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Welcome to the 12th Annual Electrochemistry Seminar of Iran

Dear attendants

On behalf of organizing committee of the 12th Annual Electrochemistry Seminar of Iran, I'm delighted to welcome you all to Tarbiat Modares University.

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

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

We whole heartedly hope that your participation in the 12th Annual Electrochemistry Seminar of Iran in Tehran will be fruitful.

Cordially
Hossein Gharibi

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Key Speaker

Professor Ali Asghar Ensafi

“The Role of Nanomaterials in Energy Sources Development and Storage Devices”

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The Role of Nanomaterials in Energy Sources Development and Storage Devices

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Abstract

Hydrogen is the most plentiful element in nature, which is an appropriate substitute for nonrenewable and environmentally destructive fossil fuels due to some advantages such as renewability, storability, portability and also being non-pollutant [1]. The main advantage of hydrogen is its environmentally friendly property since water is produced as the only by-product [2] and has an excellent energy density by weight. In the present time, platinum and platinum alloys are the best catalysts for hydrogen evaluation reaction (HER), but their application is often limited due to some limitation in platinum preparation (for instance its high cost). So the search for new methods to reduce loaded platinum in HER catalysis has been a topic of current interest [3]. Also, Electrolysis of water to produce oxygen and hydrogen (i.e., $H_2O \rightarrow H_2 + 1/2O_2$) provides a favorable route for the large-scale storage of energy from the sun or other renewable resources. Over the past several decades, electrochemical water splitting has attracted a lot of attention as a critical process in hydrogen production from electricity [4]. Moreover, Li-ion batteries have been used in energy-storage applications, due to their superior charge storage properties (including high capacity and low self-discharge rates) in comparison with other rechargeable batteries. However, to achieve super-high energy density, advanced electrode materials with high energy storage capacities must be developed to replace traditional $LiCoO_2$ cathode and graphite anode materials. Here, we introduce different new electrochemical nanomaterials for electrochemical hydrogen/oxygen generation or as a hydrogen storage, and or as supercapacitor and/or several anodes for Li-battery, based on the fabrication of several new nanohybrids. One of them is modified polyoxometalates; that was decorated on poly diallyldimethylammonium chloride–reduce graphene oxide (PDDA–rGO) and PDDA–CNT. Then, Pt nanoclusters were decorated at the surface of $[PW_{11}NiO_{39}]^{5-}$@PDDA–CNT and at $[PW_{11}NiO_{39}]^{5-}$@PDDA–rGO to fabricate new catalysts [3]. Another one is based on bimetallic silicon nanostructures (Pt–M, M: Pd, Ru, Rh) on reduced graphene oxide (rGO) [2], Pd/Pt

bimetallic nanofoam (Pd/Pt NFC) on Cu nanofoam substrate [1], Pd#LDH/rGOs modified with some polymer layers as a hydrogen storage [4,] (Al-M/LDHs) modified reduced graphene oxide (rGO) and on RuO_2-decorated exfoliated graphene oxide (RuO_2-EGO) [5], nitrogen doped graphene oxide (rNGO) rNGO/LaNi-LDH [6] and rNGO/Au$^{@}$LaNi-LDH [6], polybenzimidazole and polybenzimidazole/MoS_2 hybrids [7], . The nanocomposites and nanohybrids are characterized in detail using different electrochemical and spectroscopic methods. The nanohybrids exhibited excellent electrocatalysts for electrochemical hydrogen evolution reaction with a small Tafel slope, which is one of the best candidates among all the or lower Pt and/or non-Pt electrocatalysts for electrochemical hydrogen evolution reaction with highly competitive performance relative to various hydrogen generation electrocatalytic materials such as MoS_2 and WS_2, and Pt. Recently, we have prepared Ni_3S_2/Ball-milled silicon flour as a bi-functional electrocatalyst for hydrogen and oxygen evolution reactions (OER) [8]. The isolated island architecture of the bi-functional (HER and OER electrocatalyst) could act as the promising electrode materials for water splitting using electrochemical methods. Moreover, copper-bismuth oxide ($CuBi_2O_4$) nanoparticles were supported on nanoporous stainless steel by a simple electrochemical deposition method and then was employed as a binder-free electrode for supercapacitor application [9].

