance spectroscopy

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Abstract

In this study a modified Pt/C 10%wt catalyst have been examined for electrochemical oxidation of methanol in acidic environment for direct methanol fuel cell applications. The modifier was Polyaniline Nano fibers doped by trifilic acid (TFMSA). PANI nanofibers fabricated by in-situ electropolymerization of aniline on the surface of Pt/C coated on Glassy carbon (GC) in the presence of trifluoromethane sulfonic acid at 0°C. Platinum loading was 0.051mg.cm^{-2} in all experiments. The electrodes were characterized by electrochemical impedance spectroscopy (EIS). Nyquest plots show that the PANI nanofibers change not only the methanol oxidation mechanism by different pathway of bare catalyst (Pt/C) but also, it reduces charge transfer resistance for methanol electrooxidation. At 25 ^{o}C, methanol oxidation reaction on PANI/Pt/C exhibits potential down-shift of at least 50 mV than the bare Pt/C according to the Ip. Scanning electron microscopy (SEM) was employed to study the structure of PANI Nanofibers within electrode catalyst layer. SEM micrograph has verified the formation of high porous PANI nanofibers on Pt/C which enhance the catalytic and mechanical properties of catalyst layer.

Keywords: *Electrochemical Impedance spectroscopy, Pt/C, Methanol electro-oxidation, Direct Methanol Fuel Cell, Polyaniline Nanofibers.*

Results:

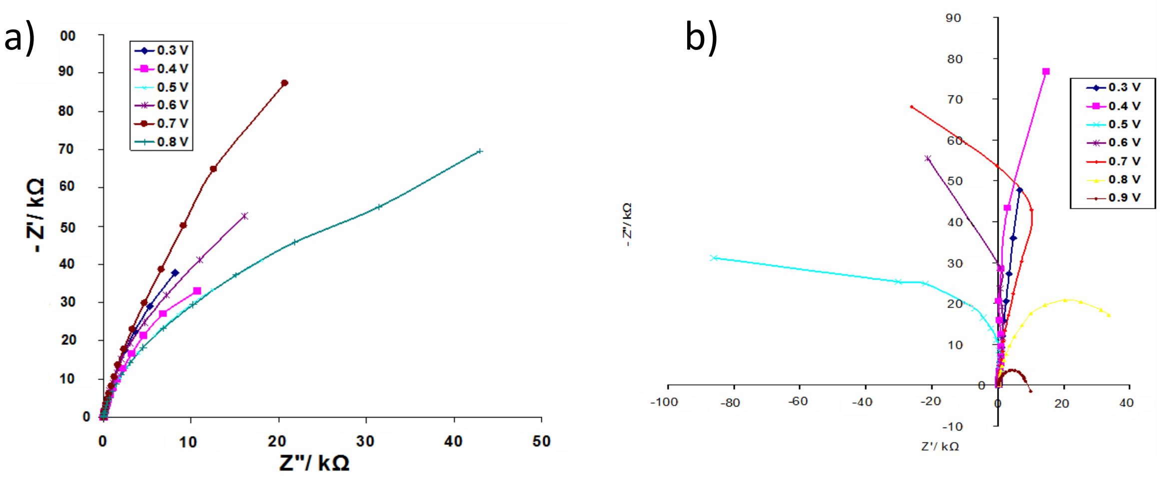

Fig. ۱ – Nyquest plots of (a) Pt/C (b) PANI/Pt/C catalysts in 3 M CH_3OH and 0.5 M H_2SO_4 with frequency range of 100 KHz to 10 mHz at various potentials of 0.3 V to ۰.۹ V vs. Ag/AgCl.

حل عددی جریان غیر هم دمای سه مولفه ای در سمت الکترود کاتد پیل سوختی با غشاء پلیمری

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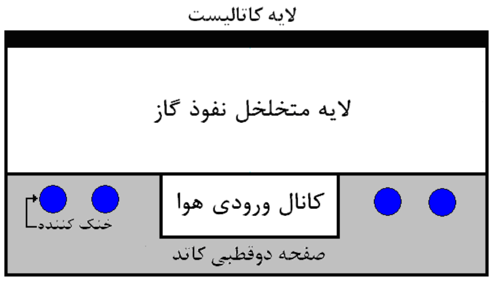
در این مقاله، فرآیندهای انتقال جرم و انتقال حرارت برای سه مولفه گازی اکسیژن، بخارآب و نیتروژن در الکترود کاتد پیل سوختی با غشای پلیمری با دو روش عددی تفاضل محدود و نرم افزار تجاری فلوئنت بررسی شده اند. مدل مطالعه شده دو بعدی، گذرا، تراکم پذیر و غیر هم دما است و در یک مقطع عمود بر جریان کانال ورودی در لایه متخلخل نفوذ گاز به کار رفته است (شکل۱). حل عددی توسط نرم افزار فلوئنت در مقطع قید شده، برای اولین بار در این مقاله انجام گرفته است بطوریکه در آن علاوه بر لایه نفوذ گاز، کانال انتقال گازهای واکنشگر نیز مدل گردیده است. مصرف اجزاء توسط معادلات فارادی به چگالی جریان کوپل شده اند و توزیع چگالی جریان الکتریکی حاصل از انجام واکنش الکتروشیمیایی در مرز لایه نفوذ گاز و لایه کاتالیست مورد بررسی قرار گرفته است. برای به دست آوردن منحنی پلاریزاسیون پیل سوختی، افت فعالسازی با استفاده از معادله تافل و افت اهمی در غشاء پلیمری لحاظ شده اند. معادلات دیفرانسیل حاکم به کار گرفته شده عبارتند از: (۱) یک معادله بقای جرم کل مخلوط و دو معادله بقای جرم اجزاء (۲) معادله مومنتوم برای مخلوط که به علت ماهیت متخلخل محیط توسط قانون دارسی بیان شده است و (۳) معادله انرژی برای کل مخلوط. به منظور ایجاد دقت مناسب، دیفیوژن هر کدام از مولفه ها بوسیله معادلات ماکسول- استفان مدل شده است. برای اطمینان از صحت کار، نتایج حاصل از دو روش عددی قید شده با همدیگر و نیز با نتایج تجربی کارهای قبلی مقایسه و تطابق خوبی مشاهده شده است.

کلمات کلیدی: *پیل سوختی با غشاء پلیمری، الکترود کاتد، حل عددی، انتقال جرم و حرارت، واکنش الکترو شیمیایی*



شکل ۱– تصویر شماتیک میدان محاسباتی (جهت جریان در کانال عمود بر صفحه است.)

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[۲] *عضو هیئت علمی دانشکده مکانیک و عضو آزمایشگاه تحقیقاتی تبدیل انرژی*

[۳] *دانشجوی کارشناسی ارشد تبدیل انرژی*

بررسی تاثیر ابعاد غشاء سلوفانی بر روی پارامترهای ارزیابی خواص غشاء در باتریهای روی-اکسید نقره

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چکیده:

به طور کلی افزایش سیکلهای باتریهای روی-اکسید نقره مهمترین عامل است که می تواند آنها را به عنوان یک منبع مؤثر انرژی معرفی نماید. یکی از عوامل و فاکتورهای کلیدی در افزایش عمر، سیکل و ظرفیت این نوع باتریها، غشاءهای بکار رفته در آنهاست. غشاءهای سلوفانی از مدتها پیش در ساختار باتریهای روی-اکسید نقره کاربرد داشته اند. در راستای بهبود کارایی باتری، ارزیابی خواصی از قبیل ابعاد، ضخامت، جذب، هیدرولیز، اکسایش، نفوذ و مقاومت الکتریکی حائز اهمیت می باشد. با توجه به آزمونهای ارزیابی انجام شده بر روی غشاء سلوفانی و اکتساب نتایج متفاوت، بهینه کردن این آزمونها مطابق با روشهای استاندارد مورد توجه قرار گرفت. همچنین به منظور اطمینان از یکنواخت بودن غشاء سلوفانی و عدم وابستگی رفتار غشاء به ابعاد آن، در این تحقیق و پژوهش شدتی یا مقداری بودن پارامتر ابعاد بر روی آزمونهای ارزیابی بررسی گردید.

آزمونهای ارزیابی در سه ابعاد مختلف و در غلظت ٪۴۰ الکترولیت KOH انجام پذیرفت و با توجه به نتایج بدست آمده، مشاهده گردید که تغییر ابعاد بر روی پارامترهای ضخامت، جذب، اکسایش، نفوذ و مقاومت الکتریکی بی تاثیر بوده و تنها بر روی هیدرولیز تاثیرگذار است که با کوچک شدن ابعاد، درصد هیدرولیز غشاء افزایش می یابد. شایان ذکر است که ابعاد غشاء در باتری روی-اکسید نقره بزرگتر از ابعاد آزمونها می باشد، لذا در کارایی سیستم خللی وارد نمی شود.

Platinume/volcane- polyaniline doped trifluoromethane sulfonic elctrodes and their electrocatalytic activity for DMFCs

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Abstract

In this work 2 electrodes were fabricated by polyaniline (PANI) and volcan wich Pt particles reduced on them. Polyaniline is synthesized by electropolymerization of aniline and trifluoromethane sulfonic acid as the proton-conductive monomer, and Platinum was reduced on to polyaniline and volcan then used in direct methanol fuel cells(DMFC s).

The efficiency of electrodes was examined for methanol oxidation reaction and the electrochemical properties of them were investigated by cyclic voltammetry, linear sweep voltammetry, chronoampermetry and electrochemical impedance spectroscopy. The surface morphology of electrodes was characterized by scanning electron microscopy. The obtained results revealed that electrode including high polyaniline is more efficient in comparison with electrodes contaning low tickness polyaniline or without polyaniline.

***Key words**: Polyaniline nanofiber, Modified electrode, methanol oxidation reaction (MOR), direct methanol fuel cell (DMFC)*,

Electrochemistry & Materials Science
الکتروشیمی و علم مواد

Metal and media effects on inhibitory performance: electrochemical approaches

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Abstract

The inhibiting action of a synthetic Schiff base [namely: N,N´- bis (salicyaldehyde)- 1,3-propandiimine] on corrosion behavior of copper in HCl and of iron in H_2SO_4 media was investigated from mechanistic points of view, through Tafel (potentio-dynamic) and electrochemical impedance (EIS) methods. The investigations revealed this molecule to be a mixed-type inhibitor (mostly anodic for iron and cathodic for copper) having physicochemical interactions with metal surface and its adsorption obeys the Langmuir isotherm. For iron system, the interactions were recognized to have some chemical properties being ascribed to the metal incomplete d-electronic configuration. The rate of corrosion was also observed to be low for copper case, comparing with iron one. This is resulting from a protective film of CuCl, forming on metal surface, detected as a double time-constant in Bode-phase diagram, causing both anodic and cathodic reactions to inhibit. This film is not stable and destroyed gradually by formation of some soluble complexes through extra coordination of chloride anions. Moreover, in presence of Schiff base, diffusion process and formation of corrosion product on metal surface were found to be prohibited, according EIS data; both Warburg line and the related time-constant disappeared. For the case of iron, however, the behavior was simple and described via conventional Randle model. Finally, the complementary investigations in electrolytes containing iodide ions showed a substantial enhancement on inhibitory performance, especially for copper system, justified by electrostatic interactions exerting between charged species.

Keywords: *Tafel polarization and impedance spectroscopy; Copper and Iron; Corrosion inhibitor; Thermodynamic and Kinetic studies; Temperature and Synergistic effect*

Mimosa Tannin as Green Inhibitor for Corrosion Protection of Mild Steel in Concentrated (30%) Hydrochloric Acid Solution

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Abstract

Corrosion Inhibitors are widely used in industrial acid pickling processes in order to alleviate the damage of the base metal and lowering the acid consumption [1]. Because of their natural source and relatively low cost as well as environmentally safe properties, natural products gained considerable attention for potential use as corrosion inhibitors. Plant essential oils and herbal extracts were studied and successfully applied as effective inhibitors for different metals in various corrosive media [2]. Among these materials, mimosa tannin, as a green inhibitor has been investigated as corrosion inhibitor for carbon steel in sulfuric solution [3]. In this research, mimosa tannin was studied for mild steel corrosion in concentrated (30%) hydrochloric acid solution by Tafel polarization and Electrochemical Impedance Spectroscopy (EIS) methods. Results showed that even in such a strongly corrosive medium, this natural product exhibits good inhibitory effect. Therefore, mimosa tannin can be used as an environmentally friendly green inhibitor for acid pickling applications.

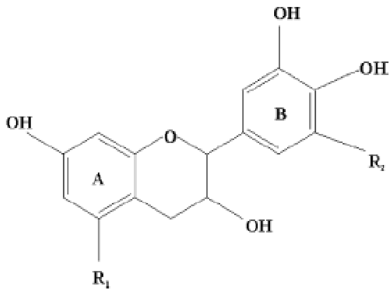

Fig. 1. Molecular structure of mimosa tannin.

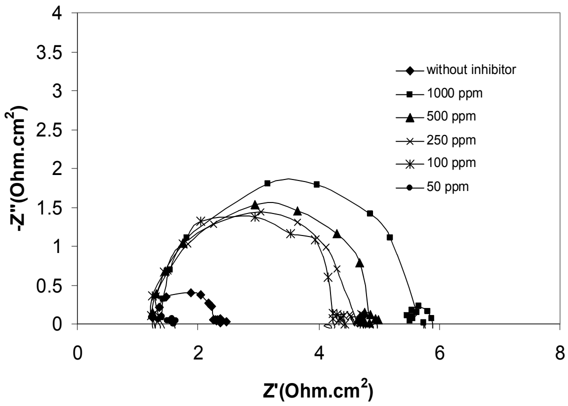

Fig. 2. Nyquist plot at various concentrations of tanni

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رسوب الکتروشیمیایی ترکیبات نیمه هادی

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چکیده

نیمه هادی ها به دلیل خواص الکتریکی و اپتیکی ویژه، از کاربرد فراوانی در صنایع اپتیک، تجهیزات فوتوولتایی، فوتوکاتالیستی، سلول های خورشیدی، حسگرها و لیزر برخوردارند. روشهای مختلفی برای تهیه مواد نیمه هادی وجود دارد که از جمله می توان به روش های رسوب بخار فیزیکی (PVD) و شیمیایی (CVD) ، سل ژل و رسوب الکتروشیمیایی اشاره نمود. علیرغم اینکه رسوب الکتروشیمیایی فلزات (به صورت تک جزئی و آلیاژی) سالیان طولانی است که شناخته شده، اما اولین گزارش استفاده از رسوب الکتروشیمیایی برای تهیه نیمه هادی مربوط به دهه ۱۹۷۰ است. با توجه به مزایای این روش، هم اکنون استفاده از این روش گسترش یافته و نیمه هادی های کالکوژنیدی (Chalcogenide) و اکسیدی با این روش تهیه می شود. در این روش طی یک واکنش الکتروشیمیایی ماده نیمه هادی بر سطح الکترود تشکیل شده و شرایط الکترولیز (پتانسیل اعمالی، غلظت یون ها و اسیدیته الکترولیت) بر مورفولوژی، ترکیب و در نتیجه خواص نیمه هادی تاثیر زیادی دارد. در این مقاله با مروری بر پژوهش های انجام شده در سالیان اخیر در زمینه تهیه مواد نیمه هادی به روش رسوب الکتروشیمیایی، چگونگی تاثیر پارامترهای این روش بر مشخصات و خواص نیمه هادی ها ارائه شده است.

واژه‌های کلیدی: *نیمه هادی ها، رسوب الکتروشیمیایی، ساختار های نانومتری*

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[۱] – استادیار

Nanostructured Magnetite/Carbon Composite as Supercapacitor Electrode

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Abstract

Electrochemical Capacitor, also know as supercapacitor, is a promising energy storage device for meeting the high-power electric market. Magnetite (Fe_3O_4) as a cheap candidate with good capacitive characteristics has attracted much attention, recently. This oxide is a newly discovered inexpensive pseudocapacitive material that exhibiting pseudocapacitance in alkali sulfites electrolytes.

In the work reported here, the combination of oxide and conductive additive was synthesized by new co-precipitation method. Iron salts ($FeCl_3$ and $FeCl_2$) were dissolved in deionized water containing carbon black. A NaOH solution was added to the solution abruptly under vigorous stirring. A black precipitate was formed immediately upon mixing. It was found that the carbon black particles sedimented simultaneously with the oxide precipitate. At the end of reaction, the precipitate was collected by filtration and washed with deionized water until the pH became neutral. The product was dried in room temperature.

The chemical composition and crystalline structure of the product were analyzed by atomic absorption and X-ray diffractometer, respectively. In order to prepare the electrode, the mixture which comprised selected composition of magnetite, carbon black mixed with binder (PTFE), and the resulting mixture was pressed on stainless steel net. The capacitive behavior of the prepared electrode from the composite was examined by electrochemical method. The electrochemical tests were carried out on electrochemical analyzer by using cyclic voltammetry, chrono potanitomery and impedance spectroscopy techniques.

The XRD pattern confirmed the magnetite structure of precipitate. The cyclic voltammetry curves showed that synthesized electrodes have significant capacitance and symmetric shape in negative potential (-1 - -0.4 V). The Results of comparing the different electrodes with different ratio of magnetite/carbon black showed that the there is an optimum ratio which the specific capacitance has the highest value. The specific capacitance of the best electrode was found to be about 250 F/g at scan rate of 2 mV/s. This value is the highest value for magnetite/cabon black composite electrode ever reported in the literatures. The chrono potentiometry curves showed that at particular ratio of magnetite/carbon black, the time of charge–discharge process is enhanced.

Keywords: *Electrochemical Capacitor, Supercapacitor, Nanostructured Magnetite, Composite*

Electrochemical impedance spectroscopy of semiconductor properties of poly-ortho-aminophenol modified graphite electrodes.

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Abstract

Poly-ortho-aminophenol(POAP) thin films on graphite working electrod were prepared by cycling the potential from -0.25 to .95V vs. Ag/AgCl in acid solution of $HClO_4$ + $NaClO_4$ containing 0.1M monomer[1]. The electrochemical properties of POAP film investigated by impedance spectroscopy in frequency range of 100 to 15mHz in different dc potential between 0.8 to 0.06V vs Ag/AgCl. The only redox process that occures in the polymer electrod without redox-couples in the solution is the doping-undoping of the polymer. Hence, the faradic reaction is localized at the metal/polymer interface[2]. The behaviour of the capacitance vs. potential and the observed capacitance values were typical of a thin film semiconductor electrode and sugegest the formation of a space charge or depletion region within the polymer film[3]. EIS measurements of the POAP modified electrodes show that the Nyquist plots are dominated by a capacitve line in low frequencies (constant phase element), we can also observe a straight line with slope slightly less than unity in the warbeurg region. The high frequency intersection with the real axis depends strongly upon the electrolyte concenteration . But, in the low frequency region, a constant capacitance value is observed for diffirent electrolyte concenteration. Moreover the low frequency capacitance increase linearity with the film thickness interface . The dependence of the electrod capacitance on the potential in the simplest case is investigated by the Mott-Schottky plot(invers squre of space charge layer capacitance, C_{sc}^{-2}, versuse semiconductor electrod potential) and calculate the flat ban potential (0.58V. vs Ag/Agcl).The negative slopes of Mott-Schottky plots of them show that we can categories them as p-type semiconductor.

Keywords: ortho-aminophenol, impedance, semiconductor

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استفاده از فرآیند الکتروفنتون در تصفیه فاضلاب‌های صنعتی

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چکیده

در سال‌های اخیر کاربرد فناوری‌های الکتروشیمیایی در زمینه آب و فاضلاب بسیار مورد توجه قرار گرفته است. علاوه بر تصفیه الکتروشیمیایی مستقیم که موجب تبدیل آندی یا کاتدی آلاینده می‌شود، تصفیه‌های غیرمستقیم نظیر تولید اکسیدکننده‌های قوی نظیر رادیکال هیدروکسیل در حال توسعه سریع است. در اثر افزایش اجزا و مقدار آلاینده‌های سمی و آلی مقاوم در مقابل تجزیه زیستی در فاضلاب، توجه به یکی از فرآیندهای اکسایش پیشرفته مثل فرآیند الکتروفنتون افزایش یافته است. فرآیند الکتروفنتون با آند متداول و کاتد پایه گرافیتی انجام می‌شود. در کاتد به علت احیای اکسیژن بطور الکتروشیمیایی، H_2O_2 تولید می‌شود. سپس افزودن Fe^{+2} به سیستم در اثر واکنش بین Fe^{+2} و H_2O_2 (واکنش کلاسیک فنتون) تولید رادیکال‌های هیدروکسیل می‌کند. در مقایسه با فرآیند فنتون متداول، فرآیند الکتروفنتون دارای مزیت کنترل بهتر فرآیند و عدم نیاز به ذخیره و نگهداری H_2O_2 است. علاوه‌براین، الکتریسیته به عنوان یک منبع انرژی پاک در این فرآیند استفاده می‌شود. لذا فرآیند کلی، آلاینده‌های ثانویه تولید نمی‌کند. مطالعات بسیاری در جهت کاربرد فرآیند الکتروفنتون در تصفیه فاضلاب تاکنون انجام شده است. بازدهی فرآیند بطور تجربی توسط محققین مختلف برای تصفیه آلاینده‌های مختلف تایید شده است. همچنین نشان داده شده است که بازدهی فرآیند با تابش نور UV یا نور مرعی طی الکترولیز بهبود می‌یابد. روش ترکیبی فرآیند الکتروفنتون و UV، فرآیند فوتو الکتروفنتون نامیده می‌شود. با تابش نور UV ، سرعت احیا Fe^{+2} بیشتر می‌شود بطوریکه اثر کاتالیستی Fe^{+2} بهبود می‌یابد. در این مقاله، مرور کاملی بر فرآیند الکتروفنتون شامل مکانیسم، جنس الکترودها و پارامترهای عملیاتی ارائه می گردد.

واژه‌های کلیدی: فرآیند الکتروفنتون، تصفیه فاضلاب، تصفیه الکتروشیمیایی، فرآیند اکسایش پیشرفته فاضلاب

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Comparison of electrochemical impedance spectroscopy and electrochemical noise measurement on corrosion of type 304 stainless steel in chloride Containing Media

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Abstract

The chloride ion is known as a aggressive species in the aqueous solution that adsorbs to the imperfect sites on the metal surface, such as defects, impurities and second – phase particles. This adsorption process could change the chemical composition and properties such as ion conductivity of the passive film.as result the passive film becomes less protectiveand breaks down at some sites where the underlying metal are exposed to the electrolyte and through anodic reactin forming a pit. In this paper the corrosion behaviour of stainless steel type 304 in different concentration oh HCl was studied using different electrochemical methode. The ENM data have been analysed in the time domain. Parameters such as the noise resistance R_n and the skewness and kurtosis of potential and current fluctuations and localization index (LI) have been determined from the analysis in the time domin. Polarization resistances R_p obtained by electrochemical impedance spectroscopy (EIS) are compared with values of the ratio of the standard deviation of the voltage and current fluctuations. A good agreement was found between corrosion data from electrochemical impedance spectroscopy(EIS) and electrochemical noise measurement (ENA).

***Key words**: Electrochemical impedance spectroscopy(EIS),Electrochemical noise measurement (ENA), Stainless steel*

Corrosion inhibition of carbon steel in sulphuric acid by some polydentate Schiff base compounds

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Abstract

The use of corrosion inhibitor is one of the most effective measures for protecting metal surfaces against corrosion in acid environments. Some organic compounds are found to be effective corrosion inhibitors for many metals and alloys.

In the present work, the efficiency of three polydentate Schiff bases as corrosion inhibitors for carbon steel in 1M sulphuric acid has been determined by electrochemical impedance spectroscopy (EIS), Tafel polarisationmeasurements. These compounds inhibit corrosion even at very low concentrations. Polarization curves indicate that all compounds are mixed inhibitors, affecting both cathodic and anodic corrosion currents. The surface adsorption of the Schiff bases has lead to a decrease in the double layer capacitance and to an increase in polarisation resistance. Adsorption of Schiff bases on the carbon steel surface is in agreement with the Langmuir adsorption isotherm model, and the calculated Gibbs free energy values confirm the chemical nature of the adsorption. Scanning electron microscopy (SEM) has been applied to identify the surface morphology of the carbon steel both in the absence and presence of the Schiff base molecules The structural and electronic properties of these inhibitors, obtained using AM1, PM3, MNDO and MINDO/3 semi-empirical self-consistence field methods, are correlated with their experimental efficiencies.

Keywords: *Corrosion inhibition, Polydentate Schiff bases, Carbon steel, Adsorption, Quantum chemical calculations*

Quantum Electrochemistry
الکتروشیمی کوانتمی

Storage of Molecular Hydrogen in Alkali Metal Atom Decorated $B_{12}C_{48}$ Nanocage: A Density Functional Theory Study

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Abstract

We study the capability of the alkali-metal (Li, Na) doped $B_{12}C_{48}$ for hydrogen storage using the density functional theory. It is found that the alkali metal atoms are strongly bound at the centers of the pentagons of the $B_{12}C_{48}$, creating $Li_nB_{12}C_{48}$ and $Na_nB_{12}C_{48}$ complexes (n=1-12). This bonding can be ascribing to the charge transfer between the alkali atoms and $B_{12}C_{48}$ structure. The charge reallocation induces an electric field principally around the positively charged Li and Na atoms, which polarizes the H_2 molecules but does not make them dissociate. It is demonstrated that the doping of alkali metal atoms in $B_{12}C_{48}$ nanocage remarkably enhances the molecular hydrogen adsorption capacity, which is higher than that for other conventionally known fullerene complexes. It has been shown that the total numbers of hydrogen molecules adsorbed over 12 Li and Na atoms are 36 and 60 with the gravimetric densities of ~8.5 and 11 wt%, respectively. Moreover, the alkali metal atoms do not cluster in the $B_{12}C_{48}$, which promote the reversible hydrogen adsorption.

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Chemisorption of Hydrogen on the Zigzag Boron-Nitride Nanotubes: A Density Functional Study

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Abstract

Nowadays, it is known that nanotubes can be use as one class of candidate materials for the effective storage of hydrogen, a green source for energy. Hence, many experimental and theoretical groups have been investigated the process of hydrogen adsorption on the nanotube medium. Hydrogen can interact with nanotube via two different mechanisms: physisorption (molecular adsorption) and chemisorption (atomic adsorption). Ma et al. found experimentally that BNNTs may be used to store hydrogen and about 70% of adsorbed hydrogen is chemisorbed. In this work, we systematically investigated the chemisorption of hydrogen on the BNNT structure using first-principles calculations within density functional theory (DFT). To this aim, different model of chemisorption process with B1-N1, B1-N2, B1-B2, and B1-N3 hydrogen positions on the surface of nanotube at 10 and 14 atom layers were considered in the calculations. The geometry parameters near the chemisorption region, binding energies, dipole moment and electronic properties, density of states, were discussed. Furthermore, the calculated bond lengths of atoms in the chemisorption region at the B3LYP/6-31G* level. The data indicate that the chemisorption of hydrogen atoms significantly changes the B-N and B-B distances of the tube in the chemisorption. Although the interaction energies for 14 layers are about 3 Kcal/mol higher than the 10 layers, but there is similar trend for various hydrogen additions in different type tube layers. Specifically, dipole moment and bond gapes varies are mostly affected in chemisorption process hydrogen attached for B1-N3 case of 10 and 14 layers tubes. Also, calculated dipole moments and bond gapes for H (B1-N2) and H (B1-B2) are comparable with H(B1-N1) and H(B1-N3).

Keywords: *Boron-nitride nanotube, chemisorption, DFT*

مطالعه انتقال پروتون بر روی اکسیژن جذب شده بر سطح پلاتین برای واکنش احیای اکسیژن در پیل سوختی پلیمری

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چکیده

واکنش احیای اکسیژن در پیل سوختی پلیمری، در کاتد و بر روی ذرات پلاتین انجام می گیرد. کارایی یک پیل سوختی پلیمری مستقیما متاثر از سنتیک واکنش احیای اکسیژن است. برای بهبود عملکرد پیل سوختی پلیمری علاوه بر افزودن کارایی کاتالیست و محیط انجام واکنش احیای اکسیژن لازم است، مراحل انجام واکنش احیای اکسیژن در حضور پروتون مورد درک قرار گیرد. در مطالعه حاضر، خوشه های $CF_3SO_3\text{-}Pt_2\text{-}O_{1 \text{ or } 2}$ به عنوان سطح مشترک نفیون و پلاتین با اکسیژن اتمی یا ملکولی جذب شده بر سطح آن با استفاده از محاسبات چگالی تابعی با روش B3lyp و استفاده از تابع پایه 6-31G** با استفاده از نرم افزار گوسین ۰۳ مورد بررسی قرار گرفت. مطالعات انجام شده بیانگر این است که حالت گذار انتقال پروتون بر روی اکسیژن ملکولی جذب شده بر پلاتین پایدارتر از حالت گذار آن بر روی اکسیژن اتمی جذب شده بر سطح پلاتین می باشد.

واژه های کلیدی: *واکنش احیای اکسیژن، پیل سوختی پلیمری، محاسبات چگالی تابعی، پروتون*

مطالعه کج فهمی های دانش آموزان دوره ی پیش دانشگاهی شهرتهران در یادگیری مفاهیم الکتروشیمی

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چکیده:

الکتروشیمی از جمله مباحثی است که در برنامه درسی شیمی دبیرستان گنجانده شده است و عمدتا در پیش دانشگاهی به آن توجه می شود. مربیان آموزش علوم توجه زیادی به فهمیده شدن مفاهیم علوم توسط دانش آموزان دارند . دانش آموزان همه سطوح و حتی معلمان علوم در دانش مفهومی دارای کج فهمی های هستند که بطور علمی نادرست می باشند به طوری که قادر نیستند به طور مناسب پدیده های علمی مشاهده شده را توضیح دهند .هدف از این تحقیق بررسی کج فهمی هایی است که دانش آموزان دوره ی پیش دانشگاهی در یادگیری الکتروشیمی از خود نشان می دهند. در این بررسی ۳۳۱ دانش آموز دوره ی پیش دانشگاهی از مناطق آموزشی مختلف شهر تهران پس از تدریس الکتروشیمی بوسیله پرسش نامه ای که دارای ۷سوال چهار گزینه ای و یک سوال تشریحی باز پاسخ است مورد آزمون قرار گرفتند. نتایج بدست آمده کج فهمی های گزارش شده توسط محققان مختلف از دیگر کشورها را تایید می کند ، همچنین موارد جدیدی از کج فهمی در این تحقیق مشخص شده است از جمله : نحوه ی تشخیص واکنش های اکسایش – کاهش و چگونگی انتخاب مبنا برای پتانسیل های کاهشی استاندارد. تحلیل کتاب درسی در هرمورد از کج فهمی ها نشان داد که جملات گمراه کننده ای در کتاب درسی وجود دارد که می تواند توسط دانش آموزان به طور نادرستی تفسیر شود یا به طور نامناسبی به موقعیت های دیگر تعمیم داده شود.

واژه های کلیدی: *آموزش شیمی ، الکتروشیمی ، کج فهمی و دانش آموزان دوره دبیرستان*

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Surface Electrochemistry
الکتروشیمی سطح

Covalent-modification of carbon surfaces using diazonium salts

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Abstract

The derivatization of a glassy carbon electrode surface was achieved with and without electrochemical reduction of various diazonium salts in acetonitrile solutions. The surfaces were characterized before and after their attachment by Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) to evidence the formation of a coating on carbon surface. The results are indicative of the presence of substituted phenyl groups on the investigated surface. Also, the effects of diazonium thin films at the surface of a glassy carbon electrode, modification time and salt concentration on their electrochemical responses in the presence of $Fe(CN)_6^{3-/4-}$ probe have been investigated.

Keywords *Cyclic voltammetry; Impedance spectroscopy; Diazonium salt; Glassy carbon; Ferricyanide*

بررسی الکتروشیمیایی رسوبدهی آلیاژهای نانوکریستالی آهن- نیکل با استفاده از آزمون‌های امپدانس الکتروشیمیایی

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چکیده

به دلیل خواص منحصر به فرد مواد نانوکریستالی، تکنیکهای مختلفی از جمله آلیاژ سازی مکانیکی، چگالش گاز خنثی، سل- ژل، پاشش حرارتی و رسوب دهی الکتروشیمیایی برای تولید آنها مورد استفاده قرار میگیرد که در این میان تکنیک رسوب دهی الکتروشیمیایی به دلیل خلوص بالای محصول ، عدم وجود تخلخل های عمده و تولید محصول در حجم انبوه و مدت زمان کم مورد توجه خاص قرار گرفته است. از جمله آلیاژهای قابل تولید به روش رسوب دهی الکتروشیمیایی آلیاژهای آهن- نیکل می باشد که کاربرد وسیعی در صنعت ساخت حافظه های مغناطیسی، وسایل ضبط و نگهداری اطلاعات، NEMS/MEMS و کاربردهای ضریب انبساط حرارتی پایین دارد. در این تحقیق از روش رسوب دهی الکتروشیمیایی برای تولید آلیاژ نانو کریستالی آهن- نیکل استفاده شد. به منظور جلوگیری از ورود ناخالصی و عناصر مضر به محصول، حمام کلریدی با کمترین افزودنی ها انتخاب شد. از آزمون‌های امپدانس الکتروشیمیایی برای بررسی مکانیزم رسوب‌دهی و همچنین تاثیر تغییر شدت جریان اعمالی بر مکانیزم رسوب‌دهی استفاده شد. بررسی ها نشان داد که با افزایش دانسیته جریان اعمالی، درصد نیکل و اندازه دانه در سوبات افزایش یافت. با توجه به بررسی امپدانس الکتروشیمیایی، علت این امر را می توان به جذب گونه‌های هیدروکسیدی آهن که در اثر افزایش pH در مجاورت سطح زیرلایه به علت آزاد شدن هیدروژن تشکیل شدند نسبت داد. این گونه‌ها نقش بازدارنده احیای نیکل و ایجاد شرایط غیر عادی در رسوب گذاری و همچنین انسداد محل‌های فعال رشد و جلوگیری از رشد دانه را ایفا می‌کنند. افزایش دانسیته جریان اعمالی سبب حذف این گونه ها از روی سطح شده و در نتیجه احیای نیکل افزایش یافته و شرایط برای رشد دانه ها فراهم میشود. اعمال جریان پالس با فرکانس بالا باعث افزایش آهن و کاهش اندازه دانه در رسوبات می‌شود. دلیل این پدیده، افزایش غلظت آهن در زمان های قطع جریان در نزدیک سطح زیر لایه و بالطبع آن افزایش گونه های هیدروکسیدی آهن است که باعث تشدید شرایط رسوب گذاری غیر عادی و جلوگیری از رشد دانه شده است.

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The use of electrochemical techniques for study of microbiologically influenced corrosion

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Abstract

Microbiologically influenced corrosion (MIC) occurs where the presence or activity microorganisms change localized conditions at or near the surface of a metal substratum. These microorganisms and their metabolic activity often cause the formation of biofilms on iron and steel and affect severely the kinetics of cathodic and anodic reactions and can also considerably modify the chemistry of any protective layers, leading to acceleration of localized corrosion. Several electrochemical techniques, recording of the corrosion potential E_{corr}, electrochemical impedance spectroscopy (EIS), electrochemical noise analysis (ENA), pitting scans and cyclic voltammetry (CV) has been used in studies of MIC. The aim of this study is to compare these electrochemical methods. It has been shown that the open-circuit potential indicate the mechanism of microorganisms in acceleration of corrosion. EIS has also been found to be very useful for monitoring of localized corrosion phenomena such as pitting. In fact it produces a second time constant in the low frequency region. EN measurements are obtained by monitoring the evolution of the corrosion process on two similar electrodes coupled through a zero resistance ammeter (ZRA). It is a unique technique that measures only the naturally occurring current or potential fluctuation without disturbing the system being tested. In addition, it is sensitive to localized corrosion processes. Localized index (LI) indicates the existence of pitting in samples. in the presence of MIC, LI values began to increase as the exponential phase of the growth curve advanced, reaching values of the localization index larger than 0.1, which indicates that the bacteria influences the process of localized corrosion. Finally, CV curve hysteresis can provide information on pitting corrosion rates. positive hysteresis occurs when passive film damage is not repaired and pits initiate. In the sterile medium, no significant changes have shown in electrochemical behavior of tested electrode. But in presence of bacteria, positive hysteresis was detected between anodic curves measured at positive scan and back scan. In addition to these procedures, we use microscopic techniques to confirm the existence of bacteria in pitted areas.

Keywords: *Microbiologically influenced corrosion, Electrochemical impedance spectroscopy, electrochemical noise analysis (ENA), cyclic voltammetry*

A novel electrocatalytic polyaniline electrode for glucose oxidation

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Abstract

In this contribution, we investigate the electro-oxidation of glucose on gold particles dispersed in Polyaniline matrixes on titanium plates (Au/PAni/Ti electrodes) and analyze the effect of their electrocatalytic characteristics in electrooxidation of glucose. The PAni films on titanium electrodes are prepared by cyclic voltammetry (CV) from -0.5 to 1.5V for 10 cycles in aqueous solution containing 0.1 M aniline and 0.1 M oxalic acid matrixes and then gold particle are electrodeposited in to the polymer matrixes by cathodic electrodeposition from an cyanide bath containing $KAu(CN)_2$ in presence of a citrate buffer. The electrooxidation of glucose on Au/PAni/Ti electrodes carried out using cyclic voltammetry in basic aqueous solutions. The morphology and surface analysis of Au/PAni/Ti electrodes is examined by Scanning electron microscopy(SEM) and EDAX respectively.

Keywords : *glucose; Polyaniline; gold particles; Electro-oxidation*

Surfactant & Interfacial Electrochemistry
ماده فعال سطحی و الکتروشیمی

A Newly Developed PVC Based Potentiometric Sensor for Anionic surfactants Based on Ion-Pair Carrier Complex

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Abstract

A new poly(vinyl chloride) PVC membrane electrode to determine monomer concentrations of dodecylsulphate ion (DS^-) based on a neutral ion-pair carrier complex of dodecyltrimethylammonium–dodecylbenzenesulphonate (DTA^+–DS^-), is reported here. The electrode exhibits a slope of 51.25 mV per decade for DS^- ion. The DS^- ion selective electrode (ISE) can determine monomer units down to concentrations as low as 5×10^{-6} M. The effect of some kinds of additives, i.e. alcohols, glycols and triblock polymers on the performance of the surfactant selective electrode is studied systematically. The effect of foreign anions along with primary ions on the performance of ion-selective electrode is investigated in terms of potentiometric selectivity coefficients, which were determined using the fixed interference method (FIM) at 1.0×10^{-3} M concentration of foreign anions. The sensor responds well to the surfactant ions in the presence of additives at lower concentration. The Gibbs free energy of micelle formation (□G_m) of sodium dodecylsulphate (SDS) in the presence of various additives is calculated and found to vary differently with respect to the increase in the amount of additives. The sensor worked in the wide pH range with a short response time of 30 s. The lifetime of the sensor is more than three months. The sensor was further used to determine the amount of DS^- in local detergents. This method of determining anionic surfactants was found to be quite accurate when compared with classical methods.

***Keywords**: Ion selective electrode; poly(vinyl chloride) PVC; sodium dodecyl sulfate.*

Ethylene Glycol effect on interfacial properties of binary mixtures of cationic and anionic surfactants

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Abstract:

In the present work, aggregation and adsorption at liquid-air interface were investigated for mixtures of cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) at different concentration of ethylene glycol by surface tension and conductivity measurements. The data based on plotting of surface tension (γ) as a function of solution composition and total surfactant concentration enabled us to determine critical aggregation concentration (CAC), minimum surface tension at CAC (γ_{CAC}), surface excess $(\Gamma_{\max})$, mean molecular surface area (A_{min}), the effectiveness of surface tension reduction (π_{CAC}). It was found that the surface activity of the surfactants and their mixture decreases slightly with increasing EG concentration. Analysis of variations of the specific conductivity of solution with changing total concentration in the anionic rich regions revealed a phase transition from vesicles to mixed micelle in different Ethylene Glycol-water compositions. On the basis of regular solution theory, the compositions of adsorbed film (Z) and aggregates (X) were estimated, and then the interaction parameters in aggregates (β) and in the adsorbed film phase (β^{σ}), were also calculated. The results showed synergistically enhanced ability to form mixed aggregates such as vesicle as well as surface tension reduction. But, the non ideality in mixed aggregates formation and mixed monolayer get more positive with increase in the amount of EG. This was attributed to the solvatation of the surfactant hydrophobic by EG. However, with further addition of EG the interaction parameter become more negative due to increase attractive electrostatic interaction between two surfactants.

Keywords: *Phase transition, anionic-rich, mixed micelle, mixed catanionic, surface tension, conductivity, monolayer, CTAB, SDS.*

The Polymer Interaction with Cationic and Anionic Surfactants in Catanionic Mixture Surfactants

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Abstract

The study of surfactant and polymer interactions in aqueous solutions has been a topic of intense fundamental and applied research. Surfactant-polymer systems are important in various industrial and technological fields such as cosmetics and pharmaceutical products, paints and coatings, adhesives, mineral processing and petroleum industries and many other applications. In present work, the thermodynamic parameters and aggregation characteristics were investigated in cetyltrimethyl ammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) and polyethyleneglycole (PEG) mixtures containing different concentrations of polymer by viscometry and conductometry measurements. Also, the effects of polymer were studied on the size and transition from vesicles to mixed micelles and viceversa. The plotting of specific conductivity(κ) as a function of solution composition and total surfactant concentration enabled us to determine two critical concentrations, one known as the CAC (critical aggregate concentration, also designated as C_1 or T_1), and the other as C_2 (also designated as T_2), characterize interaction of polymer with surfactant. Also, we previously studied this system by using surface tension measurements. We compared the obtained data from viscometry and conductometry with surface tension data.

The thermodynamic parameters of micellization (ΔG^0_{mic}, ΔH^0_{mic} and ΔS^0_{mic}) for these mixtures were also calculated.

Keywords: *CAC, Conductometry, Viscometry, PEG*

تعیین ثابت پیوند میسل های کاتیونی/ غیر یونی

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چکیده

در مطالعه حاضر، پیوند سورفکتانت کاتیونی (الکیل تری متیل آمونیم برماید) به ماکرومولکول میسل تریتون ایکس- صد (Triton X-100) با تکنیک پتانسیومتری مورد بررسی قرار گرفته است. روش وایمن برای پتانسیل پیوند جهت تعیین ثابت های پیوند ماکروسکوپی سورفکتانت های یونی به میسل غیر یونی به کار برده شد. ثابت های پیوند، ایزوترم های پیوند و انرژی آزاد پیوند محاسبه شدند.

واژه‌های کلیدی: *ثابت پیوند، الکترود انتخابگر یون گزین، میسل مخلوط، تریتون ایکس- صد، آلکیل تری متیل آمونیم- برماید.*

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Bioelectrochemistry
بیو الکتروشیمی

A DNA Biosensor Based on Peptide Nucleotide Acids Using 1,1′-Dianthrimid as a New Electroactive Indicator

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Abstract:

Peptide nucleic acid (PNA) is a DNA mimic that binds strongly and specifically to complementary DNA or RNA oligomers, but in contrast to DNA its backbone does not carry any electric charge. An electrochemical hybridization biosensor is presented based on thiols derivative PNA molecules self-assembled monolayer (SAM) on gold electrode along with introduction of 1,1′- Dianthrimid, as an electroactive label. PNA probes were attached covalently through cysteine linker. This biosensor is described for voltammetric detection of target DNA sequence related to P53 gene. The immobilized probe could selectively hybridize with the target DNA to form a hybrid on the surface despite the bases being attached to the SAM. The clear changes in the peak currents of 1,1′- Dianthrimid , an electroactive label, were observed upon hybridization of probe with the target using differential pulse voltammetry (DPV). Effective discrimination against non-complementary DNA and point mutation was also obtained.

Keywords: *Peptide nucleic acid, Self-assembled monolayer, 1,1′- Dianthrimid, DNA biosensor*

Electrocatalytic oxidation of Rifampicin in pharmaceuticals using room temperature ionic liquids (RTILs) modified glassy carbon electrode

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Abstract

Rifampicin (RIF); 3-[(4-methyl-1-piperazinyl)imino]- methyl rifamycin, is an important antibiotic drug which is widely used for the chemotherapy of tuberculosis. Rifampicin along with isoniazid, ethanbutol and pyrazinamide has been classified as a first line drug characterized as highly effective, orally administered, well tolerated and nontoxic. Different analytical techniques such as high performance liquid chromatography (HPLC), spectrophotometry uv-vis, thermospray and eletrospray mass spectrometry and gas chromatography have been used for the detection of RIF or the simultaneous detection of RIF and the other antituberculosis drugs. In addition, a variety of electrochemical techniques such as differential pulse polarography (DPP) and voltammetry at different electrode materials such as carbon paste electrode (CPE) and different modified electrodes such as DNA- modified carbon paste electrode have been used for the determination of RIF. The increased anodic peak currents shows electrocatalytic effects on the oxidation of Rifampicin on the Room temperature modified glassy carbon electrode (denoted as RTIL/GCE). Our IL/GCE was prepared by simply and rapidly attaching room temperature ionic liquids onto the glassy carbon electrode surface.

Keywords: *Room temperature ionic liquids, Rifampicin, Modified glassy carbon electrode*

Glucose Biosensor Based on DBD Plasma Functionalized Multiwalled Carbon Nanotubes

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Abstract

Carbon nanotube (CNT) is an attractive material for bioanalytical applications because of its unique physicochemical properties. Functionalization of CNT has further improved its performance in biosensors. In the present study, a new plasma treatment (PT) process using helium activation followed by ammonia treatment is used to functionalize MWCNTs for glucose biosensing. The SEM micrographs and FTIR spectra clearly demonstrated that the carbon skeleton structure of the resultant PT-CNTs was not destroyed and amine groups of different forms were successfully coupled to CNTs in the PT process. By using glucose oxidase (GOD) as a model enzyme, the direct electron transfer between the redox active center of GOD and the PT-CNT/GC electrode was investigated with cyclic voltammetry method. A pair of well-defined, quasi-reversible redox peaks of the immobilized GOD on the surface of PT-CNT electrode was observed in 0.1 M phosphate buffer solution (PH 7.4) with a cathodic peak potential of -0.4653 V and peak potential separation of 0.03 V (vs Ag/AgCl). The experimental results also demonstrated that the immobilized GOD retained its bio-electrocatalytic activity and can specifically catalyze the oxidation of glucose. This glucose biosensor has a sensitivity of 0.966 $nA.\mu M^{-1}$, a linear range from 16.64 µM to 114.1 µM, a low detection limit of 6.7 µM, and a fast response of 50 s. Furthermore, the electron transfer coefficient (α) and heterogeneous electron transfer rate constant (k_s) are 0.45 and $1.8s^{-1}$ respectively, indicating the great facility of electron transfer between GOD and PT-CNT. This remarkable performance indicates that PT-CNTs may be good candidate materials for electrochemistry studies of electroactive enzymes and the construction of the related third-generation enzyme biosensors for clinical and/or industrial applications.

Keywords: *Carbon nanotube, Functionalization, Glucose Biosensor, DBD Plasma*

اندازه‌گیری ضریب اکتیویته‌ی آمینواسید و الکترولیت در مخلوط الکترولیت آبی $(Water+NaCl+NaNO_3+Glycine)$ با استفاده از الکترود یون گزین

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چکیده

معمولا جداسازی و خالص‌سازی آمینواسیدها در حضور الکترولیت‌ها انجام می شود. بسیاری از فرآیندهای جداسازی بیومولکول‌ها، مانند رسوب‌گذاری، ته‌نشینی نمک پروتئین‌ها و استخراج میسلی آمینواسیدها و پپتیدها، به طور مستقیم به برهم‌کنش مولکول‌های آمینواسید و الکترولیت بستگی دارد. با توجه به موارد فوق در این تحقیق ضریب اکتیویته الکترولیت از طریق اندازه‌گیری‌های الکتروشیمیایی برای سیستم دو الکترولیتی $(Water+NaCl+NaNO_3+Glycine)$ در دمای ۳۰۸/۱۵K با استفاده ازالکترودهای یون‌گزین سدیم $(Na^+$ glass) و کلرید $(Cl^-$ solid-state) انجام گرفت. در سیستم فوق ضریب اکتیویته‌ی متوسط یونی NaCl در پنج مولالیته‌ی مختلف ($۰.۰۵،۰.۱،۰.۲،۰.۴،۰.۶kg.mol^{-1}$) محاسبه شد. در انتها از یک معادله‌ی چند جمله‌ای برای بیان رابطه‌ی نسبت ضریب اکتیویته‌ی متوسط یونی NaCl در مخلوط $(Water+NaCl+NaNO_3+Glycine)$ به ضریب اکتیویته‌ی متوسط یونی NaCl در مولالیته‌های یکسان در مخلوط (water+NaCl) استفاده شد سپس بکمک آن بتوان ضریب اکتیویته آمینو اسید محاسبه گردید. بیشتر کارهای قبلی بر اساس سیستم‌های تک الکترولیتی انجام شده است و در میان سیستم‌های چندالکترولیتی مخلوط $(Water+NaCl+NaNO_3+Glycine)$ برای اولین بار در این تحقیق مورد مطالعه قرار گرفته است. نتایج نشان می‌دهد با افزایش قدرت یونی محلول ضریب فعالیت آمینواسید کاهش می‌یابد. هر سری از آزمایش‌ها سه بار انجام شد که نتایج یکسان آن‌ها نشان‌دهنده‌ی صحت ازمایشات است.

واژه‌های کلیدی: *ضریب فعالیت، آمینواسید، الکترودهای یون‌گزین*

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The Selective Oxidation and Voltammetric Determination of Cysteamine at the Surface of Functionalized Carbon Nanotube Modified GC Electrode

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Abstract

In this work, the functionalized carbon nanotube (CNT) electrode was fabricated by electrodepositing of 1, 2-naphthoquinone-4-sulfonic acid sodium (Nq) on single wall carbon nanotube (SWNT) modified glassy carbon electrode (GCE). This electrode was characterized by scanning electron microscopy (SEM) and the results showed that Nq can rapidly and effectively be deposited on the surface of SWNT film with high stability. The electrochemical properties of functionalized SWNT/GCE with Nq (SWNT-Nq/GCE) were studied by cyclic voltammetry, double step potential chronoamperometry and differential pulse voltammetry methods. The results indicated that SWNT could improve the electrochemical behavior of Nq and greatly enhances its redox peak currents. The SWNT-Nq/GCE exhibited a pair of well-defined redox peaks. The experimental results also demonstrated that the deposited Nq species on SWNT could participate in Michael addition reactions with cysteamine (β-mercaptoethylamine, an aminothiol) and SWNT-Nq exhibited a high performance with decrease the overpotential by more than 710 mV. The effect of pH value, number of scans and Nq concentration was investigated. The selectivity of the reaction has been assessed with no interference from tyrosine, lysine, methionine, tryphtophan, alanin, glutathione, *D*-penicillamine and *L*-cysteine. The presented method has highly selectivity for voltammetric determination of cysteamine in the dynamic range 5.0×10^{-6} M - 2.7×10^{-4} M with a detection of limit (3σ) of 3.0×10^{-6} M.

Keywords: cysteamine, voltammetric determination, single wall carbon nanotube, Michael addition reactions, modified glassy carbon electrode

Electrocatalytic Oxidation of Methanol on Pt Electrode Modified by Nickel ions Dispersed into

Poly-6-amino-m-cresol

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Abstract

Poly-6-amino-m-cresol (poly AMC) film was prepared by using the repeated potential cycling technique in phosphate buffer (pH=3) at the surface of Pt electrode. Then transition metal ions of Ni(II) were dispersed to the polymer by immersion of the modified electrode in a 1.0 M nickel chloride solution. The electrochemical characterization of this modified electrode exhibits stable redox behavior of the Ni(III)/Ni(II) couple. Also, cyclic voltammetric experiments showed that methanol is electrooxidized at the surface of this Ni(II) dispersed polymeric modified Pt electrode [Ni/P-AMC/MPE]. The mechanism of methanol oxidation changes from diffusion control at low concentration to a catalytic reaction at higher methanol concentration. The effects of both scan rate and methanol concentration on the anodic peak height of the methanol oxidation were discussed.