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Content of tables

A hydrothermal-electrochemical synthesis of MnO$_2$ nanostructures for Zn-Air applications

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Abstract

In recent years, metal-air batteries that are receiving attention for both fundamental and industrial viewpoints, because they exhibit high specific energy density compared to other energy storage devices, in particular the Li-ion systems. Among metal–air batteries, the zinc–air batteries represents a safe, environmentally friendly and potentially cheap and simple way to store and deliver electrical energy for both portable and stationary devices as well as for electric vehicles [1]. In the development of zinc-air batteries, the high performance electrocatalysts for air cathode is an important issue [2]. MnO$_2$ has attracted great attention due to its favorable Oxygen Reduction Reaction activity, redox stability, low-cost and abundance [3].

In this work, manganese dioxide nanostructures were prepared by a hydrothermal-electrochemical method. The syntheses were performed in a closed, Teflon-lined stainless steel reaction vessel as a two-electrode system by constant current mode with a current density of 10 mA⁄cm^2 at 80 and 110 °C. Prepared samples have been characterized using X-ray diffraction (XRD), morphology of the samples has been characterized by field-emission scanning electron microscopy (FESEM). The pore structures of the prepared samples were tested by N$_2$ adsorption-desorption measurements. The electrochemical behaviors of prepared samples were investigated by electrochemical techniques including polarization curve and galvanostatic discharge.

The XRD patterns of the as-prepared samples indicating that purely crystalline □-MnO$_2$ were successfully synthesized. The FESEM images showed that the nanoclusters of MnO$_2$ were composed. The size of nanoparticles were about 1–20 nm that reduced by increasing the synthesis temperature. The N$_2$ adsorption-desorption measurements results showed that isotherms of these samples were of typical IV classification and exhibited clear hysteresis loops which were characteristic of mesoporous materials. The results of electrochemical tests revealed that the peak power density of Zn-Air batteries were 80 mW/cm^2 which increased to

120 mW/cm^2 when temperature of MnO_2 synthesis was raised from 80 to 110°C. The cells galvanostatic discharge showed maximum discharge current density of 150 and 300 mA/cm^2 for cells, respectively.

Keywords: *MnO_2 nanostructure, hydrothermal-electrochemical synthesis, Zinc-air battery.*

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Electrochemical Determination of the Anticancer Drug Amsacrine at a ds-DNA Modified Graphene Carbon Paste Electrode and its Application as a Label-Free Electrochemical Biosensor

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Abstract

DNA has a key role in the process of life as heritage data are carried with it. DNA is an important target for smaller molecules such as medicines, metals, and carcinogens [1].

The interaction between several anticancer medicines with DNA has been investigated using different methods. Although, these methods are time-consuming and expensive and need more materials, Recently, the electrochemical investigation of interaction between anticancer drugs and DNA has been increased. Among these methods, DNA electrochemical biosensors are one of the main groups [2]. Amsacrine is a well-known anticancer agent with a good activity against refractory acute leukemias as well as Hodgkin's and non-Hodgkin's lymphomas [3]. In current research, based on the interaction between dsDNA and amsacrine, amsacrine was determined by a simple, fast, reliable, and sensitive DNA biosensor. After optimizing the main experimental parameters, This DNA-coated GPE was fabricated to evaluate its performance analytically. A linear dynamic range of 7.0×10^{-7}– 10×10^{-4} M was obtained for amsacrine. Ultimately, the proposed biosensor was found to be capable of successfully analyzing human serum and urine samples.