Keywords: *Methanol; Electrocatalytic oxidation; Cyclic voltammetry*

Electrocatalytic Determination of L-Cysteine at Venylferrocene Modified Carbon Nanotube Paste Electrode

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Abstract

In this work, the electrochemical behavior of L-cysteine studied at the surface of venylferrocene modified multi-wall carbon nanotube paste electrode (VMMWCNTPE) in aqueous media. The results showed that VMMWCNTPE has high electrocatalytic activity for L-cysteine electrooxidation. Cyclic voltammetry (CV), double potential-step chronoamperometry and square wave voltammetry (SWV) teqniques were used to investigate the suitability of venylferrocene into VMMWCNTPE matrix as a mediator for electrocatalytic oxidation of L-cysteine in aqueous solutions with various pH. It has been found that under the optimum condition (pH 7.00) in cyclic voltammetry, the oxidation of cysteine at the surface of VMMWCNTPE occurre at a potential about 220 mV less positive that than an unmodified carbon paste electrode. Under the optimmum conditions, the electrocatalytic oxidation peak current of L-cysteine shows two linear dynamic ranges with a detection limit of 0.051 µM. The linear calibration ranges was 0.082 µM - 0.6 µM and 0.6 µM -180 µM using square wave voltammetric technique. Finally, this modified electrode was also examined as a selective, simple and precise new electrochemical sensor for the determination of L-cysteine in real samples.

Keywords: *L-Cysteine, Venylferrocene, Cyclic voltammetry, Electrocatalysis, modified multi-wall carbon nanotube paste electrode*

Electrocatalytic Oxidation of Methanol on Ni (II)–N,N-bis(Salicylidene) Phenylenediamine Modified GC Electrode

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Abstract

The electrocatalytic oxidation of methanol at the surface of glassy carbon electrode (GCE) modified with Ni(II)–N,N-*bis*(salicylidene) phenylenediamine or Ni(II)-salophen complex was presented. The prepared complex of nickel (II) with salophen was solved in ethanol, and then dropped on the surface of GCE to give electroactive films that strongly adhered on the electrode surface. This modified electrode was used for the electrocatalytic oxidation of methanol in alkaline solutions using various electrochemical techniques such as cyclic voltammetry (CV), chronoamperometry (CA) and electrochemical impedance spectroscopy (EIS). The electrooxidation of methanol was observed as large anodic peaks and early stages of the cathodic direction of potential sweep around the 20 mV vs. Ag|AgCl|KCl_{sat}. A mechanism based on the electrochemical generation of Ni (III) active sites and their subsequent consumptions by methanol was discussed. EIS studies were employed to unveil the charge transfer rate as well as the electrical characteristics of the catalytic surface. For the electrochemical oxidation of methanol at 5.0 M concentration, charge transfer resistance of nearly 0.936 kΩ was obtained, while the resistance of the electrocatalyst layer was ca.111.6 Ω.

Keywords: *Nickel-salophen complex, Electrocatalysis, Modified electrodes, Methanol, Glassy carbon*

اکسایش الکتروکاتالیستی سیستئین با ایندیگوکارمین در سطح الکترود کربن شیشه‌ای

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چکیده

سیستئین ترکیبی فعال زیستی با اهمیت فراوان است و به عنوان مرکز فعال درآنزیم های مشخص، مانند سیستئین پروتئاز ودیگر پپتید ها می باشد. از آن به عنوان محافظ تابش، پادزهر و آنتی اکسیدان استفاده می شود. همچنین درتهیه بسیاری از آنتی بیوتیک های اختصاصی، برای درمان آسیب های پوستی و به عنوان عامل محافظت کننده در برابر پرتوهای فعال استفاده می شود. بنابراین برای اندازه گیری آن، توسعه روش های ساده و سریع ضروری است. اندازه گیری سریع سیستئین با الکترود های از جنس کربن و فلز به خاطر اضافه ولتاژ بالا وآلوده کردن سطح الکترود بوسیله محصولات اکسیداسیون بسیار مشکل است. بنابراین الکترودهای اصلاح شده شیمیایی با حد واسط فعال قرار گرفته در سطح الکترود برای اکسیداسیون الکترو کاتالیزی سیستئین مورد استفاده قرار گرفته است. در این کار توانایی ایندیگو کارمین برای اکسایش کاتالیستی سیستئین در محلول بافر با استفاده از روشهای ولتامتری چرخه ای و کرنو آمپرومتری با پله پتانسیل دو گانه مورد مطالعه قرار گرفت. الکترو اکسیداسیون سیستئین تحت شرایط بهینه در سطح الکترود کربن شیشه ای در حضور اصلاح گر در پتانسیل های مثبت کوچکتر نسبت به الکترود کربن شیشه ای در غیاب اصلاح گر دیده شد. منحنی کالیبراسیون با گستره ۱۰$^{-۲}$ ۱/۵- ۱۰$^{-۴}$ ۱/۰ مولار سیستئین و ضریب همبستگی ۰/۹۸۸۹ بدست آمد. همچنین حد تشخیص اندازه گیری سیستئین در این کار ۱۰$^{-۵}$ ۴/۴ مولار می باشد.

واژه های کلیدی: *الکترو کاتالیستی، اصلاحگر، سیستئین.*

تعیین حساس سیستئین به روش ولتامتری با استفاده از الکترود خمیر کربن حاوی نانو لوله کربنی و اصلاح شده با اصلاحگر جدید ١٤(٤-هیدروکسی فنیل)-١٤-H-دی بنزو[a,j]-زانتن

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چکیده

الکترود خمیر کربنی حاوی نانو لوله کربنی که با ترکیب آلی جدید ۱۴(۴-هیدروکسی فنیل)-۱۴-H-دی بنزو[a,j]-زانتن اصلاح شده است بعنوان یک الکترود حساس برای آنالیز سیستئین به کار رفته است. این الکترود خصوصیات کاتالیزی برای اکسیداسیون سیستئین از خود نشان می‌دهد و همچنین اضافه ولتاژ اکسیداسیون این ترکیب را کاهش می‌دهد. پارامترهای مختلف مانند pH و ترکیب درصد الکترود بهینه شدند و مکانیسم اکسیداسیون سیستئین از طریق ولتامتری چرخه‌ای مورد بررسی قرار گرفته است. آنالیز با روش ولتامتری پالس تفاضلی دو محدوده خطی غلظت ۴ µM تا ۰/۰۸ mM و ۰/۲ mM تا ۰/۸ mM با حد تشخیص ۲ µM نشان می‌دهد. الکترود اصلاح شده فوق یک پاسخ بسیار پایدار الکتروشیمیایی نسبت به غلظت سیستئین از خود نشان می‌دهد و دارای طول عمری طولانی است. این الکترود برای تعیین غلظت سیستئین در نمونه های دارویی و سرم شبیه سازی شده انسانی با موفقیت مورد استفاده قرار گرفت.

واژه‌های کلیدی: *الکترود خمیر کربنی، الکترود اصلاح شده، نانو لوله کربنی، ۱۴(۴-هیدروکسی فنیل)-۱۴-H-دی بنزو [a,j]-زانتن، سیستئین*

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Nanogold-modified carbon paste electrode for the determination of atenolol in pharmaceutical formulations by differential pulse voltammetry

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Abstract

A gold nanoparticles modified carbon paste electrode (nanoAu-CPE) has been used for the determination of atenolol (ATN) in drug formulations by cyclic voltammetry, differential pulse voltammetry (DPV) and chronoamperometric methods. The electro-oxidation and detection of atenolol has been studied using EG&G. the results revealed that the modified electrode show an electrocatalytic activity toward the anodic oxidation of atenolol by a marked enhancement in the current response in buffered solution at pH of 10.0. The anodic peak potential shifts negatively of 80.0 mV when compared with that on bare CPE. The linear analytical curve was observed in the 1.96×10^{-6} to 9.09×10^{-4} $molL^{-1}$ range with correlation coefficient of 0.994. The detection limit of this simple method is 7.2×10^{-8} M which was lower than other similar work. The method was then successfully applied to the determination of atenolol in tablets. The percentage recoveries in urine ranged from 92.0% to 109.8%. The effect of pH, pulse amplitude and step potential on the voltammetric response were also studied. In brief the use of carbon paste electrode has the advantages of diversity of paste modification and the convenience in manipulation ant the method show good sensitivity and selectivity.

Keywords: *Gold nanoparticles modified CP electrode; Atenolol; Differential pulse voltammetry; Drug formulation; Urine*

Study and determination of trace amount of dopamine by cyclic and differential pulse voltammetry on the modified gold electrodes by self-assembly 1/6-hexandithiol and nano gold particles

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Abstract

In recent years, many researchers have paid a great attention to using sensors for measuring neuromediators. Modified electrodes with self-Assembled monolayer (SAM) can be used as a base for making may bio sensors and other electrochemical sensors. "Dopamine" and the other neuromediators can oxidized easily, therefore, electrochemical methods according to anodic oxidation can be applied to control their concentration. Some interferences can create problems in measuring of dopamine and the process becomes complex. In many cases the unmodified electrode surface is covered with collecting oxidation products on gold electrode (Au) decreases its sensitivity and selectivity of the method. There are different ways to remove or reduce the problem and one of them is using modified monolayer on the gold electrode surface. Au nano particles (AuNPs) have high surface area and also its catalytic effect on the oxidation of Dopamine (DA), increases the sensivity and decreases its detection limit. In this project, First, unmodified Au electrode surface was studied. The surface of Au electrode is then modified by 1,6-Hexandithiol (HDT) and electrochemical behavior of monolayer in the presence of a electron transfer reaction $[k_3Fe(CN)_6]^{4-/3-}$ was studied by cyclic and differential pulse voltammetry. The pH effect and also catalytic effect of gold nano particles on the modified electrode Au/HDT/AuNPs were also investigated. By using the Au/AuHDT/AuNPs at dynamic range of 10-100 μM, with the detection limit of 2.96×10^{-6} M for the dopamine was obtained at the pH=7.2. Parameters such as the electron transfer coefficient by tofel equation, and diffusion coefficient, D for oxidation of dopamine by chorono amperometry and chorono coulometry method's was also determined. The nano-Au electrode shows excellent sensitivity, and good selectivity. The modified electrode was successfully applied for the determination of the dopamine in the real sample.

Keywords: *Self Assembly; 1/6 hexandithiol (HDT); Dopamine. Gold electrode differential pulse voltammetry (DPV)*

PVC-basedN,N’bis[2(salcylideneamino) ethyl] ethane-1,2-dimin (L) Sensor for Ce(III) Ions

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Abstract

Apolyvinyl chloride(PVC) based membrane sensor for cerium ions was prepared by employing PVC-based- N,N’-bis[2-(salcylideneamino)ethyl]ethane-1,2-dimine(L) as an ionophore,and o-nitrophenyloctyl ether (o-NPOE) as plasticizer. The plasticized membrane sensor exhibit a Nernestian response for Ce(III) ions over a wide concentration range (1×10^{-5}-1 $\times10^{-1}$M) with a limit of detection as low as 3×10^{-6}M. It has fast response time (<12s) and can be used for 4 months.The sesor revealed a very good selectivity with respect to common alkali, alkaline earth and heavy metal ions.The response of the proposed sensor is independent of pH 4.0 to 8.0 and 3.5 to 7.5 for 1×10^{-2} M and 1×10^{-3} M Ce^{3+} ion concentrations, respectively. Functioning of the electrode was also investigated in mixed solvent media using methanol-water, acetone-water and DMSO-water mixtures. It was found that the assembly works well up to 20% nonaqueous content without showing any appreciable change in the working concentration range or slope. In acetone medium, a significant change in emf, slope, measuring range and detection limit is observed. This may be due to the dynamic complex formation and decomplexation between L and Ce (III) in the water-acetone mixture.It was used as an indicator electrode in potentiometric titration of fluoride ,and carbonate, and oxalate anions and determination of cerium in simulated mixtures. A standard deviation of ±0.9 mV was observed.The results shows that the recovery of Ce^{3+} ions is quantitative in all cases and the sensor can be used for the determination of Ce^{3+} in real samples having different analytical matrixes.

Keywords: *Cerium selective electrode; Polyvinyl chloride;Membrane electrodes; sensor*

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a-، مربی پایه۸ و b دانشیار دانشگاه ارومیه cاستادیاردانشگاه آزاد مراغه

Novel Potentiometric Membrane Sensor based on ethyl 1, 2, 3, 4-tetrahydro-6-methyl-4-phenyl-2-thioxopyrimidine-5-carboxylate for Detection of Lanthanum (III) Ions at Trace Levels

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Abstract

A PVC membrane La (III) ion-selective electrode has been constructed using ethyl 1,2,3,4-tetrahydro-6-methyl-4-phenyl-2-thioxopyrimidine-5-carboxyla-te (ETMPTC) as a neutral ionophore. This electrode responds to La (III) ion with a sensitivity of 19.9 ± 0.3 mV/decade over the range 9.3×10^{-8} to 1.0×10^{-1}M at pH 3.0-10.0. The limit of detection was 1.7×10^{-8} M. It has a response time of < 20s and can be used for at least 3 months without any divergence in potentials. The proposed electrode shows fairly good discrimination of La (III) ion from several cations. The effect of organic solvents on electrode response was examined. The results show that this electrode can be used in ethanol media until 20% (v/v) concentration without interference. The isothermal temperature coefficient of this electrode amounted to 0.00013 V/ °C. This sensor not only was used as an indicator electrode in potentiometric titration of lanthanum ion against EDTA but also was used to determination of La^{3+} concentration in the presence of certain interfering ions.

Keywords: *La^{3+}-selective electrode; PVC membrane; Potentiometry*

Strontium Ion-Selective Electrode Based on 18-crown-6 in PVC Matrix

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Abstract

A potentiometric strontium-selective electrode based on using of 18-crown-6 in PVC matrix for measurement of strontium ion is reported. The electrode was prepared by coating the surface of a graphite by a membrane containing dioctylphtalate (DOP), 18-crown-6 and carbon powder in poly(vinylchloride)(PVC) in tetrahydrofuran (THF). The membrane composition such as 18-crown-6, PVC, DOP, carbon, the thickness of coated membrane, pH, and possible interfering cations and anions were investigated and optimized electrode were found. The electrode exhibits significantly enhanced response toward strontium ions over the concentration range 1×10^{-7} to 1×10^{-2} M with slope of 27.35 mV per decade change. Fast and stable response, good reproducibility, long-term stability is demonstrated. The electrode has a response time of 20-25 second and can be used for at least 6 weeks without any considerable divergence in their potential response. The proposed electrode shows fairly good discrimination of strontium from several cations. The electrode was used for direct potentiometric measurements of strontium ions over the concentration range 1×10^{-7}- 1×10^{-2} M. The practical utility of the electrode has been demonstrated by using it successfully as an indicator electrode in the potentiometric titration of Sr^{2+} with EDTA.

Keywords: *potentiometry, ion selective electrode, 18-crown-6, Strontium*

A selective modified bentonite - porphyrin carbon paste electrode for determination of Mn (II) by using anodic stripping voltammetry.

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Abstract

A novel voltammetric sensor based on chemically modified bentonite–porphyrin carbon paste electrode has been introduced for the determination of trace amount of Mn(II) in wheat flour, wheat rice and vegetables. In this method Mn(II) gives well-defined voltammetric peak at the pH range of 3.5–7.5. For the preliminary screening purpose, the catalyst was prepared by modification of bentonite with porphyrin and characterized by thermogravimetric method (TG) and UV–vis spectroscopy. The detection limit (three times signal-to-noise) with 4 min accumulation is 1.07×10^{-7} mol L^{-1} Mn(II). The peak currents increases linearly with Mn(II) concentration over the range of 6.0×10^{-7} to 5.0×10^{-4} mol L^{-1} ($r^2 = 0.9959$). Statistical treatment of the results gave a relative standard deviation lower than 2.3 %. The chemical and instrumental parameters have been optimized and the results showed that 1000-fold excess of the additive ions had not interferences on the determination of Mn(II).

Keywords: *Modified bentonite; Porphyrin; Manganese; Modified carbon paste electrode; Voltammetry*

Highly Selective and sensitive membrane electrode for determination of Salicylate based on Complex of Ni (II)

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Abstract

The potentiometric response properties and applications of a tetra – coordinate Ni(II) complex with relatively high selectivity toward salicylate ion (sal$^-$) are described. the complex of Ni was used as a carrier into plasticized poly (vinyl chloride) (PVC) membrane. The influence of several variables was investigated in order to optimize the potentiometric response and selectivity of the electrode. the resulting membrane electrode incorporating 29.0% PVC, 63.0% dioctyl phthalate (DOP) as plasticizer, 2% methyltrioctylammonium chloride (MTOAC) as a cationic additive and 6% carrier (all w/w) demonstrated a Nernstian response slope of -59.5±1.0 mV/decade over the concentration range of 7.0 10^{-7}-1.0 10^{-1} M sal$^-$.

The electrode exhibits a fast response time (≤20s), a detection limit of 5.0 . 10^{-7}M, and can be used over a wide pH range of 6.0-9.5. It was successfully applied to the determination of salicylate ion in real samples.

Keywords: salicylate, membrane selective electrode, potentiometry, ionophore

The application of extracted humic acid from forest soil in production of the ion selective electrode to measure Calcium ion

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Abstract

Humic acid is solid and insoluble in water, acid and alcohol But is soluble in stronge basic solution. Up to now base on many researches studies in this field the cationic and chaylite producing transformation properties of It's metal ions has been demonstrated so in this regard in can be used as an ion selective electrode for measurement of the heavy metal ions an transitional ones. The humic acid was extracted from forest soil of Naharkhoran Gorgan's –Iran base on the protocol of the international society of Humic materials. Then by mixing the mentioned acid with PVC in the ratio of 1:1, the membrane of the diameter 1cm has been obtained which the Bufferic solution of Calcium (pH=6.75) at the various concentrations measured by the resulted electrode. The response of electrode is linear at the rang 10^{-1} - 10^{-6} M of Calcium ion concentration and further more is response had Nernest'slope. The another studied investigations on Ca^{2+} Bufferic solutions in Different pH's demonstrated that the pH rang from 4-6 is not influenced of the potential ranges. The Detection Limit (DL) parameter of the mentioned ion selective electrode is reported as 0.223 PPm with response time 60 seconds which could be used for 4 weeks.

Keywords: *extracted Humic acid, ion selective electrode , ion meter , Calcium ion*

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Measurement of Calcium ion with membrane electrode of humic acid in aqutic media

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Abstract

Humic acid is solid and insoluble in water, acid and alcohol But is soluble in stronge basic solution. Up to now base on many researches studies in this field the cationic and chaylite producing transformation properties of It's metal ions has been demonstrated so in this regard in can be used as an ion selective electrode for measurement of the heavy metal ions an transitional ones. The humic acid was extracted from forest soil of Naharkhoran Gorgan׳s –Iran base on the protocol of the international society of Humic materials. Then by mixing the mentioned acid with PVC in the ratio of 1:1, the membrane of the diameter 1cm has been obtained which the Bufferic solution of Calcium (pH=6.75) at the various concentrations measured by the resulted electrode. The response of electrode is linear at the rang 10^{-1} - 10^{-6} M of Calcium ion concentration and further more is response had Nernest'slope. The another studied investigations on Ca^{2+} Bufferic solutions in Different pH's demonstrated that the pH rang from 4-6 is not influenced of the potential ranges. The Detection Limit (DL) parameter of the mentioned ion selective electrode is reported as 0.223 PPm with response time 60 seconds which could be used for 4 weeks.

Keywords: *extracted Humic acid, membrane electrode , ion meter , Calcium ion*

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اندازه گیری سرب (II) با استفاده از الکترود پوشانیده یون گزین ساخته شده به روش Dip-Dry بایونوفور Benzo 18-Crown-6 در ماتریکس پلیمری

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چکیده

روش پتانسیومتری با استفاده از الکترودهای یون گزین در مقایسه با سایر روشهای تجزیه ای مانند اسپکتروسکوپی جذب اتمی، کروماتوگرافی و... دارای مزایای سهولت کاربرد، سرعت و ارزان قیمت بودن آن است. دراین کار تحقیقاتی، یک غشاء انتخابگر یون با استفاده ازبنزو-۱۸-کرون-۶ (B18C6) بعنوان مبادله کننده یون، در ماتریکس پلی وینیل کلراید(PVC) و نرم کننده دی اکتیل فتالات(DOP) تهیه شد و از این غشاء در ساخت الکترود حساس به یون Pb^{+2} استفاده گردید.

در ابتدا مقدار یونوفور بنزو– ۱۸- کرون – ۶ در ساختار غشاء بهینه سازی گردید و مشاهده شد که با افزایش مقدار یونوفور و کاهش مقدار PVC پاسخ نرنستی غشاء به یون Pb^{+2} کاهش می یابد. همچنین اثر نوع نرم کننده نیز بر روی پاسخ الکترود بررسی شد و بین دی اکتیل فتالات (DOP) و دی بوتیل فتالات (DBP) که به عنوان نرم کننده مورد استفاده قرار گرفتند، پاسخ نرنستی برای DOP مناسب تر بود. پاسخ الکترود در محدوده غلظتی M10^{-1} 1/0 تا 10^{-} ^{5}M 1/0 نرنستی می باشد.

اثر تداخلی کاتیونهای مختلف از قبیل Ag^{+} K^{+}، Na^{+}، Co^{+2}، Cd^{+2}، Mg^{+2}، Ni^{+2}، Ca^{+2}، Zn^{+2}، Fe^{+2} و Cu^{+2} بر روی پاسخ الکترود نسبت به Pb^{+2} بررسی شد و نتایج بدست آمده در اندازه گیریهای پتانسیومتری نشان می دهند، که این الکترود به کاتیونهای دوظرفیتی Fe^{+2}، Cd^{+2}، Ni^{+2}و تک ظرفیتی Ag^{+} هم پاسخ نرنستی می دهد. اثر عوامل مختلف از قبیل pH محلول، پاسخ زمان و اندازه میله های گرافیتی در پا سخ دهی الکترود بررسی شد. در نهایت الکترود در تیتراسیون پتانسیومتری تشکیل کمپلکس بین EDTA و کاتیون Pb^{+2}، با استفاده از محلول استاندارد EDTA مورد استفاده قرار گرفت. پاسخ الکترود تهیه شده در محدوده ی غلظتی $۱۰^{-۵}$ 1/0 تا $۱۰^{-۱}$ 1/0مولار شیب تقریبا ثابتی برابر ۲۸/۸ میلی ولت دارد. این الکترود در محدوده pH (3-5) پاسخی مستقل از pH دارد.

واژه های کلیدی: *پتانسیومتری ، بنزو۱۸-کرون ۶ ، الکترود یون گزین*

۱-استاد تمام –عضو هیات علمی تمام وقت دانشگاه فردوسی مشهد و عضو هیات علمی نیمه وقت دانشگاه آزاد اسلامی مشهد .

۲ – مربی – عضو هیات علمی تمام وقت دانشگاه آزاد اسلامی مشهد . ۳- کارشناس ارشد شیمی

Determination of Hydrogen Peroxide Using Poly (M-Toluidine)-Nickel Modified Carbon Paste Electrode

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Abstract:

Highly sensitive and selective determination of H_2O_2 is greatly practical importance in chemical, biological, clinical, environmental and many other fields. Many methods such as spectrophotometry, fluorimetry, fluorescence, chemiluminescence and electrochemical methods have been developed for this purpose. Electrochemical methods have been proved to be an inexpensive and effective way for hydrogen peroxide determination. However the major limitation of these techniques is the high operating potential required for detecting H_2O_2. One of the possibilities how to overcome above problems is the use of mediators. Different electron transfer mediators such as, cobalt phthalocyanine, platinum, vanadium doped zirconias, Prussian blue, nickel oxide, nickel schiff base complex and copper complex have been used for determination of hydrogen peroxide. Electrochemical polymerization offers the advantages of reproducible deposition in terms of film thickness and loading, allowing the immobilization procedure of a nickel -based electrocatalyst very simple and reliable. In the present work, the poly (M-toluidine) film was prepared by using the repeated potential cycling technique in an acidic solution at the surface of carbon paste electrode. Then transition metal ions of Ni (II) were incorporated to the polymer by immersion of the modified electrode in a 0.2 M NiS04. The electrocatalytic ability of Ni(ll)/poly (M-oluidine)/modified carbon paste electrode (Ni/PMT/MCPE) was demonstrated electrocatalytic oxidation of hydrogen peroxide with cyclic voltammetric and chronoamperometric methodes in the alkaline solution. The effects of scan rate and hydrogen peroxide concentration on the anodic peak height of hydrogen peroxide oxidation were also investigated. The catalytic oxidation peak current showed two linear ranges ($8*10^{-6}$ to $1*10^{-4}$ and $1*lO-^{4}$ to $2*10-^{2}$ M) with different slopes dependent on the hydrogen peroxide concentration and the detection limit (3σ) were $6.5*10^{-6}$ and $2.2*10-^{5}$ M respectively. The catalytic reaction rate constant, (k_h), was calculated $5.5*10^{+2}$ M^{-1} S^{-1} by the data of chronoamperometry. The modified electrode was used successfully in real sample analysis.

***Keyword's**: Electrocatalytic oxidation, hydrogen peroxide, Ni/PMT/MCPE.*

Simultaneous determination of ascorbic acid and dopamine at a bis(4'-(4-pyridyl)-2,2':6',2''-terpyridine)iron(II) thiocyanate carbon past modified electrode

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A carbon paste electrode modified with bis(4'-(4-pyridyl)-2,2':6',2''-terpyridine)iron(II) thiocyanate, $[Fe(pyterpy)_2](SCN)_2$, where pyterpy = 4'-(4-pyridyl)-2,2':6',2''-terpyridine, have been applied to the electrocatalytic oxidation of ascorbic acid which reduced the overpotential by about 200 mV with obviously increase the current response. Due to its strong electrocatalytic activity towards ascorbic acid, the modified carbon paste electrode can resolve the overlapped voltammetric waves of ascorbic acid (AA) and dopamine (DA) into two well-defined voltammetric peaks with peak-to-peak separation in potentials of about 200 mV. This property allows to selective determination of ascorbic acid in the presence of dopamine [1,2]. Relative standard deviations for AA and DA determinations were less than 3.0% and AA and DA can be determined in the ranges of $8.33\times1o^{-6} - 2.92\times10^{-3}$ and $2.00\times10^{-6} - 7.40\times10^{-4}$ M, respectively. The treatment of the voltammetric data of AA showed that it is a pure diffusion-controlled reaction, which involves one electron in the rate-determining step. The transfer coefficient (α) for the electrocatalytic oxidation of AA and diffusion coefficient of this substance under the experimental conditions were also investigated. The modified electrode shows good selectivity, stability and anti-fouling properties. The proposed method was successfully applied to the determination of AA, and DA in vitamin C and dopamine hydrochloride injections samples.

Anodic Stripping Voltammetry Determination of Silver ion at Carbon Paste Electrode Modified with Carbon Nanotube

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Abstract

Silver is a naturally occurring metal that is extensively utilized in the photographic and imaging industry and other lesser uses. It is known to be discharged to the environment from its industrial applications, and this leads to the possibility for exposure to aquatic and terrestrial organisms. The toxicity of silver ranges through several orders of magnitude depends on the silver forms. While the ionic form of silver has been shown to be toxic to a variety of aquatic organisms other forms of silver, other than ionic silver, are significantly less toxic [1]. With due attention to this instance, the need of a rapid & accurate analytical method for silver determination is essential.

Carbon nanotubes (CNTs) have specific and unique properties and are widely used in analytical science especially because of their catalytic property. CNTs are one of the most commonly used building blocks of nanotechnology. With one hundred times the tensile strength of steel, thermal conductivity better than all but the purest diamond, and electrical conductivity similar to copper, but with the ability to carry much higher currents [2].

In this work a carbon paste electrode (CPE) modified with CNT were used to sensitive determination of silver ion. The main goal of this work is to improve a simple, rapid and efficient electrochemical method for the determination of trace amount of silver ion. The linear calibration graph was obtained in the concentration range 1×10^{-8} to 1×10^{-5} mol L^{-1} and detection limit was 1.8×10^{-9} mol L^{-1}. Many coexisting ions had little or no effect on the determination of silver ion. The procedure was applied to determination of silver ion in natural waters.

***Keywords**: Anodic Stripping Voltammetry, Carbon Nanotube, CNT, Carbon Paste Electrode, Silver ion*

Electroanalytical studies on cobalt(II) selective potentiometric sensor based on 3, 3'-(dodecylazanediyl)bis(N-(2-(2-aminoethylamino)ethyl)propanamide) in poly(vinyl chloride)

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Abstract

Dendrites are unique synthetic macromolecules with highly branched structure and cascade shape. Their interior has been shown to be capable of encapsulating various molecules. They can act as hosts for guest molecules capable of binding via non-covalent interactions such as Van der Waals interaction or hydrogen bonding. Dendrites can be functionalized with various functional groups and hence allow design of several novel applications, such as directional excitation energy transfer at molecular level. We in this research design first generation dendrite for ionophore with high ability for adsorption of Co(II). A Co^{2+} ion-selective membrane sensor has been fabricated in a poly(vinyl chloride) matrix based on a recently synthesized 3,3'-(dodecylazanediyl)bis(N-(2-(2-aminoethylamino)ethyl)propanamide) as a neutral carrier, sodium tetraphenylborate (NaTPB) as an anionic excluder and dioctylphthalte (DOP) as a solvent mediator. The electrode exhibits a Nernstian response over a wide concentration range (6.58×10^{-7} to 1.0×10^{-1} M) between pH 2.5 and 8.5 and the limit of detection is 2.46×10^{-7} M. The response time of the sensor is about 5 s and it can be used over a period of 4 months without any divergence in potential. The proposed membrane sensor revealed good selectivity for Co^{2+} over a wide variety of other metal ions. The electrode has been used as an indicator electrode in potentiometric titration of Co^{2+} with EDTA and direct determination of Co^{2+} in wastewater of the electroplating industry.

Keywords: *Cobalt-selective electrode; amidoamine compound; PVC membrane; Potentiometry*

اندازه گیری ولتامتری هیدروکلروتیازید با بکارگیری الکترودخمیرکربن اصلاح شده با فروسن دی کربوکسیلیک اسید

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چکیده

در این کار، اکسیداسیون الکتروکاتالیستی هیدروکلروتیازید بوسیله الکترود خمیر کربن اصلاح شده با فروسن دی کربوکسیلیک اسید بررسی شده است. تکنیک های ولتامتری چرخه ای و کرونوآمپرومتری برای بررسی توانایی فروسن دی کربوکسیلیک اسید به عنوان یک حد واسط برای اکسیداسیون اکتروکاتالیستی هیدروکلروتیازید در محیط های آبی بکارگرفته شد. اکسیداسیون هیدروکلروتیازید در سطح الکترود اصلاح شده حدود ۳۰۰ میلی ولت در پتانسیل های کم مثبت تر نسبت به الکترود اصلاح نشده در $pH = 9.0$ رخ می دهد. ثابت سرعت واکنش بوسیله داده های کرونوآمپرومتری محاسبه و مقدار آن معادل 3.38×10^{-2} بدست آمده است. تحت شرایط بهینه، اکسایش اکتروکاتالیستی هیدروکلروتیازید حد تشخیص $0.037 \mu M$ را نشان میدهد. محدوده خطی در آن در محدوه $0.08 - 5.8 \mu M$ و $5.8 - 500 \mu M$ بوسیله تکنیک ولتامتری موج مربعی بدست آمد. در نهایت، این روش پیشنهادی به عنوان یک سنسور الکتروشیمیایی حساس و ساده و ارزان قیمت برای اندازه گیری هیدرو کلروتیازید در نمونه های حقیقی مانند دارو و ادرار بکار برده شده است.

واژه‌های کلیدی:هیدروکلروتیازید، فروسن دی کربوکسیلیک اسید سیکلیک ولتامتری، الکتروکاتالیز.

۱- *استاد دانشکده شیمی دانشگاه صنعتی اصفهان.*

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Voltammetric determination of hydrochlorothiazide using ferrocenedicarboxylic acid modified carbon paste electrode

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Abstract

The electrocatalytic oxidation of hydrochlorothiazide has been studied by ferrocenedicarboxylic acid modified carbon paste electrode. Cyclic voltammetry and chronoamperometry were used to investigate the suitability of ferrocenedicarboxylic acid as a mediator for the electrocatalytic oxidation of hydrochlorothiazide in aqueous solution. The oxidation of hydrochlorothiazide occurs at a potential about 300 mV less positive than with the unmodified carbon paste electrode at pH 9.0. The catalytic reaction rate constant, k_h, was calculated and equal 3.38×10^2 cm^3 mol^{-1} s^{-1} using chronoamperometry. Under the optimized conditions, the electrocatalytic oxidation peak current of hydrochlorothiazide showed two linear dynamic ranges with a detection limit of 0.037 µmol L^{-1} hydrochlorothiazide. The linear calibration ranges were 0.08-5.8 µmol L^{-1} and 5.8-500 µmol L^{-1} hydrochlorothiazide using square wave voltammetric method. Finally, the proposed method was also examined as a selective, simple and precise electrochemical sensor for the determination of hydrochlorothiazide in real samples such as drug and urine.

Keywords: *Hydrochlorothiazide, Ferrocenedicarboxylic acid, Cyclicvoltammetry, Electocatalysis.*

Voltammetric behavior and determination of isoniazid in pharmaceuticals using room temperature ionic liquids (RTILs) modified glassy carbon electrode

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Abstract

Isoniazid (INH); pyridine-4-carboxylic acid hydrazide, is an antituberculosis agent which is now widely used together with other antituberculostatic agents for chemotherapy of tuberculosis. The importance of this drug is its wide-spread use and efficiency in the treatment of pulmonary tuberculosis. Reported analytical techniques for the determination of INH include capillary electrophoresis with electrochemical detection, visible spectrophotometry, UV spectrophotometry, UV spectrofluorimetry, flow-injection chemiluminescence, colorimetry, potentiometry, titrimetry, oxidimetry, liquid chromatography, high-performance liquid chromatography and high-performance thin-layer chromatography. In addition, a variety of electrochemical techniques such as dc-polarography, differential-pulse polarography(DPP) and voltammetry at different electrode materials such as glassy carbon electrode (GCE), gold, hanging mercury drop electrode (HMDE), carbon paste electrode (CPE) and different chemically modified electrodes (CMEs) with multi-walled carbon nanotubes (MWNTs), overoxidized polypyrrole (OPPy) film, have been utilized and studied in the electrochemical oxidation and determination of INH. Room temperature ionic liquids glassy carbon electrode (IL/GCE) exhibited catalytic activity toward the electro-oxidation of INH which showed good selectivity and reproducibility for determination of isoniazid. Our Room temperature modified glassy carbon electrode (denoted as RTIL/GCE) showed a good electrocatalytic effect on the oxidation of RIF. RTIL/GCE was prepared by attaching ionic liquids onto the glassy carbon electrode surface.

Keywods: *Room temperature ionic liquids, Isoniazid, Modified glassy carbon electrode*

سنتزو شناسایی الکترود کربن اصلاح شده با لیگاند شیف باز (Salen) تثبیت شده بر روی مخلوط اکسیدهای فلزی SiO_2-Al_2O_3 به عنوان سنسور با حساسیت بالا برای تعیین Cu^{+2} به روش ولتامتری چرخه ای

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چکیده

در سالهای اخیر اصلاح شیمیایی الکترودهای کربن به عنوان سنسور بسیار مورد توجه قرار گرفته است. ولی از مهمترین معایب این روش حل شدن اصلاح گر در محلول آبی و خارج شدن آن ازدرون الکترود می باشد که خود باعث آلودگی محلول آبی و کاهش کارایی الکترود و تکرار نا پذیری نتایج بدست امده می شود. در این پروژه بر خلاف روشهای قدیمی که برای اصلاح الکترود کربن انجام می شد، سالیسیل آلدهید (اصلاح گر) با پیوند کووالانسی به سطح بستر مخلوط اکسیدهای فلزی SiO_2-Al_2O_3 اصلاح شده با ۳-آمینو پروپیل تری متوکسی سیلان متصل شد و سپس برای تهیه الکترود کربن از آن استفاده شد. الکترود کربن اصلاح شده با این روش معایب روشهای قدیمی تهیه الکترود کربن اصلاح شده را نداشت و نسبت به آنها حد تشخیص بسیار پایین و گزینش پذیری بسیاربالایی برای تعیین Cu^{+2} داشت.

واژه‌های کلیدی: *شیف باز، ولتامتری چرخه ای ، سنسور، SiO2-Al2O3، Cu^{+2}.*

۱- دانشجوی دکتری دانشگاه صنعتی اصفهان.

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Characterization of modified carbon paste electrode by using Salen Schiff base ligand immobilized on SiO_2-Al_2O_3 as a highly sensitive sensor for anodic stripping voltammetric determination of copper(II)

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Abstract

The wish of this work is to develop a Schiff base ligand covalently linked onto the SiO2-Al2O3 mixed-oxide as a new modifier of carbon paste electrode for highly sensitive voltammetric determination of copper(II). It is also an easy and inexpensive way for determination of copper(II). For the preliminary screening purpose, the Schiff base ligand was prepared by modification of SiO2–Al2O3 mixed-oxide and characterized by TG, CHN elemental analysis and FTIR spectroscopy. Linear response to copper (II) was found in the 3.4×10−10 to 3.3×10−7 mol L−1 (r2 = 0.9994) concentration range, with a detection limit estimated at 1.8×10-10 mol L−1 (3Sb/m). The multiple determinations (n = 3) of copper (II) in the concentration of 5.0×10−4, 1.8×10-5, 2.0×10−7, 1.0×10−8 mol L−1, following a preconcentration detection–regeneration cycle, displayed a relative standard deviation of lower than 1.07%. The developed sensor could also be used to determine the copper(II) in tap water and real samples. The copper content of the samples were comparable with the results obtained through AAS method.

Keyword: *Shiff-base, Voltammetry, SiO2–Al2O3 mixed-oxide, Salen Schiff base ligand, copper (II).*

Modified multi-wall carbon nanotube past electrodeby new compound [1,1(1,2-ethanediyl bis(nitrilo methylidyne)- bis- 2-naphtol)] for study and determination of acetaminophen in real sample

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Abstract

Drug analysis plays important roles in drug quality control, and has great impacts on public health. there for, a simple, sensitive and accurate method for the determination of active ingredient are very important. acetaminophen or paracetamol (ACOP) is an effective and safe analgesic agent used worldwide for the relief of mild to moderate pain associated with headache, backache, arthritis and postoperative pain. in recent years, intensive investigations have been carried out on chemically modified electrodes (CMEs), due to their fast, selective, reproducible, sensitive, response and low cost for a chemical analysis . the electro oxidation of acetaminophen has been studied by modified carbon nanotube past electrode by 1,1 – [1,2–ethanediyl bis (nitrilo methylidyne)- bis-2-naphtol]. in Briton-Rabinson (B-R) buffer solution using cyclic voltammetry, chronoclumetry, chronoamperometry and differential pulse voltammetry for study and determination of acetaminophen. a three electrode assembly was employed to the experiment in a 50 ml glass cell containing an Ag\Agcl electrode as reference electrode. a platinum wire counter electrode and the working electrode was a modified carbon paste electrode (MCNPE). Cyclic voltammetry was used to investigate the redox properties of this modified electrode at various scan rates. The obtained catalytic peak current, was linearly dependent on the acetaminophen concentrations in the range of 0.74×10^{-4} to 8×10^{-7} M and the detection limit for ACOP was 4×10^{-8} in DPV. the diffusion coefficient (D) , and the kinetic parameters such as electron transfer coefficient (α) and heterogeneous rate constant (K) were also determined using electrochemical approaches. the modified electrode showed good sensitivity, selectivity, and was employed for the determination of acetaminophen in the real samples .

Keywords: *Nanotube; Shiff base; Acetaminophen; Differential pulse voltammetry; Drug formulation; Urine*

Electrooxidation of catechol in the Presence of Ethyl benzoylacetate and its Digital Simulation

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Abstract

In this work, electrooxidation of catechol has been studied in the presence of ethyl benzoylacetate as a carbon nucleophile in acetonitrile-water mixed solvent using cyclic voltammetry, square wave voltammetry and controlled potential coulometry**.** Cyclic voltammetry of catechol in the buffered solution showed one anodic and corresponding cathodic peak which corresponds to the transformstion to corresponding *o*-quinone and vice versa within a quasi-reversible two electron process. But, cyclic voltammogram of catechol in the presence of ethyl benzoylacetate showed one anodic peak in anodic scan of potential, whereas in the reverse scan the cathodic peak disappeard. Effect of potential scan rate on the electrochemical behavior of catechol in the presence of ethyl benzoylacetate showed that the electrodic process is diffusion controlled. Also, with increasing the nucleophile concentration, the ratio of cathodic peak current to anodic peak curent increased. Controlled potential coulometry technique indicated that in the electrochemcial oxidation of catechol in the presence of ethyl benzoylacetate 2 mole electrons per 1 mole catechol transferred. Also, an Scheme for electrooxidation of catechol was proposed and tested by digital simulation. Based on EC mechanism, the homogeneous rate constant of 1,4- Michael addition reaction has been estimated.

Keywords: *Electrooxidation, Digital simulation, Catechol.*

الکترود خمیر کربن اصلاح شده با مشتقات کینونی جدید برای اندازه‌گیری ولتامتری دوپامین

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چکیده

در کار تحقیقاتی حاضر، از یک الکترود خمیر کربن اصلاح شده با ماده ۲و′۲-[۳و۶ دی اکسا- ۱و۸- اکتاندیل بیس(نیتریلو اتیلیدین)]- بیس- هیدروکینون برای بررسی اکسایش الکتروکاتالیتیکی دوپامین استفاده شده است. اندازه‌گیری دوپامین در محلول آبی با استفاده از روشهای ولتامتری چرخه‌ای، ولتامتری موج مربعی و کرونوآمپرومتری انجام گرفت و پارامترهایی نظیر ضریب نفوذ و ضریب انتقال الکترون مربوط به اکسایش دوپامین در سطح الکترود اصلاح‌شده تعیین شد. در شرایط بهینه و در سطح الکترود مذکور، اکسایش دوپامین در پتانسیل حدود ۲۹۰ میلی‌ولت کمتر مثبت نسبت به الکترود اصلاح‌نشده صورت می گیرد. اندازه‌گیری کمّی دوپامین با روش ولتامتری موج مربعی انجام گرفت و حد تشخیص در حد ۰/۸۲ میکرومولار بدست آمد. همچنین از این روش بهمراه روش افزایش استاندارد برای تعیین دوپامین در فراورده‌های دارویی استفاده شد.

واژه‌های کلیدی: *دوپامین، الکترود اصلاح‌شده، اکسایش الکتروکاتالیتیکی، ولتامتری*

A novel hydroquinone derivative modified carbon paste electrode for voltammetric determination of Dopamine

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Abstract

A chemically modified carbon paste electrode with 2, 2'-[3, 6-dioxa-1, 8-octanediylbis (nitriloethylidyne)]-bis-hydroquinone was employed to study the electrocatalytic oxidation of dopamine in buffer solution using cyclic voltammetry, square wave voltammetry and chronoamperometry. The diffusion coefficient ($D=7.4\times10^{-6}$ cm^2 s^{-1}), and the kinetic parameter such as the electron transfer coefficient, ($\alpha=0.33$) of dopamine oxidation at the surface of 2, 2'-[3, 6-dioxa-1, 8-octanediylbis(nitriloethylidyne)]-bis-hydroquinone was determined using electrochemical approaches. It has been found that under an optimum condition (pH= 7.0), the oxidation of dopamine at the surface modified electrode occurs at a potential about 290 mV less positive than that of an unmodified carbon paste electrode. The catalytic oxidation peak currents show a linear dependence on the dopamine concentrations and linear analytical curves were obtained in the ranges of 3.0×10^{-5}M–2×10^{-3} M of dopamine with square wave voltammetry. The detection limit (2σ) was determined to be 8.2×10^{-7} M with square wave voltammetry. This method was also used for the determination of dopamine in the pharmaceutical preparation (Dopamine injection) by standard addition method.

Keywords: *Dopamine, Modified electrode, Electrocatalytic oxidation, Voltammetry.*

اثر یون لیتیم بر رفتار ولتامتری چرخه ای نانوذرات دیوکسید سرب

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چکیده

در طول دهه گذشته، تحقیقات گسترده ای در زمینه سنتز و کاربرد دیوکسید سرب و نانوساختارهای آن که یون لیتیم در درون ساختار بلوری آنها وارد شده است، انجام شده است. ورود لیتیم به شبکه بلوری دیوکسید سرب می تواند باعث ایجاد نقص در شبکه و تشکیل ترکیبات اسپینلی شود. لیتیم وارد شده در ساختار بلوی دیوکسید سرب می تواند به عنوان ماده فعال در باتری های لیتیمی به کار گرفته شود ولی تاکنون گزارشی در زمینه اثر حضور یون لیتیم در محلول سنتز شیمیایی و یا الکتروشیمیایی دیوکسید سرب بر رفتار ولتامتری چرخه ای آن ارائه نشده است. در این کار، نانوذرات دیوکسید سرب به روش ولتامتری چرخه ای از طریق اکسایش مستقیم الکترود سرب در محلول اسید سولفوریک سنتز شد. مورفولوژی و اندازه ذرات نانوذرات حاصل به کمک دستگاه میکروسکوپ الکترونی روبشی (SEM) بررسی شد. رفتار ولتامتری چرخه ای الکترود حاصل در غلظت های مختلف یون لیتیم مورد بررسی قرار گرفت. نتایج حاصل از آزمایشات نشان داد که پارامترهای شاخص پیک های اکسایش و کاهش در ولتاموگرام های چرخه ای دیوکسید سرب (I_p^a، I_p^c، E_p^a و E_p^C) می توانند به شدت تحت تأثیر یون لیتیم قرار گیرند. نتایج نشان داد که غلظت های کم یون لیتیم از طریق ورود به ساختار بلوی دیوکسید سرب، انجام نیم واکنش های کاهش و اکسایش را برای دیوکسید سرب سخت و کند می نمایند. این اثر منفی در غلظت های کمتر از ۰/۲ M به وضوح مشاهده می شود. با افزایش غلظت یون لیتیم، علاوه بر عامل ورود یون لیتیم به شبکه بلوری که منجر به نقص شبکه می شود، حضور یون لیتیم در الکترولیت باعث افزایش شدید هدایت الکتریکی محلول شده و در نتیجه اثر مثب بر پارامترهای ذکر شده خواهد داشت به گونه ای که در غلظت ۱ M از یون لیتیم، اثر افزایش هدایت محلول بر اثر نقص شبکه غالب شده و منجر به کاهش پتانسیل پیک های اکسایش و کاهش و نیز افزایش قابل توجه در ارتفاع پیک های ردوکس دیوکسید سرب می شود.

واژه های کلیدی: *یون لیتیم، نانوذرات دیوکسید سرب، ولتامتری چرخه ای*

Voltammetric determination of dopamine and uric acid using α-cyclodextrine-multi walled carbon nanotube modified carbon paste electrode

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Abstract

In 0.2 M Britton-Rabinson buffer solution (pH 6.0) ,the carbon paste electrode modified with α-cyclodextrine incorporated multi walled carbon nanotube (> 95%) exhibits a strong catalytic effect toward the electro-chemical oxidation of dopamine (DA)and uric acid (UA) .the peak current increases linearly with the concentration of DA in the two range of 5×10^{-7} - 1.4×10^{-5} And 2.2×10^{-5} - 1.6×10^{-4} and for UA in the range of 7×10^{-7} -2.2×10^{-5} . the detection limit for DA is 1.7×10^{-7} ML-1 and for uric acid is 4.7×10^{-6}.using square wave voltametry(SWV) for simultaneous measurement ,we obtained two peaks for DA and UA in the same solution which the separation between the two peaks is about 170 Mv . the recovery for Dopamine injection obtained 97%.

Keyword: *Cyclodextrine;Dopamine;Uric acid; Square wave voltammetryα–*

Prepation of New Amperometric Sensor for Lactic Acid Using Chitosan and Glutaraldehyde Dopped with Nile Blue

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Abstract

Lactic acid is mainly composed of the l-form in mammals, which is produced from pyruvic acid under anaerobic conditions it may also be produced by bacterial fermentation in the gastrointestinal tract. D-Lactic acid, found in human physiologic fluids, generally is produced from the metabolism of carbohydrate by the action of D-lactate dehydrogenase in presence of intestinal bacteria. The increase of concentration of blood lactate is a sensitive indicator of human medical disorders such as acidosis. Otherwise, in foodstuffs lactic acid is also produced by bacterial fermentation [1]. Its quantitative determination is of great relevance for monitoring metabolic states and possible disorders as well as fermentation processes. Different techniques have been employed for determination of lactic acid such as immobilization enzyme fluorescence capillary analysis (IE-FCA) [2], high-performance immunoaffinity [3], biosensor [4] capillary electrophoresis [5] and etc. This paper describes a novel electrochemical sensor which is very sensitive and could be a useful tool in determination of lactic acid in different samples. This sensor has been used as an amperometric sensor for the detection of lactic acid. The sensor was developed by dropping chitosan and glutaraldehyde solutions doped with Nile Blue onto the surface of an anodized glassy carbon electrode. After drying the prepared sensor in room temperature for 24 h the electrode used for amperometric determination of lactic acid. The electrochemical characterization of this sensor using different electrochemical techniques exhibits stable redox behavior. Electrochemical behavior of sensor studied using cyclic voltammetric, chronoamperometric and hydrodynamic amperometric techniques. The experimental results showed that lactic acid was electrooxidized on sensor. The sensor has shown stable response in long time. The relative standard deviation for lactic acid (3 repetitions using the same electrode) is 0.109 and detection limit was determined as 13.8 μM.

***Keywords**: Lactic acid, Chitosan, Glutaraldehyde, Nile Blue*

Electrodeposition of polypyrrole–modified multiwalled carbon nanotube composite film on glassy carbon electrode and its application for determination of some species

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Abstract

In this paper, the films of overoxidized polypyrrole (PPyox) directed modified multi-walled carbon nanotubes (MWNTs) have been electrochemically coated onto glassy carbon electrode (GCE). Electroactive monomer pyrrole was added into the solution containing surfactant and MWNTs. Then, electropolymerization was proceeded at the surface of GCE, and a novel kind of conducting polymer/carbon nanotubes (CNTs)composite film with the orientation of CNTs were obtained correspondingly. Finally, this obtained polypyrrole (PPy)/MMWNTs film modified GCE was oxidized at a potential of +1.8 V. It can be found that this proposed PPyox/MMWNTs composite film modified GCE exhibited excellent electrocatalytic properties for some species and could be used as a new sensor for practical applications. Compared with previous CNTs modified electrodes, MWNTs were oriented towards the outside of modified layer by PPyox and surfactant, which made the film easily conductive. Moreover, this proposed film modified electrode was more stable, selective and applicable.

Keywords: *Overoxidized polypyrrole; Modified Carbon nanotubes; Electrocatalytic oxidation*

Preparation of Iodide-selective polymeric membrane electrode

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Abstract

A PVC membrane electrode based on bis(N-2-bromophenylsalicyldenaminato)copper(II) as ionophor was prepared. The electrode tested by inorganic anions and showed a good selectivity for iodede ion.This sensor showed Nerstian behaviour with a slope of a -57.8 mV per decade at 20°C. The proposed electrode exhibited a wide linear range from 4×10^{-5} to 1×10^{-1}M with a detection limit of 5×10^{-6}M. The electrode response was independent of pH in the range of 3.0 to 10.0 . The response time is about 10-20 s and be used for at 2 months without considerable deterioration. The proposed sensor was applied as an indicator electrode in potentiometric titration of I^- with Ag^+ ion, and to determine the iodide in samples of water and a sample of mouthwash.