Keywords: *Amsacrine, Graphene, Carbon paste electrode, DNA*

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A Label-Free Electrochemical Biosensor Based on Carbon Paste Electrode Modified with Graphene and ds-DNA for the Determination of the Anti-Cancer Drug Tamoxifen

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Abstract

In nanotechnology and biosensor technology, DNA serves as an excellent building block for the construction of new devices since being stable, low-cost, and easily adaptable [1]. In rational design of drugs, a structural guideline can be attained via the interaction between DNA and small molecules, which contributes to an improved synthesis of new drugs with higher selective activities and clinical efficacy and lower toxicities. Drug binding interactions with DNA have been investigated through various techniques. The interaction mechanism can be evidenced through observing DNA electrochemical signals before and after interacting with its targeted drug. Also, these drugs can be quantified by this interaction besides determining new drugs targeting DNA [2]. As an oral nonsteroidal antiestrogen drug, Tamoxifen has been widely utilized and developed via several methods for the prevention and treatment of breast cancer [3]. In this study, we constructed a carbon paste electrode modified with graphene and ds-DNA and studied the electrochemical interaction of ds-DNA and Tamoxifen. The DPV response to ds-DNA-GPE to various tamoxifen concentrations, as well as a calibration curve for tamoxifen detection with the help of the proposed biosensor under the optimal experimental conditions. A linear relationship was exhibited to exist between the tamoxifen concentration over the range of 8.0×10^{-7}– 8.5×10^{-5} M and the peak current at ds-DNA-GPE by the calibration graph. Furthermore, the proposed method was applied to tamoxifen determination in human blood serum and urine samples.

Keywords: *tamoxifen, Carbon paste electrode, DNA, Graphene*

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A Sensitive Electrochemical DNA Biosensor for Anticancer Drug Topotecan Based on Graphene Carbon Paste Electrode

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Abstract

A main anti-cancer medicine is topotecan (TPT), which is a water-soluble derivative of camptothecin. TPT is so effective for treatment of human ovarian cancer, cervical and small cell lung cancer [1].Some methods have been applied to determine topotecan and only a few voltammetric methods was used to study the electrochemical behavior of topotecan. The study of interactions between drug and DNA is of present overall interest and importance, particularly to design novel DNA-targeted medicines. Among the methods used to study the interaction between DNA and drug, electrochemical techniques are particularly promising because of their high sensitivity and selectivity along with reasonably low costs [2]. Graphene is a low-cost substance with excellent mechanical, electrical and thermal features and it has been recently considered considerably. Owing to mentioned features, graphene is a good alternative for using in electrochemical biosensor [3].In current research, the interaction of topotecan with DNA is investigated with a graphene paste electrode and in solution phase via DPV. Based on the interaction between dsDNA and topotecan, topotecan was determined by a simple, fast, reliable, and sensitive DNA biosensor. After optimizing the main experimental parameters, This DNA-coated GPE was fabricated to evaluate its performance analytically. A linear dynamic range of 7.0×10^{-7}– 9.0×10^{-5} M was obtained for topotecan. Ultimately, the proposed biosensor was found to be capable of successfully analyzing human serum and urine samples.

Keywords: *topotecan, Drug-DNA interaction, Graphene*

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Protection of 316L Stainless Steel by $Mn_{0.5}Mg_{0.5}Fe_2O_4$/Chitosan in HCl and H_2SO_4 Media

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Abstract

The use of corrosion inhibitors is one of the most economical and simplest method for overcoming the corrosion problems [1-3]. From the standpoint of safety, the expansion of non-toxic and effective inhibitors is required. Chitosan is a natural polycationic copolymer and is one of the important biopolymers that extensively used in pharmaceutical applications, such as in tissue engineering materials, drug carriers [4]. Chitosan is rich in hydroxyl and amino groups, so it is a good potential inhibitor. Umoren et al. were estimated the inhibition action of chitosan on the corrosion of mild steel in 0.1 M HCl solution. They found that chitosan inhibit corrosion of mild steel even at a very low concentration and inhibition efficiency increases with a rise in temperature up to 96 %at 60°C and then drops to 93 % at 70 °C, while it slightly increases with an increase in chitosan concentration [5]. The inhibition action of 2-N,N-diethylbenzene ammonium chloride N-oxoethyl chitosan and 12-ammonium chloride N-oxododecan chitosan on the corrosion of carbon steel in 1 M HCl has been evaluated. The results illustrate that the inhibition efficiency of 2-N,N-diethylbenzene ammonium chloride N-oxoethyl chitosan in 1 M HCl at varying temperature is higher than for chitosan and 12-ammonium chloride N-oxododecan chitosan [1]. The main aim of this study is investigation of inhibition action of $Mg_{0.5}Mn_{0.5}Fe_2O_4$/chitosan nanocomposite on the corrosion of 316L stainless steel in 2 M HCl and 1 M H_2SO_4 solutions. The synthesized nanocomposite was evaluated using X-ray diffraction (XRD) and field emission scanning electron micrographs (FESEM). The corrosion behavior of 316L stainless steel was estimated by using electrochemical methods including potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) methods in both acidic media in the absence and presence of various concentration of chitosan, $Mg_{0.5}Mn_{0.5}Fe_2O_4$ and $Mg_{0.5}Mn_{0.5}Fe_2O_4$/chitosan nanocomposite. In order to designed the effect of temperature on the behavior of nanocomposite, polarization measurements in the temperature range of 25-65 °C was carried out for different concentration of three mentioned inhibitor.