Keywords: *Iodide-selective electrode, polymeric membrane, potentimetry*

Using of MWCNTs modified glassy carbon electrode for adsorptive stripping voltammetric determination of ultratrace levels of RDX explosive

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Abstract

Glassy carbon electrodes modified with multi-wall carbon nanotubes (MWCNTs) show extremely useful for highly sensitive adsorptive stripping voltammetric measurements of the RDX high explosive down to the sub-□g/l level. Operational parameters have been optimized and the stripping voltammetric performance has been studied using cyclic voltammetry and electrochemical impedance spectroscopy. The adsorptive stripping response shows wide linear dynamic range, with a detection limit of 0.2 nM and good precision of of <4% (RSD, n=8). This modified electrode can be properly used for determination of RDX in the environmental samples with satisfactory results.

Keywords : Multiwalled carbon nanotube, RDX, Explosive, Adsorptive stripping voltammetry.

بیوسنسور دوپامین براساس پلی آنیلین دوپه شده با نانولوله های کربن (MWCNT) چنددیواره

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چکیده

پلی آنیلین (PANi) ، بعنوان یکی از مهمترین پلیمر های هادی در سالهای اخیر بشدت مورد مطالعه قرار گرفته است. از کاربرد های بسیار مهم آن می توان در زیست حسگرها ، مواد الکتروکرومیک ، ابزارهای فوتوولتایی ، باتری های قابل شارژ و غیره اشاره نمود. عموماً روش های الکتروپلیمریزاسیون و پلیمریزاسیون شیمیایی برای تهیه فیلم های PANi استفاده می شود. در این کار تحقیقاتی PANi دوپه شده با نانولوله های کربن چند دیواره (MWCNT) بروش اکسیداسیون شیمیایی با استفاده از HCl بعنوان دوپه کننده ،تهیه شد. ساختار لایه تهیه شده با استفاده از میکروسکوپ الکترونی پویشی (SEM) مطالعه شد نتایج نشان دادکه نانو ترکیب PANi – MWNT بعنوان زیست حسگرقابل استفاده بوده و با مطالعات FTIR مشخص شدکه نانوذرات PANi حاوی گروههای عاملی کربوکسیلیک اسید در انتها و روی دیواره جانبی MWCNT تشکیل شده اند. زیست حسگر PANi – MWNT برای تعیین رفتار دوپامین بعنوان ترکیب الکتروفعال و داروی هورمونی اعصاب استفاده شد. تاثیر سرعت روبش های مختلف بر روی رفتار زیست حسگر مطالعه شد و ضریب انتقال (α) و ثابت سرعت انتقال بار (Ks) محاسبه شد. سینیتیک واکنش کاتالیزوری با استفاده از تکنیک کرونوآمپرومتری مطالعه شد. میانگین مقدار ضریب انتشار(D) و ثابت سرعت واکنش شیمیایی (K) برای دوپامین با استفاده از تکنیک کرونوآمپرومتری ارزیابی شد.

واژه‌های کلیدی: *زیست حسگر، پلی آنیلین، دوپامین، FTIR, SEM*

Determination of vitamin C at a new derivative of hydroquinone-TiO_2 nanoparticles modified carbon paste electrode

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Abstract

Ascorbic acid (AA) or vitamin C is present in many biological systems and in multivitamin preparations, which are commonly used to supplement inadequate dietary intake. AA has been used for prevention and treatment of common colds, mental illness, cancer and in some clinical manifestations of HIV infections. In addition, it is widely used in foods as an antioxidant for the stabilization of color and aroma, with subsequent extension of the storage time of the products. Therefore it is essential to develop simple and rapid methods for its determination in routine analysis.

Titanium dioxide (TiO_2) is a versatile material with a wide range of uses, from pigments to photocatalysts and dimensionally stable electrode applications. Recently, there has been considerable interest in using TiO_2 nanoparticles as film-forming materials because they have high surface area, optical transparency, desirable biocompatibility, and relatively good conductivity. Various TiO_2 films have also been used to immobilize proteins or enzymes on electrode surfaces, for mechanistic studies of proteins or fabrication of electrochemical biosensors.

In this paper, the preparation and suitability of a new derivative of hydroquinone-TiO_2 nanoparticles modified carbon paste electrode was described as an electrocatalyst in the electrocatalysis and determination of ascorbic acid in an aqueous buffer solution. Cyclic voltammetry (CV), differential pulse voltammetry (DPV) and chronoamperometry (CHA) was used and some parameters such as the diffusion coefficient of AA (D), electron transfer coefficient (α) and heterogeneous rate constant (k_h) were determined.

Keywords: *Vitamin C, TiO_2 nanoparticle, Modified carbon paste electrode, lectrocatalysis*

اندازه گیری روی در نمونه های غذایی و دارویی با روش ولتامتری عاری سازی جذبی

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چکیده

روی در گذشته از نظر سمیت و همچنین اثر آن بر روی سلامتی بشر مورد آزمایش قرار گرفته است. در حالیکه مقادیر کم روی برای فرایند های فیزیولوژیکی بدن ضروری است، مقادیر اضافی آن برای سلامتی بشر تهدیدی جدی محسوب می شود. بیشترین مقدار مجازمصرف روزانه روی یک میلی گرم بر کیلوگرم وزن بدن می باشد. بنابراین اندازه گیری و کنترل روی در نمونه های غذایی و دارویی امری مهم به شمار میرود. در این طرح از روش ولتامتری عاری سازی کاتدی جذبی با استفاده از الکترود قطره جیوه برای اندازه گیری فلز روی در نمونه های غذایی و دارویی استفاده شد. این روش بر پایه جذب فلز روی در سطح الکترود قطره جیوه با استفاده از معرف کاپفرون بعنوان معرف تشکیل دهنده کمپلکس می باشد. ولتاموگرامهای عاری سازی پالسی تفاضلی در نواحی با پتانسیل منفی ثبت شدند. نتایج بدست آمده نشان داد که رابطه بین جریان پیک در برابر غلظت بین ۰/۱۵ –۳۲۰ نانوگرم بر میلی لیتر خطی بود. حد تشخیص روش ۰/۰۵۹ بود.انحراف استاندارد نسبی در غلظت ۵۰ نانوگرم بر میلی لیتر ٪۱/۸ بود. در ادامه برای بدست آوردن غلظت روی در نمونه های حقیقی از روش افزایش استاندارد استفاده شد.

واژه های کلیدی: *ولتامتری عاری سازی کاتدی جذبی، فلز روی، نمونه های غذایی و دارویی*

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Determination of ultratrace amount of enrofloxacin by adsorptive cathodic stripping voltammetry using copper(II) as an intermediate

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Abstract

In this work, a simple and sensitive electroanalytical method was developed for the determination of enrofloxacin (ENRO) by adsorptive cathodic stripping voltammetry (ADSV) using Cu(II) as a suitable probe. The complex of copper (II) with ENRO was accumulated at the surface of a hanging mercury drop electrode at −0.10V for 40 s. Then, the preconcentrated complex was reduced and the peak current was measured using square wave voltammetry (SWV). The optimization of experimental variables was conducted by experimental design and support vector machine (SVM) modeling. The model was used to find optimized values for the factors such as pH, Cu(II) concentration and accumulation potential. Under the optimized conditions, the peak current at −0.30V is proportional to the concentration of ENRO over the range of 10.0–80.0 nmol L^{-1} with a detection limit of 0.33 nmol L^{-1}. The influence of potential interfering substances on the determination of ENRO was examined. The method was successfully applied to determination of ENRO in plasma and pharmaceutical samples.

Keywords: *Enrofloxacin, Support vector machine, Copper(II), Adsorptive cathodic voltammetry*

تعیین ولتامتری جذبی عاری سازی مقادیر بسیار ناچیز انرو فلوکساسین بااستفاده از مس(II)به عنوان حدواسط

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چکیده

یک روش ولتامتری کاتدی جذبی عاری سازی حساس و گزینش پذیر برای تعیین مقادیر بسیار ناچیز انرو فلوکساسین بر سطح الکترود جیوه قطره آویزان با استفاده از مس(II) ارائه و توسعه داده شده است.کمپلکس مس(II) با این دارو در پتانسیل ۰/۱- ولت به مدت ۴۰ ثانیه بر سطح الکترود قطره جیوه آویزان تغلیظ شد. سپس پیک ناشی از کاهش کمپلکس تغلیظ شده با تکنیک ولتامتری موج مربعی تعیین شد. پارامترهای موثر برآزمایش از قبیل غلظت مس(II) ، pH . پتانسیل جایگری با استفاده از بردارهای نگه دارنده ماشین بهینه شد.تحت شرایط بهینه، پیک احیای این کمپلکس در ۰/۳- متناسب با غلظت انرو فلوکساسین در محدوده ۰/۸۰- ۱۰/۰ نانومولاراست از طرفی حد تشخیص روش ۰/۳۳ نانومولار بدست آمد. روش پیشنهاد شده برای تعیین انرو فلوکساسین در سرم خون و داروها با نتایج رضایت بخش بکار گرفته شده است.

واژه‌های کلیدی: *ولتامتری کاتدی جذبی عاری سازی ، انرو فلوکساسین، الکترود جیوه قطره آویزان، بردارهای نگه دارنده ماشین.*

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Electrocatalytic determination of isoprenaline on a MWCNTs-CoHCF nanocomposite electrode

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Abstract

The electroanalytical determination of isoprenaline on a multiwalled carbon nanotubes (MWCNTs)-Cobalt hexacyanoferrate (CoHCF) nanoparticles paste electrode was studied by cyclic voltammetry and electrochemical impedance spectroscopy (EIS). CoHCF nanoparticles were chemically deposited on the MWCNTs and the resulted nanocomposite was characterized by FT-IR, scanning electron microscopy (SEM), atomic absorption spectroscopy, and electrochemical methods. This new electrode exhibits greatly improved stability and enhanced electrocatalytic activity toward the oxidation of isoprenaline owing to the synergetic effects between CoHCF and MWCNT nanoparticles. Under the optimized condition, this electrochemical sensor shows very good detection limit of 0.2 μM with a precision of lower than 3% (RSD, n=8). The proposed procedure was successfully applied for the determination of isoprenaline in the pharmaceutical and biological samples.

Keywords : *Multiwalled carbon nanotube, Cobalt hexacyanoferrate nanoparticles, Isoprenaline.*

اندازه گیری روی در نمونه های غذایی و دارویی با روش ولتامتری عاری سازی جذبی

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چکیده

روی در گذشته از نظر سمیت و همچنین اثر آن بر روی سلامتی بشر مورد آزمایش قرار گرفته است. در حالیکه مقادیر کم روی برای فرایند های فیزیولوزیکی بدن ضروری است، مقادیر اضافی آن برای سلامتی بشر تهدیدی جدی محسوب می شود. بیشترین مقدار مجازمصرف روزانه روی یک میلی گرم بر کیلوگرم وزن بدن می باشد. بنابراین اندازه گیری و کنترل روی در نمونه های غذایی و دارویی امری مهم به شمار میرود. در این طرح از روش ولتامتری عاری سازی کاتدی جذبی با استفاده از الکترود قطره جیوه برای اندازه گیری فلز روی در نمونه های غذایی و دارویی استفاده شد. این روش بر پایه جذب فلز روی در سطح الکترود قطره جیوه با استفاده از معرف کاپفرون بعنوان معرف تشکیل دهنده کمپلکس می باشد. ولتاموگرامهای عاری سازی پالسی تفاضلی در نواحی با پتانسیل منفی ثبت شدند. نتایج بدست آمده نشان داد که رابطه بین جریان پیک در برابر غلظت بین ۰/۱۵ -۳۲۰ نانوگرم بر میلی لیتر خطی بود. حد تشخیص روش ۰/۰۵۹ بود.انحراف استاندارد نسبی در غلظت ۵۰ نانوگرم بر میلی لیتر ٪۱/۸ بود. در ادامه برای بدست آوردن غلظت روی در نمونه های حقیقی از روش افزایش استاندارد استفاده شد.

واژه های کلیدی: *ولتامتری عاری سازی کاتدی جذبی، فلز روی، نمونه های غذایی و دارویی*

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Electrocatalytic oxidation and simultaneous determination of uric acid and ascorbic acid at glassy carbon electrode modified with iron(III) complex adsorbed on multi-walled carbon nanotubes

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Abstract

This article reports the highly selective and sensitive uric acid quantification in the presence of ascorbic acid using glassy carbon electrodes (GCEs) modified with iron (III) 5-Br PADAP complex adsorbed on multi-walled carbon nanotubes. The electrocatalytic activity of modified MWCNT deposited on GCEs has allowed an important decrease in the overvoltages for ascorbic acid oxidation (440 mV), making possible the clear definition of the oxidation processes of ascorbic acid and uric acid. The differential pulse voltammetry was applied for determination ascorbic acid and uric acid. For uric acid, A linear response range from 5μmol L^{-1} to 5 mmolL^{-1} was obtained. The sensitivities were, $(9.8\pm0.2)\times10^4$ μAM^{-1} (r = 0.994) and $(10.7\pm0.2)\times10^4$ μAM^{-1} (r = 0.994) in the presence and absence of 1.0 mM ascorbic acid, respectively. The sensor was successfully used for the quantification of uric acid in serum samples.

Keywords: *Carbon nanotubes; Uric acid; Ascorbic acid; Electrocatalytic oxidation*

Determination of Hydrogen Peroxide Using Poly (M-Toluidine)-Nickel Modified Carbon Paste lectrode

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Abstract:

Highly sensitive and selective determination of H_20_2 is greatly practical importance in chemical, biological, clinical, environmental and many other fields. Many methods such as spectrophotometry, fluorimetry, fluorescence, chemiluminescence and electrochemical methods have been developed for this purpose. Electrochemical methods have been proved to be an inexpensive and effective way for hydrogen peroxide determination. However, the major limitation of these techniues is the high operating potential reuired for detecting H_20_2. One of the possibilities how to overcome above problems is the use of mediators. Different electron transfer mediators such as, cobalt phthalocyanine, platinum, vanadium doped zirconias, Prussian blue, nickel oxide, nickel schiff base complex and copper complex have been used for determination of hydrogen peroxide. Electrochemical polymerization offers the advantages of reproducible deposition in terms of film thickness and loading, allowing the immobilization procedure of a nickel -based electrocatalyst very simple and reliable. In the present work, the poly (M-toluidine) film was prepared by using the repeated potential cycling techniue in an acidic solution at the surface of carbon paste electrode. Then transition metal ions of Ni (II) were incorporated to the polymer by immersion of the modified electrode in a 0.2 M $NiS0_4$. The electrocatalytic ability of Ni(ll)/poly (M-oluidine)/modified carbon paste electrode (Ni/PMT/MCPE) was demonstrated electrocatalytic oxidation of hydrogen peroxide with cyclic voltammetric and chronoamperometric methodes in the alkaline solution. The effects of scan rate and hydrogen peroxide concentration on the anodic peak height of hydrogen peroxide oxidation were also investigated. The catalytic oxidation peak current showed two linear ranges (8X10"^{6} to 1 x10"^{4} and 1 xiO"^{4} to 2x10"^{2} M) with different slopes dependent on the hydrogen peroxide concentration and the detection limit (3a) were 6.5x10"^{6} and 2.2x10"^{5} M respectively. The catalytic reaction rate constant, (k_h), was calculated 5.5x10^{+2} M"V^{1} by the data of chronoamperometry. The modified electrode was used successfully in real sample analysis.

***Keywords**: Electrocatalytic oxidation, hydrogen peroxide, Ni/PMT/MCPE.*

Electrocatalytic Oxidation of L-Glutathione (GSH) by Ferrocyanide at the Surface of Carbon Paste Electrode

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Abstract

Reduced glutathione (GSH) (Y-L-glutamyl-L-cycteinyl-glycine), is the major non-protein thiol in living cells, with cellular concentrations ranging from 0.5 to 10 mM. This tripeptide containing a sulfurhydryl group plays important biological functions in the organism, including protein and DNA synthesis, enzyme activity, metabolism and cell protection.The electrocatalytic oxidation of L-glutathione (GSH) has been studied by ferrocyanide at the surface of carbon paste electrode (CPE). Cyclic voltammetry and chronoamperometry techniques were used to investigate the suitability of ferrocyanide as a mediator for the electrocatalytic oxidation of L- glutathione in aqueous solution with various pH. Results showed that pH 7.00 is the most suitable for this purpose. In the optimum pH, the electrocatalytic ability about 425 mV can be seen and the rate constant (k) for L-glutathione coupled catalytically to ferrocyanide was calculated 2.3 x 10^{3} M"^{1} *s*\ Also, an electron transfer coefficient (a) for ferrocyanide in the presence of glutathione was determined 0.470 using various electrochemical approaches such as Tafel plot. The catalytic oxidation peak current was linearly dependent on the L-glutathione concentration and a linear calibration curve was obtained in the ranges of 6.1 x10"^{5} " 1.0x10"^{3} M of L-glutathione with cyclic voltammetry method. The detection limit (3a) was determined as 5.5 xi0"^{5}.

Keyword: *Glutathione; Ferrocyanide; Carbon paste electrode*

Conversion & Storage of Electrochemical Energy
تبدیل و ذخیره انرژی الکتروشیمیایی

Dispersion of Pt nanoparticles onto the Vulcan XC-72 using different solvents for development of PEM fuel cell

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Abstract

A novel method with ethylenediaminetetraacetic acid disodium salt (EDTA-2Na) as a stabilizing agent was developed to prepare highly dispersed Pt nanoparticles on carbon (vulcan xc-72) in different solvents to use as proton exchange membrane (PEM) fuel cell catalysts. These nanocatalysts were obtained when the EDTA-2Na/Pt ratio was maintained at 1:1. And the Pt/Vulcan catalyst exhibited large electrochemical active surface areas, very high electrocatalytic activity. The Pt/XC-72R catalyst with narrow size distribution was prepared by this method.

Keywords: *Ethylenediaminetetraacetic acid disodium salt stabilizer, Pt/C, electrocatalyst, solvent*

Study of Synergism Effect between Multi-Wall Carbon Nanotubes and VulcanXC-72R at Micro Porous Layer

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Abstract

In this work, the effect of multi-wall carbon nanotubes (MWCNT) at micro porous layer (MPL) on Oxygen reduction reaction (ORR) was studied. We utilized different percentages of MWCNT and VulcanXC-72R at the MPL of gas-diffusion electrode (GDE) with different Pt loading in the catalyst layer. The performance of the electrodes in ORR was studied by linear sweep voltametery (LSV), electrochemical impedance spectroscopy (EIS), and chronoamperometery method The structure of MPL was investigated by scanning electron microscope (SEM), mercury porosimetry and gas permeability techniques. In addition, the optimum value of polytetrafluoroethylene (PTFE) for MWCNT at MPL was determined.

Our results indicate that in the presence of MWCNT at MPL, the performance of GDE increases since the following conditions exist: a) 60 wt% MWCNT and 40 wt% VulcanXC-72R with Pt loading 0.115 mg.cm^{-2}; b) 80 wt% MWCNT and 20 wt% VulcanXC-72R with Pt loading 0.5 mg.cm^{-2}; and c) 40 wt% MWCNT and 60 wt% VulcanXC-72R with Pt loading 1 mg.cm^{-2}.

***Keywords**:, proton exchange membrane fuel cell (PEMFC), Oxygen reduction reaction (ORR), synergism, multi-wall carbon nanotube (MWCNT), gas diffusion electrode (GDE) and micro porous layer(MPL).*

Synthesizing and optimization of high porous polyaniline nanofibers in catalyst layer for High performance methanol oxidation on Pt/C substrate

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Abstract

Electro-oxidation of methanol on conventional Pt/C catalyst releases some poisonous species such as CO which strongly bond on catalyst and prevent from ongoing methanol oxidation. This phenomenon in turn decreases the performance of direct methanol fuel cell. To overcome such deficiencies of methanol oxidation on surface of Pt/C as common catalyst of fuel cells, among diverse methods, using the conductive polymer, polyaniline (PANI) was chosen. The in situ electropolymerization of aniline was done on substrate of Glassy carbon (GC) painted Pt/C at 0°C. Methods of polyaniline synthesis; cyclic voltammetry, galvanostatic and potentiostatic methods were examined to get the best approach to reach porous and stable polyaniline. Trifluoromethane sulfonic acid (TFMSA) is used as dopant. Platinum loading used in all experiments is 0.51mg.cm^{-2}. The modified catalyst behavior was characterized by cyclic-voltammetry, electrochemical impedance spectroscopy. Scanning electron microscopy was applied to study the structure of synthesized PANI on whole layers of catalyst. Results verified that, the galvanostatic method is the best method among others for synthesizing the PANI, and in the presence of methanol, PANI/Pt/C exhibited lower overpotential than that of Pt/C, indicating the higher methanol tolerance of the modified catalyst.

Keywords: *Methanol electro-oxidation, Direct Methanol Fuel Cell, Pt/C Nanoparticle, Polyaniline Nanofiber.*

اصلاح لایه‌های نفوذ گازی پیل‌های سوختی تبادل یون پروتون

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چکیده

لایه‌های نفوذ گاز نقش بسیار کلیدی را در بهبود عملکرد پیل سوختی ایفا می‌کنند و براساس سه مفهوم هدایت الکتریکی بالاتر، مدیریت آب بهتر و عبورپذیری گاز بالاتر طراحی می‌شوند. ورقه‌های کربنی ، پارچه‌های کربنی و فلزات سینتر شده به طور گسترده به عنوان لایه نفوذ گازی مورد استفاده قرار می‌گیرند. اما استفاده از نانو مواد شامل فیبرهای نانو کربنی و نانو لوله‌های کربنی موجب کاهش مقاومت تماسی، بهبود توزیع گاز و مدیریت آب بهتر می‌گردد. لذا در این تحقیق، این امر بصورت آزمایشگاهی مورد بررسی و تحقیق قرار گرفته است. لایه‌های نفوذ گاز با استفاده از نانو مواد اصلاح شده و در یک پیل سوختی منفرد آزمایشگاهی مورد بررسی قرار گرفت. آنالیزهای مختلفی نظیر زاویه تماس و توزیع اندازه ذرات روی نمونه های اصلاح شده انجام می شود. مورفولوژی سطحی نمونه ها با تصویر میکروسکوپ الکترونی به دست می آید. در نهایت، از لایه نفوذ گازی با مخلوط ۵۰٪ وزنی کربن بلک و ۵۰٪ وزنی نانو تیوب کربنی و ۳۰ درصد وزنی PTFE در ساخت مجموعه الکترود- غشا (MEA) پیل سوختی استفاده شده و سپس در پیل سوختی آزمایشگاهی تست گردید. عملکرد پیل سوختی براساس منحنی پلاریزاسیون با لایه نفوذ گازی اصلاح شده بهتر از حالت اصلاح نشده بود. همچنین ولتاژ مدار باز با استفاده از این لایه نفوذ گازی، در ۷۰ درجه سانتی گراد و با استفاده از هیدروژن و اکسیژن در حدود۰/۹ ولت به دست آمد.

واژه های کلیدی: *پیل سوختی غشاء تبادل پروتون، لایه نفوذ گازی، میکرولایه متخلخل، نانو لوله‌های کربنی*

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مطالعه پارامتری شرایط عملکردی پیل سوختی و مشخصات فیزیکی GDL بر عملکرد پیل سوختی با غشاء پلیمری

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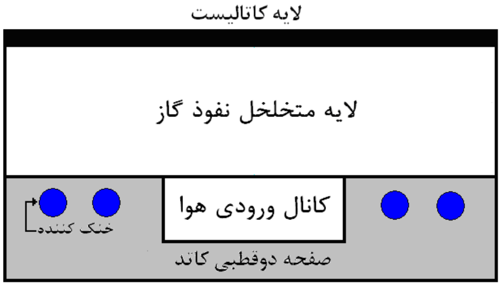
چکیده:

لایه نفوذ گاز(GDL) یکی از اجزاء بسیار مهم پیل سوختی با غشاء پلیمری است که نقش توزیع گازهای واکنشگر و افزایش سطح موثر را بر عهده دارد. با توجه به اهمیت درک چگونگی تاثیر شرایط عملکردی پیل سوختی و مشخصات فیزیکی لایه نفوذ گاز روی عملکرد پیل، لازم است روی این پارامترها مطالعه دقیقی انجام گیرد. در این مقاله اثر پارامترهای عملکردی دما و فشار و نیز مشخصات فیزیکی ضریب تخلخل، نفوذ پذیری و ضخامت لایه نفوذ گاز الکترود کاتد بر عملکرد پیل بررسی شده است. برای این کار، لایه متخلخل نفوذ گاز بوسیله مدلی دو بعدی و غیر هم دما در مقطع عمود بر جریان کانال ورودی (شکل ۱) با روش عددی تفاضل محدود صریح مدل شده است. در این مقاله نشان داده می شود که با افزایش مقادیر پارامترهای دما، فشار و ضریب تخلخل، میزان جریان تولیدی و در نتیجه کارآیی پیل افزایش می یابد. طبق نتایج به دست آمده در این مطالعه، تغییر نفوذ پذیری لایه نفوذ گاز در بازه مطالعه شده اثر ناچیزی بر عملکرد پیل دارد. با افزایش ضخامت لایه نفوذ گاز، گازهای واکنش دهنده به طور یکنواخت تر به محل های واکنش الکترو شیمیایی در مرز لایه کاتالیست رسیده و از سر تا سر محل های ممکن برای واکنش، استفاده بهتری می گردد. اما در مقابل، افزایش ضخامت لایه نفوذ گاز باعث افزایش افت های نفوذ می شود و مقاومت در مسیر گازرسانی به محل های واکنش افزایش می یابد. در این مقاله این دو عامل به خوبی نشان داده شده اند و در نتیجه ضخامتی بهینه برای لایه نفوذ گاز مدل شده به دست آورده شده است. نتایج در یک حالت پایه با نتایج تجربی موجود مقایسه شده است.

کلمات کلیدی: پیل سوختی غشاء پلیمری، لایه نفوذ گاز کاتد، مدل دو بعدی و غیر هم دما، مطالعه پارامتری



شکل ۱– تصویر شماتیک میدان محاسباتی (جهت جریان در کانال عمود بر صفحه است.

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Electrochemistry & Materials Science
الکتروشیمی و علم مواد

Metal and media effects on inhibitory performance: electrochemical approaches

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Abstract

The inhibiting action of a synthetic Schiff base [namely: N,N´- bis (salicyaldehyde)- 1,3-propandiimine] on corrosion behavior of copper in HCl and of iron in H_2SO_4 media was investigated from mechanistic points of view, through Tafel (potentio-dynamic) and electrochemical impedance (EIS) methods. The investigations revealed this molecule to be a mixed-type inhibitor (mostly anodic for iron and cathodic for copper) having physicochemical interactions with metal surface and its adsorption obeys the Langmuir isotherm. For iron system, the interactions were recognized to have some chemical properties being ascribed to the metal incomplete d-electronic configuration. The rate of corrosion was also observed to be low for copper case, comparing with iron one. This is resulting from a protective film of CuCl, forming on metal surface, detected as a double time-constant in Bode-phase diagram, causing both anodic and cathodic reactions to inhibit. This film is not stable and destroyed gradually by formation of some soluble complexes through extra coordination of chloride anions. Moreover, in presence of Schiff base, diffusion process and formation of corrosion product on metal surface were found to be prohibited, according EIS data; both Warburg line and the related time-constant disappeared. For the case of iron, however, the behavior was simple and described via conventional Randle model. Finally, the complementary investigations in electrolytes containing iodide ions showed a substantial enhancement on inhibitory performance, especially for copper system, justified by electrostatic interactions exerting between charged species.

Keywords: *Tafel polarization and impedance spectroscopy; Copper and Iron; Corrosion inhibitor; Thermodynamic and Kinetic studies; Temperature and Synergistic effect*

The effect of Thiourea inhibition for A517-Gr.B Quench tempered steel in 0.5M sulfuric acid

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Abstract

Corrosion inhibitors are widely used in acid solutions during pickling and descaling. In this study has been used Thiourea as corrosion inhibition of A517-Gr.B quench tempered in 0.5M sulfuric acid. Techniques such as weight loss measurement, Potentiodynamic polarization and electrochemical impedance spectroscopy at 25^0 C have been using for inhibition efficiency of Thiourea. The results obtained showed that the inhibition efficiency increases with an increase in Thiourea concentration. Inspection of the values of surface coverage (θ) indicate that the adsorption process obeys the Langmuir isotherm.

Keywords*: A517-Gr.B steel; Sulfuric acid; Inhibitor; Thiourea; Corrosion behavior*

Corrosion inhibition of carbon steel in sulphuric acid by some polydentate Schiff base compounds

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Abstract

The use of corrosion inhibitor is one of the most effective measures for protecting metal surfaces against corrosion in acid environments. Some organic compounds are found to be effective corrosion inhibitors for many metals and alloys.

In the present work, the efficiency of three polydentate Schiff bases as corrosion inhibitors for carbon steel in 1M sulphuric acid has been determined by electrochemical impedance spectroscopy (EIS), Tafel polarisationmeasurements. These compounds inhibit corrosion even at very low concentrations. Polarization curves indicate that all compounds are mixed inhibitors, affecting both cathodic and anodic corrosion currents. The surface adsorption of the Schiff bases has lead to a decrease in the double layer capacitance and to an increase in polarisation resistance. Adsorption of Schiff bases on the carbon steel surface is in agreement with the Langmuir adsorption isotherm model, and the calculated Gibbs free energy values confirm the chemical nature of the adsorption. Scanning electron microscopy (SEM) has been applied to identify the surface morphology of the carbon steel both in the absence and presence of the Schiff base molecules The structural and electronic properties of these inhibitors, obtained using AM1, PM3, MNDO and MINDO/3 semi-empirical self-consistence field methods, are correlated with their experimental efficiencies.

***Keywords**: Corrosion inhibition, Polydentate Schiff bases, Carbon steel, Adsorption, Quantum chemical calculations*

Synthesis and electrochemical studies of a number of new phosphorous ionic

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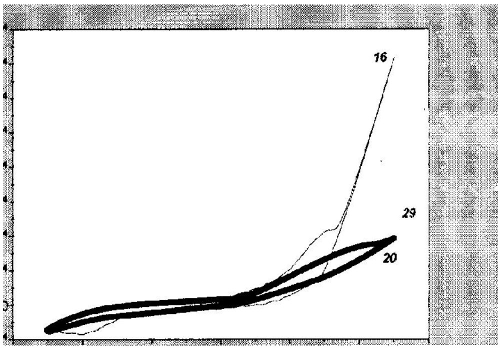
Abstract

Ionic liquids is new category in organic chemistry that have many applications because of their high polarities and boiling points. This type of materials abberivated as IL. RTIL are the ILs that have boling points near the room temperature. Room temperature ionic liquids (RTILs) are non-flammable, non-volatile and thermally stable solvents and as much as very promising replacements for the traditional volatile organic solvent. Surfactants in RTILs can significantly increase the solubility of many solutes and modify the properties of RTILs as solvents. Ionic liquids, as a class of novel environmental ''green solvents'', have remarkable new properties and promising applications in many fields. This is because they have a number of desirable characteristics, including negligible volatility, non-flammability, high thermal stability, low melting point, and controlled miscibility with organic compounds, especially some heterocyclic compounds. In this research fifteen new phosphorous ILs had been syntheszed. Their electrochemical studies specially cyclic voltammetry were been done after characterization of them with spectroscopic methods. The following picture is the CV of a number of this type new compounds.



Keywords: *Ionic Liquids, Synthesis, Phosphorous, Electrochemical Studies, Cyclic Voltammetry*

Synthesis, Characterization and electrochemical studies of a number of new silver isonicotinic hydrazide complexes

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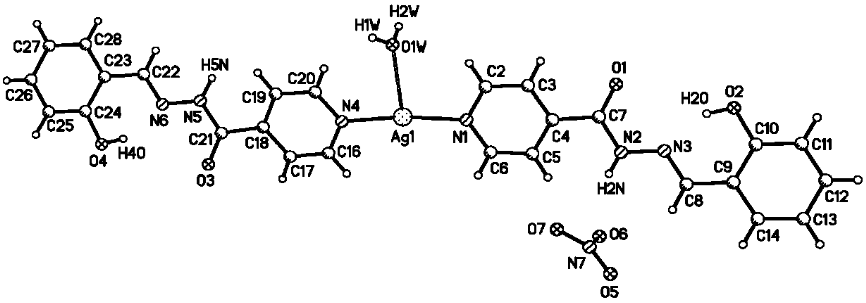
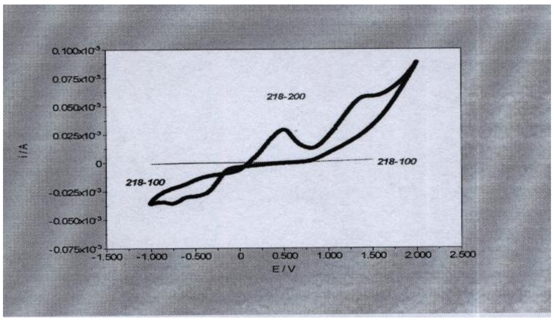
Abstract

Silver complexes have different uses in a number of industrials. This because of their anti bacterial and anti fungal properties. Silver compounds have some uses in batteries and electrical systems. In this research ten new silver isonicotinic hydrazide complexes had been synthesized. Their electrochemical studies especially cyclic voltammetry were been done after characterization of them with spectroscopic methods. The following pictures show, up) the X-ray ORTEP of one of silver complexes and down) is the CV of a number of this type new compounds.





Keywords: *Ionic Liquids, Synthesis, Phosphorous, Electrode*

Impedance Spectroscopy Studies of PbS and PbO Semiconductors

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Abstract

In recent years, electrodeposited thin film semiconductors are popular in the field of solar cells, optoelectronic devices, photoelectrochemical cells, etc. particularly lead sulfide and lead monoxide have received considerable attention because of their potential applications in a variety of semiconducting devices. In this study, we have electrodeposited the PbS and PbO thin layers potentiostatically on lead substrates and electrochemical impedance spectroscopy was used for studying the structure of the electrodeposited semiconductor layers in dark and under light illumination, N_D and V_{fb} values were calculated from Mott-Schottky plots and the effect of illumination by polychromatic light is studies. For a semiconductor in depletion condition, space charge capacitance can be obtained by impedance measurements. The values of C_{SC} can be determined experimentally as a function of potential By using Mott-Schottky equation. Hence, the value of the free charge carrier concentration, N_d, can be calculated from the slop of $1/C_{SC}^2$ versus V plot and flat band potential, V_{fb}, can be obtained from the intercept on the potential axis. It is observed that these two important semiconducting parameters are different under light illumination from their values in the dark condition. It is also observed a significant decrease in R_s, R_{ct} and R_{sc} resistances which show light assisted promotion of charge carriers and good photoconductivity.

Keywords: *Semiconductor, impedance spectroscopy, Mott-Schottky plot*

اثر بازدارندگی تیواوره بر فولاد استحکام بالای کوئنچ تمپرشده A517- Gr.B در محیط سولفوریک اسید ۰/۵ مولار

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چکیده:

بازدارنده های خوردگی به طور گسترده برای محلول های اسیدی در اسیدشویی و پوسته زدایی به کار می روند. دراین تحقیق از تیواوره به عنوان بازدارنده در سولفوریک اسید ۰/۵ مولار برای فولادهای کوئنچ تمپر A517-Gr.B استفاده شده است. روشهایی همچون کاهش وزن، پلاریزاسیون پتانسیودینامیک و امپدانس الکتروشیمیایی در دمای ۲۵°C برای مطالعه راندمان بازدارندگی تیواوره به کار گرفته شده است. نتایج بدست آمده نشان داده که با افزایش غلظت تیواوره راندمان بازدارندگی افزایش پیدا کرده است. بررسی مقادیر پوشانندگی سطح (θ) نشان می دهد که جذب تیواوره روی فولاد مورد نظر، از ایزوترم جذب لانگمیر پیروی می کند.

کلمات کلیدی: *فولاد A517-Gr.B، سولفوریک اسید، بازدارنده، تیواوره، رفتار خوردگی*

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Inhibition of mild steel corrosion by N, N' – bis (2-hydroxybenzilidene)-1, 1-diaminoalkyls in 1 M HCl solutions

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Abstract

Acid solutions are widely used in various industries for the pickling of ferrous alloys and steels. To avoid base metal attack and to ensure the removal of corrosion products/scales alone, inhibitors are extensively used. Inhibitors are compounds that control, reduce, or prevent reactions between a metal and its surroundings when added to the medium in small quantities. Usually, organic compounds are widely used in industry for preventing corrosion in acidic environments. Some Schiff bases have recently been investigated as corrosion inhibitors for various steels in acid media. These substances generally become effective due to the presence of an imine (-CH=N) group and conjugated double bonds. Besides the imine group, substitution of different groups also affects the inhibition properties.

In this study, the inhibition effect of Schiff bases N, N′- bis (2-hydroxybenzilidene)-1, 1-diaminoethan (I), N, N′- bis (2-hydroxybenzilidene)-1, 1-diaminopropan (II), N, N′- bis (2-hydroxybenzilidene)-1, 1-diaminoisobutan (III) on the corrosion of mild steel in 1 M HCL has been studied by polarization, electrochemical impedance spectroscopy (EIS) and weight loss measurements. The inhibition efficiencies obtained from all methods employed are in good agreement. Results show compound III to be the best inhibitor with a mean efficiency of 97% at 10^{-3} M additive concentration. The temperature effect on the corrosion behavior of steel in 1 M HCl without and with the inhibitors at 10^{-3} M was studied in the temperature range from 308 to 348 K. The inhibitors were adsorbed on the steel surface according to the Langmuir adsorption isotherm model. From the adsorption isotherm some thermodynamic data for the adsorption process (K and ΔG_{ads}) are calculated and discussed. The polarization data have shown that inhibitors act as mixed anodic–cathodic nature for mild steel in acid solution.

Keywords: *Corrosion inhibition; mild steel; Schiff base; HCl solution*

Corrosion inhibition of mild steel by plant extract in HCl medium

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Abstract

Corrosion inhibitors are chemical compounds usually used in small concentrations whenever a metal is in contact with an aggressive medium. A number of heterocyclic compounds have been reported as corrosion inhibitors and the screening of synthetic heterocyclic compounds is still being continued. Though many synthetic compounds showed good anticorrosive activity, most of them are highly toxic to both human beings and environment. These toxic effects have led to the use of natural products as anticorrosion agents which are eco-friendly and harmless. In recent days many alternative eco-friendly corrosion inhibitors have been developed.

In the present work the inhibition effect of strychnos nux vomica extract on the corrosion of steel 304 in 5% and 15% aqueous hydrochloric acid solution has been investigated by Tafel polarization and electrochemical impedance spectroscopy (EIS). The corrosion inhibition efficiency increases on increasing plant extract concentration till 3000 ppm. The effect of temperature on the corrosion behaviour of steel in 5% and 15% HCl with addition of plant extract was studied in the temperature range 50 – 80ºC. Plant extract is able to reduce the corrosion of steel more effectively in 15% HCl than in 5% HCl. The adsorption of this plant extract on the mild steel surface obeys the Langmuir adsorption isotherm. HPLC analysis of plant extract shows that this plant extract contains strychnine and brucine and are responsible for the corrosion inhibition properties of this plant extract.

Keywords: *Corrosion; inhibitor; strychnine; electrochemistry; impedance*

The inhibitive effect of some bis-N,S-bidentate Schiff bases towards Al corrosion in acid solution: electrochemical and theoretical studies

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Abstract

Corrosion of aluminum and aluminum alloys has been a subject of numerous studies due to the importance of these materials in contemporary civilization due to its great industrial applications. It is very important to add a corrosion inhibitor to decrease the corrosion rate of aluminum and its alloys in such solutions. Various attempts have been made to study the corrosion of aluminum and its alloys, and their inhibition by organic inhibitors in acid solutions.

In this study, corrosion inhibition of aluminum in 1.0M HCl was investigated in the absence and presence of different concentrations of Schiff bases N-[(E)-1-(2-thienyl)methylidene]-N-(4-{[(Z)-1-(2 thienyl)methylidene]amino}phenyl)-amine (PA), N-[(Z)-1-(2-thienyl)methylidene]-N-[4-(4-{[(Z)-1-(2-thienyl)methyl-lidene]-amino}benzyl)phenyl]amine (BPA), N-[(Z)-1-(2-thienyl)met-hylidene]-N-[4-(4-{[(Z)-1-(2-thienyl)methylidene]amino}phenoxy)-phenyl]amine (PPA), N-[(E)-1-(2- thienyl-)methylidene]-N-{4-[(4-{[(Z)-1-(2-thienyl)methylidene]amin-o}-phenyl)sulf-ony-l]phenyl}amine (PSPA) Weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurements were employed. Impedance measurements showed that the charge transfer resistance increased and double layer capacitance decreased with increase in the inhibitor's concentration. Potentiodynamic polarization study showed that the inhibitors acted as mixed type inhibitors. Obvious correlations were found between corrosion inhibition efficiency and some quantum chemical parameters such as energy of highest occupied molecular orbital (HOMO), energy of lowest unoccupied molecular orbital (LUMO), HOMO–LUMO energy gap and electronic density etc. The adsorption of these compounds on the aluminum surface obeys a Langmuir adsorption isotherm and has a mixed physisorption and chemisorption mechanism.

***Keywords**: Aluminum, Corrosion inhibitors, Bis-N,S-bidentate Schiff bases, Quantum chemical calculations*

Pyrimidine-2-thione derivatives as corrosion inhibitors for mild steel in acid solution

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Abstract

Acid solutions are generally used in the industry in many important fields. Some of them are acid pickling, industrial cleaning, oil-well acidizing, acid descaling, etc. In order to reduce the degree of metal attack and rate of consumption of the acid, corrosion inhibitors are added to the pickling solutions. Heterocyclic compounds containing nitrogen, oxygen or sulphur have long been known to protect the metallic surface from corrosion.

The present study was undertaken to investigate the inhibition of corrosion of mild steel in 1 M sulphuric acid by some derivatives of pyrimidine-2-thione by two techniques weight loss and electrochemical techniques (potentiodynamic polarization and electrochemical impedance spectroscopy (EIS)). The choice of these compounds is based on molecular structure considerations, i.e., these are organic compounds having the same adsorption centers but they only differ in the substituent type at the ortho and para position of phenyl group. Under the present experimental condition pyrimidine-2-thione derivatives were found to be efficient inhibitors for the acid corrosion of mild steel and the inhibition efficiency of up to 98% was obtained. Effect of temperature on the mechanism and also on the efficiency of the corrosion inhibition process was studied using the Arrhenius approximation of the rate law. Thermodynamic parameters for the corrosion process were obtained and interpreted. The adsorption of the pyrimidine-2-thione derivatives, on the mild steel surface in the acid medium (1 M H_2SO_4) obeyed the Langmuir adsorption isotherm. Density functional theory calculations were performed to characterize certain features of the molecular structures, including the electronic parameters related to the inhibition effectiveness of these inhibitors.

Keywords: *Mild steel, Pyrimidine-2-thione derivatives, Corrosion inhibition, EIS, Sulfuric acid*

The behavior of Tween-20 as an inhibitor of steel corrosion in 1 M sulfuric acid (H2SO4)

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Abstract

The inhibiting action of tween-20 nonionic surfactants on the corrosion of steel in 1M sulfuric acid (H_2SO_4) was studied by tafel polarization methods, electro chemical impedance and weight loss. The results showed that in a same temperature the inhibition efficiency increased with the inhibitor concentration, while it decreases with an increase in temperature, in general, on the other hand, increasing the immersion time causes to increase the inhibition efficiency, in general the adsorption of surfactants obeys the Langmuir equation. Polarization cures show that tween-20 is cathodic type inhibitor in sulfuric acid (H_2SO_4). The results obtained from weight loss, tafel polarization and impedance are in good agreement.

Keywords: *Nonionic surfactants; Tween; Sulfuric acid; Steel; Inhibitor*

Bis-Pyrrolidiniummethyl-urea as corrosion inhibitor for mild steel in sulphuric acid medium

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Abstract

Sulphuric acid finds applications in industrial acid cleaning, acid descaling and oil well acidizing. Inhibitors are commonly employed in these environments to minimize the base metal corrosion by acids. Mild steel (MS) is used widely in engineering for its low cost, good mechanical property and easy availability; therefore its corrosion inhibition in sulphuric acid is studied frequently. Most well known acid inhibitors are organic compounds especially those containing N, S, an aromatic ring and oxygen atoms.

The inhibition of corrosion of mild steel in 1 M sulphuric acid by bis-Pyrrolidiniummethyl-urea (BPMM) has been investigated using electrochemical, scanning electron microscope (SEM) and Infrared (IR) techniques. The results suggest that BPMM acts as a good inhibitor and the inhibition efficiency of BPMM increases with increasing concentration. Potentiodynamic polarization studies have shown that the inhibitor influences both the anodic and cathodic process and it behaves as a mixed type inhibitor. Double layer capacitance and charge transfer resistance values were derived from Nyquist plot obtained from AC impedance studies. The film which is formed over the metal surface is analyzed by IR spectroscopy. Further, surface morphological examination through SEM has also been carried out. The results confirm the role of BPMM as an effective corrosion inhibitor for MS in acid media.

Keywords: *Sulfuric acid, Corrosion inhibitor; SEM, Bis-Pyrrolidiniummethyl-urea*

Investigation of adsorption and inhibitive effect of bis morpholiniummethyl-urea on corrosion of mild steel in hydrochloric acid media

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Abstract

The adsorption of organic molecules at the metal/solution interface is of a great interest in surface science and can markedly change the corrosion resisting properties of metals. The protection of corroding surfaces prevents the waste of both resources and money during the industrial applications and it is vital for the extension of the life time of the equipment and limiting the dissolution of the toxic metals from the components into the environment. Therefore, the prevention from the corrosion of metals used in industrial applications is an important issue that must be dealt with. The use of inhibitors is one of the most practical methods for protecting against the corrosion and it is becoming increasingly popular. The organic molecules are recently used as corrosion inhibitors. The efficiency of these molecules is mainly dependent on their ability to be adsorbed on the metal surface, which results with the replacement of water molecules at a corroding interface.

In this study, the inhibition effect of bis morpholiniummethyl-urea (BMMU) on the corrosion behavior of mild steel (MS) in 1M HCl solution was studied using potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and linear polarization resistance (LPR) techniques. The value of activation energy (E_a) for the MS corrosion and the thermodynamic parameters such as adsorption equilibrium constant (K_{ads}), free energy of adsorption (ΔG_{ads}), adsorption heat (ΔH_{ads}) and adsorption entropy (ΔS_{ads}) values were calculated and discussed. The potential of zero charge (PZC) of the MS in inhibited solution was studied by the EIS method, and a mechanism for the adsorption process was proposed. The results showed that BMMU performed excellent inhibiting effect for the corrosion of the MS. Finally, the high inhibition efficiency was discussed in terms of adsorption of inhibitor molecules and protective film formation on the metal surface.

Keywords: *Corrosion inhibitors, Hydrochloric acid solution, Adsorption mechanism, Potential of zero charge (PZC)*

Nickel Doped Nanostructured MnO_2 as Supercapacitor Electrode

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Abstract

Manganese oxides are very promising candidates as electrode material in supercapacitors. In this work, we employed a sonochemical method to synthesis manganese oxides as the active material for the supercacitor electrode. In order to improve the electrochemical properties of the electrode, nickel ion was doped into the manganese oxide crystallite structure during the synthesis of the oxide. The oxides samples were prepared by sonochemical method from an aqueous solution of potassium bromate and manganese sulfate and addition of nickel sulfate solution at different reaction intervals.

Chemical composition analysis was carried out using potentiometric titration, atomic adsorption spectroscopy. Crystalline structure of the powder was examined using XRD technique.

The atomic absorption analysis shows that the Ni was doped with concentration of two percent. The XRD patterns show that the γ-MnO2 structure for pristine and Ni doped samples.

The electrochemical properties of the samples were examined in a three electrode system including a beaker type electrochemical cell and an aqueous solution of 0.5 M K_2SO_4 at pH 3. The electrochemical techniques such as cyclic voltammetry, chronopotentiometry and impedance spectroscopy were employed to investigate the the electrochemical properties of the samples. The cyclic voltammograms were taken at the potential ranges of – 0.2 – 1.0 V versus Ag/ AgCl and at sweep rate of 2 mVs^{-1}.

The specific capacitance of MnO2 increases in presence of Ni in the structure. The maximum specific capacitance of nickel doped samples was 220 F/g at scan rate 2mVs^{-1} in 0.5 M aqueous K_2SO_4 solution at pH=3.1.

The cyclic votammograms are relatively rectangular in shape and exhibit near mirror-image current response on voltage reversal thus indicating ideal capacitive behavior for samples. The specific capacitance for pristine samples was around 190 F/g whereas the specific capacitance for doped was around 220 F/g.

Keywords: *Nickel doped, Supercapacitor, Nanostructured Manganese oxide*

مطالعه الکتروشیمیایی پروپارگیل الکل بعنوان ممانعت کننده خوردگی برروی آلیاژمس-نیکل(۲۵/۷۵)

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چکیده

استفاده از ممانعت کننده ها، از پرکاربردترین روش ها در جلوگیری از خوردگی مواد در صنعت است. در این تحقیق مطالعه خوردگی آلیاژ مس-نیکل(۲۵/۷۵) در اسید سولفوریک نیم مولار در غیاب و حضور پروپارگیل الکل با روش های الکتروشیمیایی (AC امپدانس و پلاریزاسیون تافل)مورد بررسی قرار گرفت. نتایج بدست آمده نشان می دهد که فرآیند الکترواکسیداسیون آلیاژ مس- نیکل(۲۵/۷۵) در حضور پروپارگیل الکل کاهش می یابد. ازمنحنی تافل نتیجه گرفته شد که با افزایش مقدار پروپارگیل الکل دانسیته جریان خوردگی کاهش می یابد. نتایج AC امپدانس نشان میدهد که با افزایش مقدار پروپارگیل الکل ،مقاومت پلاریزاسیون افزیش می یابد. همچنین فرآیند برهم کنش بین ماده آلی و سطح الکترود به صورت جذب سریع پروپارگیل الکل بر روی سطح آلیاژ مس- نیکل(۲۵/۷۵) است که بستگی به انرژی جذب وغلظت پروپارگیل الکل دارد.

واژه های کلیدی: *اسید سولفوریک، پروپیل الکل، پلاریزاسیون تافل، دانسیته جریان، الکترو اکسیداسیون*

Electrooxidation of Saccharose on Nickel Electrode in Alkaline Media

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Abstract:

Studies of the electro catalysis for the oxidation of organic molecules are of importance in connection with efforts to find alternative fuels to H_2 in the anodic compartment of fuel cells. H_2 is an environmentally desirable anodic fuel, considering that only water results from the coupling of its oxidation to the reduction of O_2. However, H_2 gas is difficult to handle relative to liquid fuels such as alcohols which yield CO_2 upon complete oxidation[1]. The purpose of the present work is electrocatalytic oxidation of saccharose on nickel in the alkaline solution.

Sodium hydroxides, saccharose used in this work were analytical grade of Merck origin. Electrochemical studies were carried out in a conventional three electrode cell powered by an electrochemical system comprising of EG&G model 273 potentiostat/galvanostat and Solartron model 1255 frequency response analyzer. A dual Sat'd Ag/AgCl, a Pt wire and a nickel disk electrode were used as the reference, counter and working electrodes, respectively.