Comparing the results indicated that, for both acidic media, the inhibition efficiency of $Mg_{0.5}Mn_{0.5}Fe_2O_4$/chitosan nanocomposite at all investigated temperature is higher than chitosan and $Mg_{0.5}Mn_{0.5}Fe_2O_4$. The nanocomposite was found to inhibit corrosion even at a very low concentration (0.1 g/L) and high temperature (99 % at 65°C). Because of these features and non-toxic properties of nanocomposite, we think this inhibitor can be introduced for use in the oil and gas industry.

Keywords: *Corrosion, Chitosan, Spinel, Potentiodynamic polarization, electrochemical impedance spectroscopy (EIS)*

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Sonochemical synthesis of mesoporous MnO_2 for Zinc-Air battery applications

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Abstract

MnO_2 is one of the candidate materials for the application to electrochemical capacitors, Li-ion batteries, sensors and catalysts [1]. In energy-storage devices, nano structured MnO_2 has been used as an active material because of its low cost and natural abundance as well as it being environmentally safe [2]. Sonochemical technique has proved to be useful method for generating nano structures of oxide materials with highly pure and unusual properties in short reaction times [3].

Here in, nanostructured MnO_2 was synthesized using a simple one-step sonochemical method in the presence of poly (ethylene glycol)-block poly (propylene glycol)-block-poly (ethylene glycol) (P123) as a soft template as well as a reducing agent. Prepared samples have been characterized using X-ray diffraction (XRD), morphology of the samples has been characterized by field-emission scanning electron microscopy (FESEM). The pore structures of the prepared samples were tested by N_2 adsorption-desorption measurements. The activity and stability of this catalyst was evaluated by preparing air electrodes with primary Zinc−Air batteries that consume ambient air.

The XRD results indicated that MnO_2 sample was poorly crystalline. The FESEM images showed that the nanostructure of MnO_2 was composed. The size of nanoparticles were about 10-13 nm. A BET surface area of 87 m^2/g is achieved for mesoporous MnO_2 sample. The results of electrochemical tests revealed that the peak power density of Zinc-Air batteries were 136.05 mW/cm^2. The cells galvanostatic discharge showed maximum discharge current density of 200 mA/cm^2.

Keywords: *MnO_2 nanostructure, Sonochemical synthesis, Zinc-Air battery.*

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The Electrochemistry Properties Of Ni–W Alloy Coatings Obtained By Pulse Plating From Citrate Media