Nickel modified NiOOH electrodes were used for the electro-catalytic oxidation of saccharose in alkaline solutions where the methods of cyclic voltammetery (CV), chronoamperometry (CA) and impedance spectroscopy were employed. The anodic current was proportional to the bulk concentration of saccharose and any increase in the concentration of saccharose caused an almost proportional linear enhancement of the anodic current. In CV studies, in the presence of saccharose the peak current of the oxidation of nickel hydroxide increase is followed by a decrease in the corresponding cathodic current. This suggests that the oxidation of saccharose is being catalyzed through mediated electron transfer across the nickel hydroxide layer comprising of nickel ions of various valence states [2]. Impedance spectroscopy showed that the charge transfer resistance decreases with increasing saccharose concentrations. A mechanism based on the electro-chemical generation of Ni^{3+} active sites [3] and their subsequent consumptions by saccharose have been discussed and kinetic parameters have been derived.

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Comparative study of oxidation of methanol, ethanol, 1-propanol, 2-propanol on Ni electrode

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Introduction

The electro-oxidation of alcohols is a wide research area for the development of fuel cell in this respect , a great interest exist in the studying different alcohols[1,2]. According to these proposes; we compared alcohol oxidation on Ni electrode, by using cyclic Voltammetry and impedance spectroscopy techniqes.

Experimental:

Sodium hydroxide and all alcohols used in this work were Merck products of analytical grade and were used without further purifications. Doubly distilled water was used throughout.Electrochemical studies were carried out in a conventional three electrode cell powered by an electrochemical system comprising of EG&G model 273 potentiostat/galvanostat. The system is run by a PC through M270 commercial softwares via a GPIB interface. A dual Sat'd Ag/AgCl, a Pt wire and a nickel disk electrode were used as the reference, counter and working electrodes, respectively. All studies were carried out at 298± 2 K.

Results and discussion:

Ni modified NiOOH electrode prepared after repetitive cyclic Voltammetry.It is observes that the methanol peak is higher than the other alcohol after that the peak currents of 1-propanol,ethanol and 2-propanol were obtained respectively.

Reference

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بررسی رفتار الکتروشیمیایی بازدارنده های آلی سنتزی بر خوردگی فولاد زنگ نزن۳۰٤ در محیط اسیدی

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چکیده

در تحقیق حاضر، خوردگی فولاد زنگ نزن ۳۰۴ در محیط اسید سولفوریک ۰/۵ مولار در حضور مقادیر مختلفی از بازدارنده های آلی سنتزی: اتیل-۳- [(۲- آمینو اتیل)آمینو] -۲- بوتانوات و اتیل -۳- (۲-آمینوآنیلینو)-۲-بوتانوات، در دماهای ۵۵-۲۵ درجه سانتی گراد با استفاده از تکنیک های پتانسیواستات و کاهش وزن، مطالعه گردیده است. با رسم منحنی های پلاریزاسیون، پارامترهای خوردگی (پتانسیل خوردگی، جریان خوردگی، درصد بازدارندگی و میزان پوشش سطح) بدست آمد. سپس با استفاده از پارامترهای حاصل، توابع ترمودینامیکی (انرژی فعال سازی واکنش، انرژی آزاد جذب واکنش، آنتالپی جذب و آنتروپی جذب واکنش) محاسبه شدند. با بررسی منحنی های پلاریزاسیون بدست آمده و پارامترهای خوردگی میزان تأثیر بازدارنده ها ،بر روی فولاد زنگ نزن بررسی شد. مشاهده شد، که این بازدارنده ها در محیط اسید سولفوریک تأثیر بازدارندگی خوبی روی فولادزنگ نزن دارد، که ناشی از نحوهٔ عملکرد آن روی سطح فلز است. در این تحقیق، میزان تأثیر افزایش دما بر عملکرد بازدارنده نیز بررسی شد که نشان داد، افزایش دما تأثیری منفی بر عملکرد بازدارنده دارد و باعث تشدید خوردگی چه در حضور و چه در غیاب بازدارنده می شود. همچنین به منظور انجام بررسی های سطحی از میکرسکوپ الکترونی روبشی SEM ، استفاده گردید. نتایج آزمایشها نشان داد که افزایش غلظت بازدارنده ها سبب افزایش راندمان بازدارندگی می شود. همچنین نتایج آزمایشها نشان داد که بازدارنده از نوع آندی-کاتدی می باشدو عملکرد آن در خوردگی فولاد به مکانیزم جذب فیزیکی آن نسبت داده می شود.

کلمات کلیدی: *خوردگی، پلاریزاسیون، بازدارنده ، فولادزنگ نزن، بازدارندگی.*

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Electrochemical behaviour of organic compounds on the corrosion of stainless steel in sulfuric acid solution

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Abstract

In the present research, the corrosion behavior of stainless steel in 0.5 M sulfuric acid containing different amounts of synthesized organic inhibitors: ethyl-3-[(2-aminoethyl) amino]-2-butenoate and ethyl-3-(2-aminoanilino)-2-butenoate as an inhibitor at a temperature range 25-55° C were investigated by potentiostatic and weight loss techniques. Corrosion parameters such as corrosion potentials (E_{corr}), cathodic Tafel slopes (βc), corrosion current densities (I_{corr}), inhibition efficiency (IE) and surface coverage degree (θ) were determined. Also by using these data, thermodynamic quantities such as (ΔG, ΔH, and ΔS) were calculated. An inspection of the results reveals that, by increasing the concentration of inhibitor, IE and θ are increased. This effect was more significant for stainless steel, because the inhibiting effect were attributed to the parallel absorption on the metal surface. We have also studied the effect of temperature on the corrosion parameters in the presence and absence of inhibitor, which proved that, by increasing the temperature, the rate of corrosion rate will be increased. Also, SEM was used surface analysis. Results show that increasing the concentration of inhibitor, increase the efficiency of inhibitor. Results also indicate that the inhibitor in question is of mixed type inhibitor, and this performance in control of corrosion of steel is attributed to physical adsorption.

Keywords: *Corrosion, Polarization, Inhibitor, Stainless steel, Inhibition*

The Corrosion Inhibition Study of Mild Steel in Hydrochloric Acid Solution Containing New S2N2-Schiff Bases by Electrochemical and Quantum Techniques

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Abstract

Mild steel is widely used in store tanks, petroleum refineries, and so on. The main problem of using mild steel is its dissolution in acidic solutions. Acid solutions are widely used for removal of undesirable scale and rust in many industrial processes. Inhibitors are generally used in these processes to control metal dissolution in acid. In this paper, the Schiff bases containing sulphur and nitrogen as heteroatom; N-[(Z)-1-phenylemethyleidene]-N-{2-[(2-{[(Z)-1-phenylmethylidene]amino}phenyl)disulfanyl]phenyl}amine,2-[({2-[(2-{[(Z)-1-(2 hydroxyphenyl)methylidene]amino}phenyl)disulfanyl]phenyl} imino)methyl]phenol , N-[(Z)-1-(4-methylphenyl)methylidene]-N-{2-[(2-{[(Z)-1-(4-methylphenyl) methylidene]amino}phenyl)disulfanyl]phenyl}amine; are synthesized. The efficiency of these S2N2-Schiff bases as a corrosion inhibitor for mild steel in 2.0 M HCl has been investigated. Potentiodynamic polarization measurements, electrochemical impedance spectroscopy "EIS", weight loss measurements and quantum chemical methods are used to study the effect of Schiff bases on the corrosion inhibition of the mild steel. Potentiodynamic polarization measurements suggest that the inhibitors

have a mixed anodic–cathodic nature but these inhibitors have somewhat greater influence on the cathodic process because these compounds shift the corrosion potential towards more negative values. The impedance measurements show that the inhibition efficiencies increase with increasing concentration of inhibitors. The impedance response is similar to a parallel combination of a capacitor (Cdl) and a resistor (Rct) both are in series with another resistor (RΩ). This is the standard Randels circuit without diffusion control. The results from potentiodynamic polarization, impedance and weight loss measurements are in good agreement. The

results show that these compounds have good inhibiting properties for mild steel corrosion in acidic media. Adsorption of Schiff bases on the surface of mild steel, in hydrochloric acid solution, follows the Longmuir adsorption isotherm. The negative values of ΔGads obtained from these studies indicate that the inhibitors are strongly adsorbed on the steel surface. The results from Arrhenius plots show that the inhibition efficiency increases with increasing temperature and the activation energy

is lower in the presence of inhibitor. The lower activation energy in presence of inhibitor is shown chemisorption of inhibitors on the surface of mild steel. Also, the quantum chemical parameters show the same results in inhibition efficiency.

***Keywords**: Corrosion inhibition, Mild steel, S2N2-Schiff base, Impedance, Polarization*

Corrosion behavior of electroless Ni-P-Au coatings composite in 3.5% NaCl solution

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Abstract:

The aim of this study is to explore the effect of gold nanoparticles (AuNPs) on the corrosion resistance of nano-composite coating Ni-P-Au. In this work AuNPs were synthesized by sonochemical reduction method and polyvinylpyrrolidon (PVP) (M_w=1300000) was used as a stabilizer. The nano-composite coating of Ni-P-Au was obtained by adding synthesized AuNPs to the Ni-P electroless plating solution. Electrochemical impedance spectroscopy (EIS) and polarization measurement have been used to evaluate the coating resistance. The Ni-P-Au coating showed the highest surface resistance compared with Ni-P.

Keywords: *Gold nanoparticles, Electrochemical impedance spectroscopy, Ni-P electroless plating, Nano-composite coatings.*

The influence of Ni percent on the corrosion behavior of Cu-Ni alloys in neutral chloride solutions

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Abstract

The electrochemical behavior of copper–nickel alloys with different Ni content (5–65%) in neutral chloride solutions of pH 7 was investigated. The effects of chloride ion concentration and immersion time were also studied. Different electrochemical methods such as polarization and electrochemical impedance spectroscopy (EIS) techniques were used. The results show that the increase in nickel content decreases the corrosion rate of the alloys in the neutral chloride solution.The increase of chloride concentration up to 0.3 mol dm−3 increases the corrosion rate. At higher concentrations ([Cl−] > 0.3 mol dm−3) the corrosion rate decreases due to the hydrolysis of Cu(I) chloride to form the passive Cu(I) oxide film. The experiment data have shown that the increase of immersion time of the alloys in the chloride solution increase the corrosion resistance of alloys.

Keywords: *corrosion, electrochemical, impedance, polarization*

بررسی رفتارالکتروشیمیایی آندهای Pb-Ca-Sn مورد استفاده در سلولهای الکترووینینگ مجتمع مس سرچشمه به روش ولتامتری چرخه ای

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چکیده

در فرایند الکترووینینگ مس سرچشمه عموما از آندهای سربی استفاده می کنند. این امر به علت مقاومت خوردگی مناسب این آندها در الکترولیت حاوی سولفات می باشد. در نتیجه استفاده از این آندها نقش بسزایی در تولید مس با خلوص قابل قبولی، ایفا می کند. برطبق تحقیقات پیشین فازهای تشکیل شده بر سطح آندهای سربی معمولا ترکیبات $PbSo_4$,α Pbo_2 ,β Pbo_2 می باشند. در این تحقیق خواص الکتروشیمیایی آندهای Pb-Ca-Sn به روش ولتامتری چرخه ای در محدوده زمانی ۰ تا ۹۶ساعت مورد بررسی قرار گرفت. نتایج نشان دهنده ی به وجود آمدن ترکیبات اکسید و سولفات سرب روی آند می باشد، که با گذشت زمان میزان این ترکیبات روی آند افزایش می یابد. همچنین در طی زمان پیکهای منحنی به سمت پتانسیلهای منفی شیفت پیدا میکند که نشان دهنده مستعد شدن آند به خوردگی می باشد.

کلمات کلیدی:*آندهای سربی،الکترووینینگ،ولتامتری چرخه ای، خوردگی،الکتروشیمیایی*

Photoelectrochemical Studies of PbS thin film

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Abstract

PbS is narrow and direct band gap semiconductor whose energy lies typically between 0.3 to 0.4 eV at room temperature. PbS thin films have been used in infrared application for decade [1]. PbS thin films have been deposited by various technique e.g., chemical bath deposition ,spray pyrolysis , vacuum evaporation and electrodeposition [2,3]. Among these methods , electrodeposition is simple , scalable and reproducible. In our present work, we studied PbS thin film by Photoelectrochemical techniques in alkaline solution. Electrochemical studies were carried out in a conventional three electrode cell powered by an electrochemical system comprising of EG&G model 273 potentiostat/galvanostat and Solartron model 1255 frequency response analyzer. A dual Sat'd Ag/AgCl, a Graphite and a Lead disk electrode were used as the reference, counter and working electrodes, respectively. PbS thin film was synthesized by electrochemical methods e.g., chronoamperometry, chronopotentiometry and cyclic voltammetry in mixed solution of Na_2S and NaOH on Lead electrode. Cyclic voltammetry of PbS thin film in 0.1M NaOH solution shows oxidation peak in darkness at 1 V/Ag-AgCl. In presence of light, the increasing oxidation peak current was observed and indicated surface states of semiconductor were activated by light (Fig.1). Electrochemical impedance spectroscopy studies showed the resistance of high frequencies and also diameter of charge transfer resistance decreased with light (Fig.2).

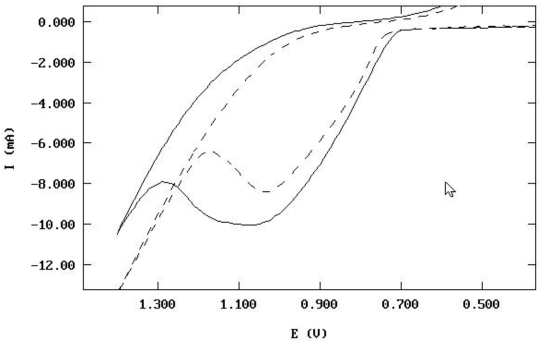

Fig. 1

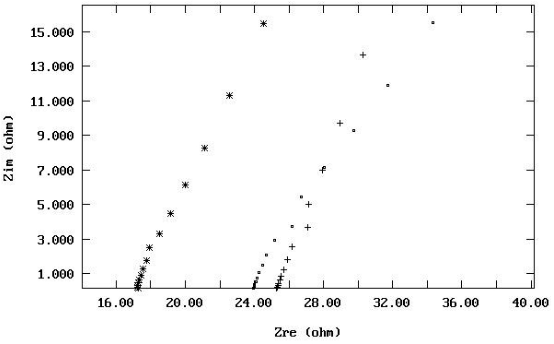

Fig. 2

Keywords: lead sulphide, semiconductor, photoelectrochemical, impedance

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Electrocatalytic oxidation and simultaneous determination of uric acid and ascorbic acid at glassy carbon electrode modified with iron(III) complex adsorbed on multi-walled carbon nanotubes

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Abstract

This article reports the highly selective and sensitive uric acid quantification in the presence of ascorbic acid using glassy carbon electrodes (GCEs) modified with iron (III) 5-Br PADAP complex adsorbed on multi-walled carbon nanotubes. The electrocatalytic activity of modified MWCNT deposited on GCEs has allowed an important decrease in the overvoltages for ascorbic acid oxidation (440 mV), making possible the clear definition of the oxidation processes of ascorbic acid and uric acid. The differential pulse voltammetry was applied for determination ascorbic acid and uric acid. For uric acid, A linear response range from 5μmol L^{-1} to 5 mmolL^{-1} was obtained. The sensitivities were, $(9.8\pm0.2)\times10^4$ μAM^{-1} (r = 0.994) and $(10.7\pm0.2)\times10^4$ μAM^{-1} (r = 0.994) in the presence and absence of 1.0 mM ascorbic acid, respectively. The sensor was successfully used for the quantification of uric acid in serum samples.

Keywords: *Carbon nanotubes; Uric acid; Ascorbic acid; Electrocatalytic oxidation*

Quantum Electrochemistry

الکتروشیمی کوانتمی

The Influence of Carbon Doping on the Adsorption Efficiency of Boron Nitride Nanotubes

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Abstract:

Nanotubes are very important in adsorption of matters especially gases. The non-carbon boron nitride nanotubes (BNNTs) are important for this purpose. Rich electron density at the sites of boron and nitrogen nuclei play important role in the adsorption of maters; therefore, the matters are much more adsorbed by the ends of nanotube. If the nanotube could adsorb the matters by atoms other than the end atoms, the efficiency of nanotube is increased. To this aim, some of boron and nitrogen atoms in the wall of BNNT are doped by carbon atoms. Density functional theory (DFT) calculations of the electric field gradient (EFG) tensors in the optimized structures reveal that those boron and nitrogen atoms which are directly connected to the doped carbons exhibit behaviors like the end atoms; therefore, they are proper candidates for adsorbing matters in addition to the end atoms.

مطالعه نقش ناخالصی کربنی در کارایی جذب نانولوله‌های بورنیترید

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چکیده:

نانولوله‌ها در جذب مواد و به‌ویژه گازها از اهمیت بسیار زیادی برخوردار هستند. نانولوله‌های بورنیترید که از دسته نانولوله‌های غیرکربنی محسوب می شوند نیز برای این منظور بسیار حایز اهمیت هستند. محیط الکترونی قوی در اطراف هسته‌های بور و نیتروژن در جذب مواد نقش مهمی دارند و به همین دلیل بسیاری از جذب‌ها از طریق دهانه نانولوله ها صورت می گیرد. حال اگر علاوه بر دهانه نانولوله، مکان دیگری نیز در سطح نانولوله از نظر محیط مشابه اتم‌های لبه‌ای باشد می‌تواند کارایی جذب نانولوله بورنیترید را افزایش دهد. بدین منظور از نقش ناخالصی کربنی به صورت کربن‌های جایگزین شده به جای اتم های بور و نیتروژن در دیواره نانولوله بورنتیرید خالص بهره گرفته شده است. مطالعه با محاسبات نظریه تابعی چگالی برای بهینه سازی انرژی ساختاری و محاسبه تانسورهای شیب میدان الکتریکی که ارتباط مستقیم با چگالی الکترونی اطراف هسته‌های چهارقطبی دارند انجام شده است. نتایج حاکی از آن هستند که اتم‌های بور و نیتروژن که در پیوند مستقیم با اتم‌های کربن جایگزین شده در دیواره نانولوله هستند خصوصیاتی همچون اتم‌های لبه‌ای پیدا می کنند که کاندیدی برای جذب مواد علاوه بر اتم‌های لبه‌ای محسوب می‌شوند.

مطالعه جذب اکسیژن بر روی نانو خوشه های پلاتین برای واکنش احیای اکسیژن در پیلهای سوختی

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چکیده

برهمکنش اکسیژن با خوشه های پلاتینی از ۴۰ سال پیش تا کنون شناخته شده است که عمدتاً مربوط به اکسید پلاتین می شود ولی جزئیات دقیق مکانیسم آن هنوز ناشناخته است. این فرایند نقش اساسی در واکنش کاتدی پیلهای سوختی و بالطبع در عملکرد آن ایفا می نماید. با توجه به اهمیت مسئله، مطالعه کوانتومی برهمکنشهای نانوخوشه های پلاتین با اکسیژن کمک شایانی در درک ابعاد ناشناخته فرایند مذکور خواهد نمود. در این تحقیق، برهمکنش بین نانوخوشه های پلاتین و مولکول اکسیژن با استفاده از تصویر اربیتالی تابع موج مطالعه گردیده است. به این منظور، اربیتالهای سیستم کمپلکس و اجزاء منفرد مستقر گردیده و سپس عدم استقرار سیستم الکترونی توسط ماتریسهای چگالی مربوطه مورد تجزیه و تحلیل قرار گرفته اند. محاسبه انتقال بار، پیوندهای برگشتی و سهم اربیتالهای مختلف در شکل گیری پیوندها جزئی از این موارد می باشند. نتایج حاصل از قطری سازی ماتریسهای چگالی حاصل بیانگر این هستند که هر دو سیستم σ و π در ایجاد برهمکنش سهیم هستند که می توانند توسط ویژه مقادیر مربوطه به صورت کمی توصیف شوند.

واژه های کلیدی: *پیل سوختی، واکنش احیای اکسیژن، نانو خوشه های پلاتین*

Theoretical and Experimental Study of Copper Electrowinning process in NICICo.

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Abstract

Solvent extraction followed by electrowinning (SX-EW) is an economical option for the processing of low –grade and oxide copper ore. Phenomenological methods were developed to simulate the copper EW processes. The simulation is used to predict the operation of the NICICo. Pilot plant put in operation in 1999. Results confirm the potential of the simulation that would subsequently be used for student training, process optimization, and to assess the performance of control strategies.

Keywords: *copper, electrowinning, modeling, NICICo.*

بررسی تـئوری و عملی فرایند الکترووینینگ مجتمع مس سرچشمه

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چکیده

فرایند الکترووینینگ برای سنگ های کم عیار و اکسیدی مس بسیار اقتصادی است.کاری که اینجا بررسی شده است، مدلسازی این فرایند جهت شرح و توصیف مراحل و کارکرد وحد الکترووینینگ است تا بتوان به یک شبیه سازی منطبق بر آن دست یافت. ورودی ها از طریق تئوری از مقالات گرفته شده است و در مرحله بعد از داده های واحد الکترووینینگ مس سرچشمه کرمان استفاده شده است و مدل کالیبره شده است. نتایج حاصل در جهت مطالعه و تحقیق فرایند، کنترل واحد و بهینه کردن شرایط عملکردی آن سود برد.نتایج قابل بررسی در این مدلسازی شامل این موارد است: میزان تولید مس در کاتد، رون تغییر فلز آهن از ورودی تا خروجی، جریان سلول ها و بازدهی جریان.

واژه های کلیدی: *مس، الکترووینینگ، مدلسازی، شبیه سازی، سرچشمه*

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Calculation of Electrochemical Half-wave Potential of Aromatic Compounds using GA-MLR and ANN methods

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Abstract

A quantitative structure-electrochemistry relationship (QSER) study has been done on the half–wave potential ($E_{1/2}$) of 47 aromatic compounds using of multiple liner regression (MLR) and artificial neural network (ANN) modeling methods. Genetic algorithm based on multiple linear regression (GA-MLR) procedure was employed for selecting of a suitable subset of descriptors. The best selected descriptors were MWCO9, Mor17u, More28u, Mor28v, Ic2, Then, selected descriptors were used as inputs for an artificial neural network. The best artificial neural network model was a fully-connected, feed forward back propagation network with a 5-4-1 architecture. Correlation coefficient between the experimental and calculated values of $E_{1/2}$ for the artificial neural network and MLR models were R = 0.995 and R = 0.955 for the training set, respectively. For the test set R was 0.987 for the ANN model and R was 0.969 for the MLR model. Standard error for the training set using neural network was SE=0.242 and for the MLR model was SE=0.307. Comparison of the results indicates that the ANN method has a better predictive power than the MLR method.

Keywords: *Half–wave potential ($E_{1/2}$), Artificial neural network (ANN), Genetic algorithm (GA), Multiple linear regression (MLR), quantitative structure-electrochemistry relationship (QSER)*

مقایسه ی محتوای کتاب های درسی شیمی دبیرستان در کشورهای ایران ، انگلیس ، امریکا و ایتالیا در زمینه ی الکتروشیمی

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چکیده:

با توجه به نتایج پژوهش های انجام گرفته در سراسر جهان ، مشخص شده است که مربیان و فراگیران گروه های سنی مختلف ، یادگیری الکتروشیمی را امر مشکلی می دانند و در درک مفاهیم آن دچار کج فهمی های متفاوتی هستند. در این پژوهش محتوای کتاب درسی شیمی دوره های متوسطه در کشورهای ایران ، انگلیس ، امریکا و ایتالیا مورد مقایسه قرار گرفته است. جمله ها ، مثال ها ، شکل ها و تصاویر بکار رفته در مورد الکتروشیمی در این کتاب ها و مزایا و معایب مطرح شده در ارتباط با یادگیری فراگیران ، مورد تجزیه و تحلیل قرار گرفته است. نتایج این بررسی می تواند به نویسندگان کتاب های درسی در بازبینی زبان نوشتاری مورد استفاده و رسانه های آموزشی بکار رفته در این کتاب ها کمک کند.

واژه های کلیدی: *آموزش شیمی ، الکتروشیمی ، کتاب های درسی*

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[۱] *استادیار شیمی فیزیک گروه شیمی دانشگاه تربیت دبیر شهید رجایی*

[۲] *کارشناس دانشگاه صنعتی شیراز*

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Surface Electrochemistry
الکتروشیمی سطح

Electrochemical Behavior of Schiff-Base Metal Complexes in Non-Aqueous Media at the Surface of Solid Electrodes

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Abstract

The synthesis and electrochemical studies of transition metal complexes containing thiolate coordination is an important area of study with implication in bioinorganic and medical chemistry [1-2]. In this work, the electrochemical behavior of newly synthesized Schiff-base metal complexes with N_2SO donor group with different electrochemical techniques was investigated in different non-aqueous media such as acetonitrile and dichlromethane as aprotic solvents at the surface of solid electrodes (Pt, Au and GC) using tetrabuthylammonium perchlorate as supporting electrolytes. It has been found that, these compounds exhibit one irreversible reduction peak due to the charge transfer without any coupled chemical reaction. The heterogeneous charge transfer rate constants, $K^{\cdot}$, the charge transfer coefficients, α , and the diffusion coefficients (D values) for this compounds in various solvents were obtained. The effect of solvent dielectric constant and the surface and catalytic effect for oxidation were investigated.