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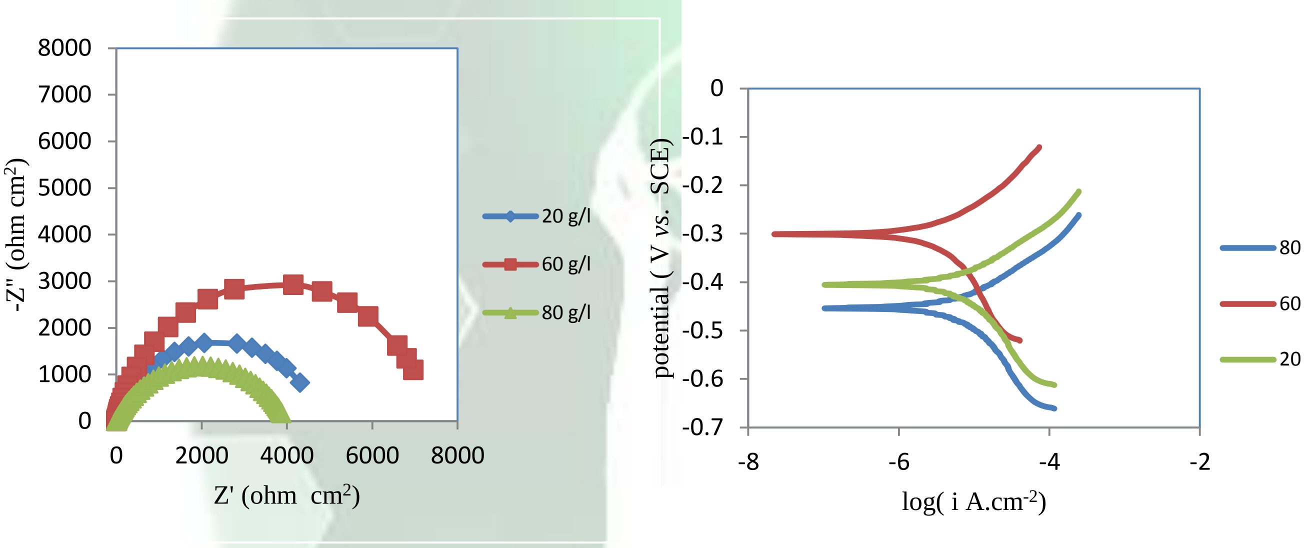
Abstract

pulse plating is an effective means of controlling the microstructure and composition of electrodeposits because it can be used to improve current distribution and modify mass transport. Thus, different problems like hydrogen evolution and uneven deposits caused by mass transport may be overcome and pH local changes minimized. Therefore, recently this method have been received many attentions especially in plating of pure nickel and it's alloys. Among them, Efforts to get plated Ni–W alloys were increased as they proved to have optimum hardness, good corrosion resistance, properly ductility and high thermal stability[1-5]. Previous studies [2] showed that, the corrosion resistance of Ni–W alloys generally increased with W content (up to 11 wt.%). Also it would generally seem that as W content in the alloy increases, grain size diminishes [2]. The objective of this work is to optimize the parameters to obtain a Ni–W alloy with high resistance to corrosion. Effects of tungstate ion concentration, average current density and duty cycle on the properties of the coatings were studied. Ni–W alloy specimens were prepared by electrodeposition using a pulse rectifier on cupper sheets. The plating bath contained 147 g/l $Na_3C_6H_5O_7{\cdot}2H_2O$, 26 g/l NH_4Cl, 26.3 g/l $NiSO_4{\cdot}6H_2O$, 20-60-80 g/l $Na_2WO_4{\cdot}2H_2O$. The optimized coating was tested at 2 two different current densities and duty cycles to study the effect of pulse parameters on the properties of deposits. The coatings were characterized by Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray Analysis (EDAX) and Vicker's micro hardness tester. Tafel Polarization and electrochemical Impedance methods were used to evaluate the corrosion resistance behavior of the coatings in 0.5M NaCl solution.

The SEM studies revealed the surface of the all coatings had cauliflower-like structure and crack-free. The coatings were obtained from the bath with 60 g/l tungstate concentration, current density of 70 mA/cm^2 and duty cycle of 10% show highest microhardness (719 HV)

and maximum corrosion resistance compared to the other coatings obtained in the 20 or 80 g/l concentration of tungstate. Also with decreasing the current density in the constant duty cycle in the 60 g/l tungstate concentration bath, microhardness decreased (637 HV) and the current corrosion increased (from 5.115 μA/cm^2 to 5.583 μA/cm^2). Increasing duty cycle in the constant current density decreased corrosion resistance of the coating to 5.868 μA/cm^2. As conclusions, beside bath tungstate concentration, pulse current density was the important factor to define chemical composition, hardness and corrosion resistance of the Ni–W coating.

Keywords: *Pulse Electrodeposition, Ni-W alloy coatings, Corrosion resistance, Microstructure characterization microhardness*



Nyquist plots (Z′′ vs Z′) and Potentiodynamic polarization curves obtained for various amounts of Sodium Tungstate concentration

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Electrochemical Determination of Isoproterenol at Silver (I) Complex-Graphene-Modified Glassy Carbon Electrode

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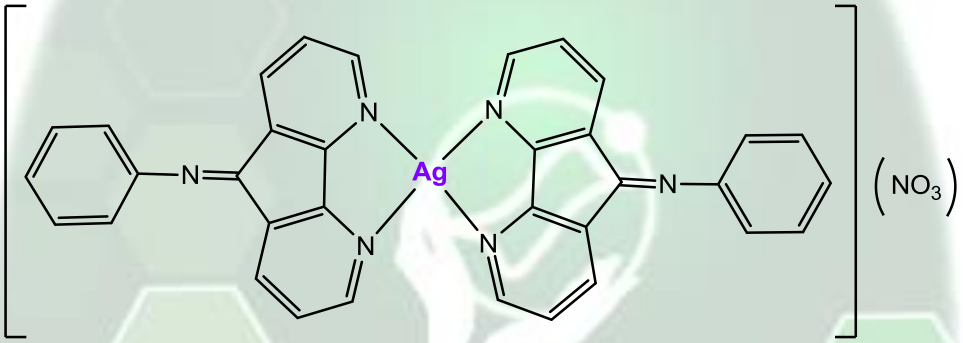
Abstract

Isoproterenol (ISO), is b-adrenergic agonist and synthetic catecholamine that is structurally related to epinephrine but acts almost exclusively on beta receptors. Its primary use is for bradycardia or heart block. By activating β_1 adrenergic receptor in the heart, it induces positive chronotropic, dromotropic, and inotropic effects. It can be used as an inhaled aerosol to treat asthma, although this is currently a rare treatment. Although it activates all beta adrenergic receptors, it works in a similar fashion to selective β_2 adrenergic agonists, e.g. salbutamol, by relaxing the airways to increase airflow. Used with caution, it can also be used to treat torsades de pointes by acquired defect, in conjunction with overdrive pacing and magnesium sulfate. The excessive amount of isoproterenol makes some side effects on human health such as palpitations, angina, Adam-Stokes syndrome, pulmonary edema, hypertension, hypotension, diaphoresis, mild tremors [1]. So, concentration determination of isoproterenol is very essential to control its dosage. Various methods have been developed for the determination of isoproterenol. Among them electrochemical method has drawn much attention by offering advantages including simplicity, good stability and low costs. Unfortunately, isoproterenol, with a large overpotential for oxidization at ordinary electrodes, is not a suitable analyte for these methods. One promising approach for minimizing overvoltage effects is the use of chemically modified electrodes [2]. Graphene is a two-dimensional carbon plane with one-atomic thickness. Since the paper on the freestanding graphene was published, the structure and property of graphene have attracted great attention owing to its particular quantum Hall effect, sensitivity, mechanical hardness, electrical conductivity and so on. These properties suggest wide applications, including field effect transistors, adsorbents, lithium-ion batteries and sensors [3]. In contrast, Ag(I) complex possesses the best catalytic activity and is still the most efficient catalyst for many reactions. Consequently, researchers are interested in the dispersion of Ag(I) complex on graphene. The electrochemical determination of isoproterenol using silver

(I)-graphene-modified glassy carbon electrode (GME) was investigated by cyclic voltammetry (scheme 1, Ag(I) complex). The results showed that the GME exhibited excellent electrochemical activity towards isoproterenol. The plot of catalytic current versus isoproterenol concentration showed two linear segments in the concentration ranges 2.1×10^{-7}–1.0×10^{-5} and 1.0×10^{-5}–1.0×10^{-4} M and a detection limit of 6.4×10^{-8} M. This method is of simplicity, rapidity, and high sensitivity and provides a practicable solution for the selective determination of isoproterenol. The method has been successfully applied to isoproterenol sample analysis.