Keywords: *Schiff base, Electrochemical behavior , Solid Electrodes.*

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Electrocatalytic properties of nickel (II) hydrotalcite for 1,2- propanol oxidation

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Abstract

Graphite electrode modified with [Ni/Al-Cl] hydrotalcite-type anionic clay has been studied with respect to the electrochemical oxidation of the Ni (II) centers. The oxidation of Ni (II) is quasi-reversible and the presence in the hydrotalcite lattice of Ni with mixed oxidation states increases the conductivity of the coverage strongly. It has been explored that these Ni redox systems act as redox mediators for the oxidation of alcohol substrates like1, 2- propanol. Sodium hydroxides, 1, 2-propanol used in this work were analytical grade of Merck origin. Electrochemical studies were carried out in a conventional three electrode cell powered by an electrochemical system comprising of EG&G model 273 potentiostat/galvanostat and Solartron model 1255 frequency response analyzer. A dual Sat'd Ag/AgCl, a graphite rod and a graphite disk electrode were used as the reference, counter and working electrodes, respectively. The [Ni/Al-Cl] HTs was prepared by co- precipitation from carbonate-free aqueous solutions of the metal ions $AlCl_3$ and $NiCl_2.6H_2o$. [1]

We studied the effect of the HTs on the oxidation of 1, 2- propanol and observed that HTs in which Me (II) is a transition metal, improve the charge transport of the material. This happened because the HTs undergone a redox reaction in the range of applied potential in according with following mechanism**:** [2]

$$\text{HT-Ni (II)} + OH^- \Leftrightarrow \text{HT }(OH^-)\text{-Ni (III)} + e^-$$

Also charge transport can be thought as due to a mixed mechanism involving an Telectron hopping along the layers, which is ascribable to an inner redox reaction and a migration of anions inside the interlayers to compensate the positive-extra-charge. In here the OH^- intercalation–deintercalation process plays a key role in the electro neutrality of the HT. It is interesting that the oxidation current of propanol on graphite electrode modified with [Ni/Al-Cl] hydrotalcite is much more than Ni rod electrode. In addition 1- propanol presented the more oxidation current than 2- propanol that is because of less steric hindrance of 1- pro to 2- pro. In particular, the sensitivity of the measurements depends both on the number of oxidisable sites and on the analyte dimension, and hence, on the dimension of the interlayer spacing.

Keywords: *chemically modified electrodes; Ni (II) hydrotalcite; 1, 2- propanol electroxidation*

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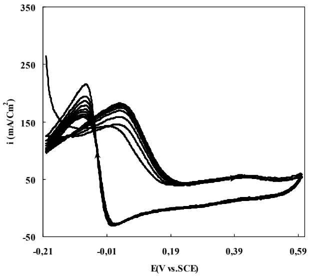

Fig. 1. Cyclic voltammograms of Au/PAni/Ti electrodes in 1M NaOH + 10mM glucose

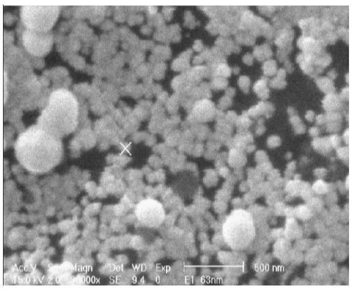

Fig. 2. SEM micrograph of PAni films containing electrodeposited gold particles

Characterization and Fabrication of Ni Nanowire

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Abstract

Porous anodic aluminum oxide (AAO) template was prepared in a two-step anodization process. High-purity aluminum foils (99.999%) were used as the starting material. Prior to anodizing, the aluminum was annealed in a vacuum of 10^{-3} Pa at 500°C for 5hr to remove the mechanical stress and obtain homogenous condition for pore growth over a large area. Anodization was carried out under a constant cell voltage 26V in a 0.36M sulfuric acid (H_2SO_4) solution at 0°C for 4hr. The formed alumina was then removed by a mixture of 6wt% H_3PO_4 and 1.8wt% H_2CrO_4 at 60°C for 4hr, and the Al sheet was reanodized under the same condition as the first step for 4hr. An etching treatment was carried out in a 5wt% H_3PO_4 solution at room temperature for 30min to remove the barrier on the bottom side of the AAO template and widen slightly the pores of the AAO template. In order to prepare Ni nanowire array we used a three-electrode electrochemical cell under constant current density that the electrolyte contained a mixture of $NiSO_4$ and H_3BO_3 solution. The morphology of the as-prepared AAO template was observed using a scanning electron microscopy (SEM). The diameter of pores was 19 nm.

Keywords: *Anodization, AAO template, Ni Nanowire, cyclic voltammetry (CV)*

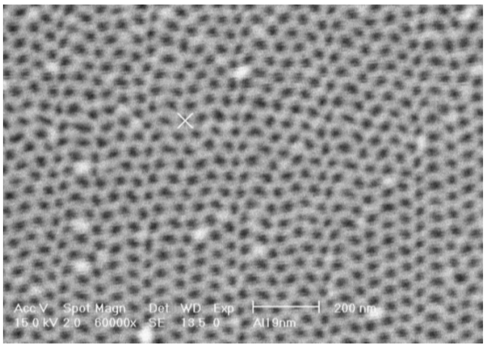

Fig1. SEM micrograph of AAO template

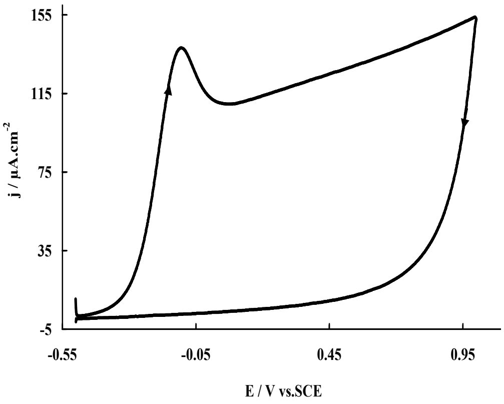

Fig2. Cyclic voltammetry of AAO electrode in $NiSO_4$ solution

Surfactant & Interfacial Electrochemistry
ماده فعال سطحی و الکتروشیمی

بررسی خواص سطح و تجمع مخلوط مواد فعال در سطح دوشاخه و تریتون-ایکس ۱۰۰

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چکیده

از آنجا که مواد فعال در سطح دوشاخه پتانسیل بالایی جهت جایگزین شدن با مواد فعال در سطح عادی را با توجه به ویژگی های منحصر به فردشان دارند، مطالعه هم افزایی مخلوط مواد فعال در سطح دو شاخه با مواد فعال در سطح عادی زمینه مناسبی برای تحقیق درباره برهم کنش آنها و چگونگی عملکردشان می باشد. می بایست توجه شود مواد فعال سطح دوشاخه در مخلوطها ویژگی متفاوتی با مواد فعال در سطح عادی نشان می دهند. از لحاظ صنعتی نیز این مطالعات مورد توجه می باشد زیرا پدیده هم افزایی سبب کاهش مقدار CMC ، افزایش کارآئی محصول و کاهش قیمت تمام شده محصول می گردد. در این پروژه مواد فعال دوشاخه خالص آلکاندیل- آلفا، اُمگا- بیس(آلکیل تری متیل آمونیم برمید) که با نماد m-n-m (m=۱۲،۱۴ n=۲) نمایش داده می شوند سنتز گردید و خواص سطح و تشکیل میسل مخلوط این مواد با ماده فعال در سطح غیر یونی تریتون-ایکس ۱۰۰ مورد بررسی قرار گرفته است. بررسی اثر طول زنجیر در گروه آبگریز بر غلظت بحرانی سطح (*CMC*)، غلظت اضافه سطحی($\Gamma_{\max}$) و حداقل مساحت سطح اشغال شده توسط مولکولهای ماده فعال سطحی *(A_{min})* در محدوده دمایی ۳۰۸ K با کمک دادهای کشش سطحی صورت گرفت. ترکیب میسل و تک لایه سیستمهای مخلوط مواد فعال در سطح با استفاده از نظریه محلول با قاعده (RST) و مدل رابینگ بررسی شد. با توجه به نقص مدل رابینگ در توصیف رفتار مخلوط مواد فعال در سطح از جمله، انرژی مازاد آزاد و ضرایب فعالیت، در این پروژه مدل سه پارامتری غریبی و همکاران در بررسی سیستم مخلوط به کار گرفته شد.

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این مدل با استفاده از معادلات وان لار و مدل غیر تصادفی بودن تشکیل میسل مخلوط ارائه شده است. این معادله شامل سه پارامتر برهمکنش β ، اندازه ρ، و انباشتگی P^* می باشد. نتایج نشان دادند که افزایش طول زنجیر افزایش برهمکنشهای مخلوط مواد فعال در سطح را در پی دارد. جهت بررسی پایداری میسلهای مخلوط ازمدل مائدا، جدایی فاز و ترمودینامیک مولکولی(مدل ناگاراجان) استفاده شده است.

واژه های کلیدی: *مخلوط مواد فعال در سطح دوشاخه،خواص سطح، هم افزایی*

The solvophobic (co-solvent) effect on intermolecular interactions of cationic and anionic mixed surfactant in mixed monolayers and mixed micelle

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Abstract

Surfactants are widely used in both industry and every day life, and the properties of aqueous solutions have received considerable attention. In recent years, however many authors have turned their attention to micelle formation and aggregation process of micelles in solvent systems constituted by mixture of water with some polar organic solvents. In the present study, the effect of EG as Cosolvent on the adsorption and association properties of cationic(Hexadecyltrimethylammonuimbromide) and anionic(Sodium dodecyl sulfate) mixed surfactant has been investigated using surface tension and conductometry measurements. Though a surface tension and conductometry study, we have obtained the change of the CMC and α with EG addition. From these data, the increase in mixed CMC value with increase EG amount in water- EG systems can be explained on the basis of two factors, (1) the structure breaking ability of EG and increase the solubility of the hydrocarbon chain of the surfactant monomers, and (2) the reduction of the dielectric constant of the medium and increase the electrostatic repulsion interaction in ionic surfactant systems. Additionally, the co-solvent effect on surfactant- surfactant interaction in binary ionic/ionic surfactants was studied using calculating the values of β parameters. It was shown that the addition of EG to solution reduces the interaction both in the mixed micelle (β^M) and in the mixed monolayer (β^σ) ,with a greater effect on the interaction in the mixed monolayer than mixed micelle. This can be attributed to a great reduce of the hydrophobic interaction in mixed monolayer due to presence of EG. In higher percentage of EG, the synergism is increased due to increase the attraction electrostatic interaction between ionic head groups after mixing.

Keywords: *Mixed micelle, Surface tension, Conductivity, Monolayer, CTAB, SDS, Ethylene glycol, interaction parameter.*

مطالعه ترمودینامیکی مواد فعال در سطح دوشاخه

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چکیده

مواد فعال در سطح دوشاخه به واسطه خواص خاصشان کاربردهای گسترده ای در زمینه های مختلف از جمله صنایع معدنی، صنایع پتروشیمی، صنایع شیمیایی، داروسازی، تحقیقات بیوشیمی و به عنوان کاتالیزور در واکنشهای آلی ومعدنی پیدا کرده اند. در این پروژه مواد فعال دوشاخه خالص آلکاندیل- آلفا، اُمگا- بیس(آلکیل تری متیل آمونیم برمید) که با نماد m-n-m (m=۱۲،۱۴ n=۲،۴) نمایش داده می شوند سنتز گردید و خواص سطح و تشکیل میسل مورد بررسی قرار گرفته است. در این بخش بررسی اثر طول زنجیر در گروه آبگریز و گروه فضاگیر و همچنین اثر دما بر غلظت بحرانی سطح (*CMC*)، غلظت اضافه سطحی(Γ_{max}) و حداقل مساحت سطح اشغال شده توسط مولکولهای ماده فعال سطحی(A_{min}) در محدوده دمایی K ۳۲۳-۲۹۸ با کمک دادهای کشش سطحی صورت گرفت. روند تغییرات *CMC* با دما U-شکل است. افزایش دما افزایش Γ_{max} را در پی دارد. سهم های مختلف انرژی آزاد که در تشکیل میسل مشارکت دارند، از طریق مدل ترمودینامیک مولکولی(ناگاراجان) بررسی گردید. تغییرات انرژی آزاد تشکیل میسل، با دما هم خوانی باروند تغییرات *CMC* دارد. از طریق پارامتر انباشتگی، شکل تجمعی میسلهای خالص مواد فعال در سطح دوشاخه پیش بینی شد که با نتایج تجربی تطابق دارد. ویژگی های ترمودینامیکی نظیر ΔH_{mic}، ΔG_{mic} و ΔS_{mic} در محدوده دمایی K ۳۲۳-۲۹۸ با کمک دادهای کشش سطحی و هدایت سنجی مورد ارزیابی قرار گرفتند. پدیده جبران آنتالپی-آنتروپی در این گونه مواد فعال در سطح دوشاخه مشاهده گردید. دمای جبران، در این گروه از مواد فعال در سطح دوشاخه تقریبا یکسان می باشد. ترتیب پایداری میسل به صورت ۱۴-۲-۱۴ >۱۴-۴-۱۴>۱۲-۲-۱۲>۱۲-۴-۱۲ است.

واژه های کلیدی: *مواد فعال در سطح دوشاخه، خواص ترمودینامیکی، خواص سطح.*

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[1] دانشجو کارشناسی ارشد دانشگاه تربیت مدرس

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The Electrolyte Effect on the Micellization and Monolayer Properties of Ionic/Ionic Surfactants Mixture

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Abstract

In the present work, the adsorption behavior at the liquid–air interface and micellization characteristics of mixtures of cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) in aqueous media containing different concentrations of NaBr were investigated by surface tension and conductometry measurements in cationic-rich and anionic-rich regions. From plots of surface tension (γ) as a function of solution composition and total surfactant concentration, we determined the critical micelle concentration (CMC), minimum surface tension at the CMC (γ_{CMC}), surface excess ($\Gamma_{\max}$), and mean molecular surface area ($A_{\min}$). On the basis of regular solution theory, the compositions of the adsorbed film (Z) and micelles (χ_{M}) were estimated, and then the interaction parameters in the micelles (β_{M}) and in the adsorbed film phase (β_{σ}) were calculated. For all mole fraction ratios, the results showed synergistically enhanced ability to form mixed micelles as well as surface tension reduction. It was observed that, for both the planar air/aqueous interface and micellar systems, the nonideality decreased as the amount of electrolyte in the aqueous medium was increased. This was attributed to a decrease of the surface charge density caused by increasing the concentration of bromide ions. Also, Analysis of the variations of the specific conductivity (κ) and surface tension (γ) with changing concentration of CTAB or SDS in the cationic-rich and anionic-rich regions revealed a phase transition from vesicles to mixed micelles.

Keywords: *Vesicles, CTAB, SDS, Conductometry*

Interaction of anionic azo dye with cationic , anionic and nonionic surfactant

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Abstract

Dye – surfactant interactions are subjects of numerous investigations. Surfactants are used as solubilizer for water in soluble dyes, to break down dye aggregates in order to accelerate absorption processes on fiber, as auxiliaries in most textile finishing processes such as wetting dispersing dyeing and finishing.

In this work, the effect of alkyl chain and head group on the interaction between an anionic dye (CONGO RED) and cationic , anionic and nonionic surfactants have been investigated using surface tension, conductometric and UV/Vis techniques. The conductance of aqueous solution of CONGO RED was measured in the presence of cationic surfactants. Six surfactants were used: DTAB , CTAB , CPC , CPB , SDS and TX-100. The interaction parameter (β^{m} , β^{σ}) , equilibrium constants and other thermodynamic were calculated on the basis of a theoretical model. The result sowed the stability of dye – surfactant complex decreased due to change trimethylammonium head group to pyridinium. The results of surface tension confirmed that there are two types of aggregation. One of them is complex and another one is mixed micelle. The results obtained from UV/Vis spectroscopy confirmed this.

Keywords: *Dye – surfactant interaction, thermodynamic, interaction parameter.*

تاثیر طول زنجیر، سر قطبی و یون مخالف روی برهمکنش مخلوط مواد فعات سطحی

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چکیده

باتوجه به اهمیتی که مواد فعال سطحی از جنبه کاربردی وتحقیقاتی دارند وهمچنین با مد نظر قراردادن این نکته که بسیاری از خواص مخلوط دوتایی این مواد متفاوت با خواص آنها در حالت خالص می باشد غلظت بحرانی میسل مخلوط دوتائی ستیل تری متیل آمونیم برمیدها (C_{16}TAB) و ستیل پیریدینیم کلرید (CPC) و ستیل پیریدینیم برمید(CPB)با Triton X-100 بوسیله روشهای کشش سطحی و هدایت سنجی تعیین شدند. با استفاده از کشش سطحی، غلظت اضافی سطح (Γ_{max})، فشار سطحی(Π_{CMC}) و حداقل مساحت سطح اشغال شده توسط مولکولهای ماده فعال سطحی، ارزیابی شدند. درجه تفکیک یون مخالف با استفاده از هدایت سنجی تخمین زده شد. نتایج نشان دادند که با افزایش طول زنجیر مواد فعال سطحی دو پیکره و رایج، پایداری میسل افزایش می‌یابد. در حالی که پارامتر برهمکنش و پایداری میسل با تغییر گروه سر از تری متیل آمونیم به پیریدینیم تغییر قابل ملاحظه ای ندارد. درجه تفکیک یون مخالف (α) نیز با افزایش طول زنجیر همولوگهای C_nTAB افزایش می‌یابد. در صورتی که افزایش طول زنجیر در همولوگهای مواد فعال سطحی دو پیکره باعث کاهش α می گردد. همچنین با تغییر یون مخالف از کلر به برم در پارامتر برهمکنش تغییر چندانی حاصل نمی شود.در ادامه با استفاده از روش ولتامتری چرخه ای (CV) ضریب نفوذ میسلهای مخلوط به دست امد و با استفاده از رابطه استوک-اینشتین شعاع هیدرودینامیکی میسلها محاسبه گردید؛نتایج حاصله بیانگر تغییرات جزئی شعاع هیدرودینامیکی میسل با تغییر گروه قطبی و یون مخالف است بطوریکه با تغییر گروه قطبی از تری متیل آمونیوم به پیریدینیم میسل رشد کرده و با تغییر یون مخالف از برمید به کلرید یک کاهش در اندازه میسل مشاهده میگردد.

واژه های کلیدی : *CPB، CPC، شعاع هیدرو دینامیکی میسل، TX-100 ، ولتامتری چرخه ای*

Bioelectrochemistry
بیو الکتروشیمی

Dopamine Biosensor based on Polyaniline Dopped –Multi-Walled Carbon Nanotube (MWCNT)

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Abstract

Polyaniline (PANi), as one of the most important conducting polymers, has been intensively investigated for many years. It is derived mainly from its promising applications in Biosensors , electrochromic materials , photovoltaic devices, rechargeable battery , etc. In general, electropolymerization and chemical polymerization methods are used to fabricate PANi films. In this work the PANi doped withmulti-wall carbon nanotube (MWCNT) was prepared by chemical oxidative polymerization, through direct route using HCl as dopant. polymerization reaction was performed. The morphology of prepared film was examined by scanning electron microscopy (SEM). FTIR results for PANi – MWNT nano composite and PANi nanoparticles indicate that carboxylic acid groups formed at both ends and on the side wall of the MWNT and this approved. The PANi – MWNT biosensor used for determination of dopamine (DA) as an electroactive material. The effect of different scan rate in the electrolyte on the behavior of the biosensor was studied and the transfer coefficient (α) and charge transfer rate constant (Ks) were calculated. The kinetics of the catalytic reaction was investigated usingchronoamperometry technique. The average value of the diffusion coefficient (D) and chemical reaction rate constant (K) were evaluated by chronoamperometric technique for DA.

Keywords *: Biosensor, Polyaniline, Dopamine, SEM, FTIR,*

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Electrochemistry and Spectroscopic studies of Pt(II) Complex, PtCl2(NN) (NN=4,7-Diphe nyl- 1,10-Phenanthroline) bound to calf thymus DNA

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Abstract

Studies of small molecules, which bind at specific sites along a DNA strand as reactive models for protein –nucleic acid interaction, provide routes toward rational drug design as well as means to develop sensitive chemical probes for DNA. In this report the Pt(II) complex, $PtCl_2$(NN) (NN = chelating dinitrogen ligand: 4,7-Diphenyl - 1,10 phenanthroline) was synthesized and characterized by spectroscopic (^1H ,^{13}C NMR) and elemental analysis techniques. and its DNA binding properties have been monitored as a function of complex-DNA molar ratio, in Tris-HCl buffer (pH=7.2), by cyclic voltammetry and UV absorption spectrophotometry method. Upon addition of the complex important changes were observed in the characteristic CV experiments showed that both the anodic and cathodic currents of the mentioned complex decreased with increasing additions of DNA. Also the anodic peak potential (Epa), cathodic peak potential (Epc), and (E1/2) all showed positive shifts, and the changes in the characteristic UV-Vis bands (hypechromism) of calf thymus DNA (CT-DNA),The experimental results show that the mode of binding of the complex to DNA is classical intercalation.

Keywords: *electrochemistry , DNA, Pt(II) complex, intercalation.*

Development of Carbon Paste Electrode Modified by Ferrocyanide-Doped Poly N,N-dimethylaniline; A Sensor for Determination of Cysteamine

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Abstract

In this work, electropolymerization of N,N-dimethylaniline film at the surface of carbon paste electrode (CPE) in aqueous solution was carried out by using potentiostatic method. Then, ferrocyanide ions adsorb at the surface of this polymer by electrostatic interaction between ferrocyanide anions and sites having positive charge of poly N,N-dimethylaniline using cyclic voltammetry method. The electrocataalytic ability of poly N,N-dimethylaniline/ferrocyanide film modified carbon paste electrode (PDMA/FMCPE) was demonstrated by oxidation of cysteamine. Cyclic voltammetry and chronoamperometry techniques were used to investigate this ability. In the optimum pH (pH 7.00) was found that the catalytic reaction rate constant, (k_h), is equal to 2.142×10^3 M^{-1} s^{-1} by the data of chronoamperometry. The catalytic reduction peak current was linearly dependent on the cysteamine concentration and the linearity range obtained was 8.00×10^{-5} M - 1.14×10^{-2} M. Detection limit was determined 7.97×10^{-5} M (2σ). This method has been successfully employed for quantification of cysteamine in real sample.

Keywords: *Poly N,N-dimethylaniline, Ferrocyanide, Carbon paste electrode, Cysteamine, Electrocatalysis*

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Electrocatalytic oxidation of nitrite on a glassy carbon electrode modified with aqua azido nitrato pyridinterpyridin manganese(II) complex and multi-wall carbon nanotubes

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Carbon nanotubes (CNTs), discovered by Iijima [1], are an interesting class of nanomaterials offering high electrical conductivity, high surface area, significant mechanical strength and good chemical stability. This has resulted in the use of CNTs to improve chemical properties of compounds such as porphyrins [2], phthalocyanines and amino-containing complexes by chemically functionalizing them with CNTs. Carbon nanotubes have been known to promote electron transfer reactions when used as electrode modifying material.

This work describes the electrochemical properties of the aqua azido nitrato pyridinterpyridin manganese(II) complex and multi-walled carbon nanotubes immobilized on a glassy carbon electrode. The constructed electrode displayed excellent electrocatalytic behavior towards the oxidation of nitrite ions (in pH 4.0), as evidenced by the enhancement of the oxidation peak current and the shift in the oxidation potential to lower values (by 120 mV) in comparison with the bare GCE. The treatment of the voltammetric data showed that it was a purely diffusion controlled reaction with the involvement of one electron in the rate-determining step. The modified electrode exhibits good catalytic activity for the oxidation of nitrite with good sensitivity over the wide concentration range of 3.33×۱۰^{-۵} - 8.33×۱۰^{-۳} M nitrite, and a detection limit of 5.29×10^{-6} M. The transfer coefficient (α) for electrocatalytic oxidation of nitrite and the diffusion coefficient of this substance under the experimental conditions were also investigated in this study.

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Electrocatalytic Oxidation of Formaldehyd by Silver Modified Polythiophenes Electrodes

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Electropolymerization of thiophene and its derivatives in acetonitrile as the solvent for electropolymerization reactions and tetrabutylammonium hydrogen sulphate (TAHS) were carried out under inert atmosphere by cyclic voltammetry technique. Those monomers which electropolymerized under the experimental conditions were immersed into silver nitrate solution to let silver reduce onto the polymer films. The coated Pt electrodes with Ag-Polythiophenes were then examined for their electrocatalytic activities by oxidation of basic formaldehyde solutions. Cyclicvoltametric studies revealed that the electrocatalytic activity of the modified electrode silver-poly 3,4-ethylenedioxythiophene was the most efficient when compared with the other electrodes.

Electrocatalytic oxidation of 6-thioguanine at a surface of *p*-aminophenol modified carbon paste electrode

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Abstract

A *p*-aminophenol modified carbon paste electrode (*p*-APMCPE) was constructed and used for the determination of an anticancer drug, 6-thioguanine (6-TG). The cyclic voltammogram showed that the electrocatalytic oxidation of 6-TG at the surface of *p*-APMCPE occurs at a potential about 840 mV less positive than that the unmodified electrode. Square-wave voltammetric results presented that the electrocatalytic oxidation peak currents of 6-TG at pH 9.0 had two linear dynamic ranges in the range of 0.2 to 8.0 and 8.0 to 350.0 μM 6-TG with a detection limit of 0.08 μM. The kinetic parameters such as electron transfer coefficient (α) and the rate constant were determined for the chemical reaction between 6-TG and *p*-aminophenol. Finally, this method was evaluated for the determination of 6-TG in 6-thioguanine tablets and urine samples.

Keywords: *Hydrochlorothiazide, Ferrocenedicarboxylic acid, Cyclicvoltammetry, Electocatalysis.*

Carbon nanotube paste electrode incorporating 14(4-Hydroxy phenyl)-14-H-dibenzo[a,j]-xanthene for sensitive voltammetric determination of cysteine

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Abstract

A chemically nanotube modified carbon paste electrode constructed by incorporating a new organic modifier 14(4-Hydroxy phenyl)-14-H-dibenzo[a,j]-xanthen was used as a sensitive electrochemical sensor for detection of cysteine. The resulting electrode exhibits catalytic properties for the electrooxidation of cysteine and lowers the overpotential for the oxidation of this compound. Different parameters like pH and composition of the electrode were optimized. The mechanism of oxidation of cysteine was investigated by cyclic voltammetry. Differential pulse voltammetric analysis of cysteine shows two linear ranges from 4 µM to 0.08 mM and from 0.2 mM to 0.8 mM. The detection limit was obtained 2µM. The modified electrode has very stable electrochemical responses toward cysteine and a long lifetime. The modified electrode was successfully used for the determination of cysteine in the pharmaceutical products and simulated human serum samples.

Keywords: *Carbon paste electrode; Modified electrode; Carbon nanotube; 14(4-Hydroxy phenyl)-14-H-dibenzo[a,j]-xanthene; Cysteine*