$[Ag(dian)_2]NO_3$

Scheme 1

Keywords: *Isoproterenol, Silver (I) complex, Graphene, glassy carbon electrode*

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Electrochemical Sensor for Epinephrine Based on a Glassy Carbon Electrode Modified With Carbon Nanotubes/Ag (I) Complex

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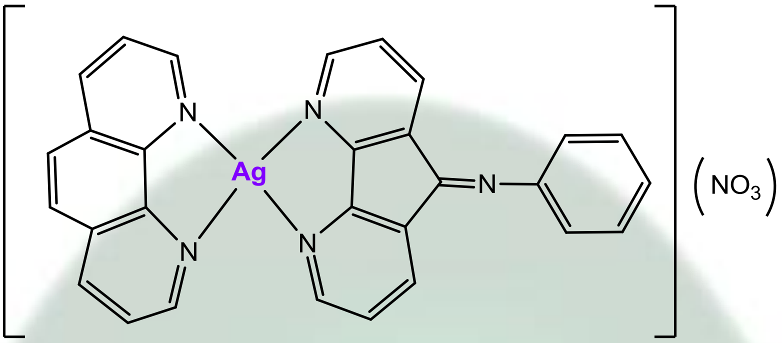
Abstract

Epinephrine, also known as adrenaline, is primarily a medication and a hormone. As a medication it is used for a number of conditions including anaphylaxis, cardiac arrest, and superficial bleeding. Inhaled epinephrine may be used to improve the symptoms of croup. It may also be used for asthma when other treatments are not effective. It is given intravenously, by injection into a muscle, by inhalation, or by injection just under the skin. The common side effects of epinephrine include shakiness, anxiety, and sweating. A fast heart rate and high blood pressure may occur. Occasionally it may result in an abnormal heart rhythm [1]. Therefore, determination of epinephrine is interesting for understanding the physiological functions. Electrochemical procedures have been developed to determine epinephrine based on this electrochemical activities. But electrochemical detection of epinephrine at the surface of bare electrodes has a high overpotential, which results in weak electrochemical responses. To solve this problem, various modified electrodes have been developed for the selective determination of epinephrine [2]. Carbon nanotubes (CNTs) have been widely used in electrochemistry due to their unique one-dimensional (1D) structural, electronic, and physical properties. In the field of chemically modified electrode, one of the most important characteristics of CNTs is their reported ability to promote electron-transfer process [3]. The CNT/Ag (I) complex modified glassy carbon electrode (CNT/Ag/GCE) exhibited high sensitivity in the detection of epinephrine (scheme 1, Ag(I) complex). It has been found that oxidation of EP at this modified electrode occurred at less positive potentials than on bare GCE. The anodic peak current observed were directly proportional to epinephrine concentration between the range of 5.0×10^{-8} and 8.0×10^{-6} M (LOD = 7.0×10^{-9} M). At the same time, this electrode also showed favorable electrocatalytic activity toward some other small biomolecules (such as dopamine, ascorbic acid and uric acid), suggesting the potential applications of CNT/Ag(I) complex for constructing biosensors.



[Ag(dian)(phen)] NO_3

Scheme 1

Keywords: *Epinephrine, Ag (I) complex, Carbon nanotubes, Glassy carbon electrode*

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Determination of Ni(II) by carbon past electrode modified with clinoptilolite nanoparticles-dimethyl glyoxime (NClino-DMG)

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Abstract

Clinoptilolite was pretreated by mechanical ball-mill method to obtain nanoparticles and it was modified by DMG. The raw and modified samples were characterized by XRD, FT-IR, SEM, BET, TG-DTG and energy dispersive analysis X-ray spectroscopy (EDX). The modified Clinoptilolite nano-particles with DMG (NClino-DMG) were used for the modification of carbon paste electrode (NClin-DMG-CPE). The modified electrode was then used for voltammetric determination of Ni(II) in aqueous solution. To determine the interaction of experimental parameters, response surface methodology (RSM) was used. The effects of some key operating parameters such as: zeolite particle size, nature and concentration of the supporting electrolytes, pH of solution, electrode ingredients and potential scan rate on the voltammetric behavior of the modified electrode were studied.

Keywords: *Clinoptilolite, Modified electrode, Voltammetric determination, RSM*

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Modification of a pencil graphite electrode with multiwalled carbon nanotubes capped gold nanoparticles for electrochemical determination of Tramadol

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Abstract

Tramadol (TRA) is a narcotic-like pain reliever that is used for the treatment of moderate to severe pain. TRA like other narcotic drugs used as a pain treatment may be abused. The analgesic potency of tramadol is between weak opioid and morphine. In several controlled clinical studies, oral and parenteral tramadol effectively relieved moderate to severe postoperative pain associated with surgery. In addition, its overdose can cause dizziness, vomiting, and nausea since it is considered as a toxic material in nature [1]. Therefore, developing a sensitive and selective method for its determination in biological samples is very important. Several analytical techniques have been reported for the determination of tramadol, such as adsorptive stripping voltammetry, gas chromatography-tandem mass spectrometry [2], liquid chromatography [3], and ultraviolet spectrophotometry. Electrochemical methods, have attracted more attention in recent years for reasons of their recognition properties, simplicity, high sensitivity, good stability, high selectivity, low cost and fast response. In this research, we introduce a new electrochemical detection method for tramadol based on a pencil graphite electrode modified with multiwalled carbon nanotubes (MWCNT) and gold nanoparticles (AuNPs). The electrochemical sensor was fabricated via immersing of a pencil graphite electrode in multiwalled carbon nanotubes suspension and then deposition of the gold nanoparticles through electrochemical method. The fabrication process of the sensor was characterized by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM). Several significant parameters such as pH, scanning rate and the amount of carbon nanotubes controlling the performance of the sensor were examined and optimized. The influence of interfering species including ascorbic acid, uric acid and citric acid were evaluated and the results showed that the developed sensor has a high selectivity for tramadol. The proposed method shows requisite accuracy, precision, sensitivity and selectivity for determination of tramadol in tablet and biological fluids.

Keywords: *Tramadol, Pencil graphite electrode, Carbon nanotubes, Gold nanoparticles, Modified electrode*

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Nickel and Nickel Hydroxide synergism in Alkaline HER as the Non Nobel Metal Nanoparticles Decorated on the Reduced Graphite Oxide

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Abstract

The development of clean electrochemical energy conversion technologies such as fuel cells and electrolyzers is considered for both of high performance and cost effective properties. Therefore, many attempts have noticed to replace Pt group metals by non-noble ones such as nickel, cobalt and etcetera. For this purpose, it is necessary to improve non noble metals catalytic activity by various methods such as development of supports, hybridization and alloying.

In this work, a novel catalyst was synthesized by hybridization of nickel and nickel hydroxide on the reduced graphite oxide ($Ni\text{-}3Ni(OH)_{2.}\ 2H_2O$ /rG) via a facile and cost effective glycerol mediated solvothermal procedure. The catalyst was evaluated toward the hydrogen evolution reaction (HER) and compared with Ni-rG and $3Ni(OH)_{2,}\ 2H_2O$/rG which had been synthesized with the same method. The structure and morphology of the samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FT-IR) techniques. After that, the catalysts were investigated for HER activity by using a conventional three-electrode electrochemical cell in alkaline media.

Fig. 1 shows the XRD patterns of the samples at three furnace temperatures. Interpretation of results clearly showed that by increasing the furnace temperature, nickel characteristic peaks appears at $2\theta = 44.3$, 51.7 and 76.2 ° which were corresponded to (111), (200) and (220) planes of cubic Ni (JCPDS 04-0850) [1]. The HER activities of three catalysts were investigated in KOH (1 M) solution. As shown in Fig. 2, $Ni\text{-}3Ni(OH)_{2.}\ 2H_2O$ /rG shows the highest electrocatalytic activity compared with others due to synergetic effect between nickel and nickel hydroxide. The edges of $Ni(OH)_2$ participate in dissociative adsorption of water and the production of hydrogen and hydroxyl intermediates [2]. Then, hydrogen adsorption and recombination into H_2 on the nearby Ni sites would be take place. For this reason, lowest tafel slope (b), onset overpotential (η_{onset}), η_{10} (overpotential at 10 mA cm^{-2}) and η_{50} as well as highest exchange current density (j_0) were obtained for $Ni\text{-}3Ni(OH)_{2.}\ 2H_2O$ /rG.

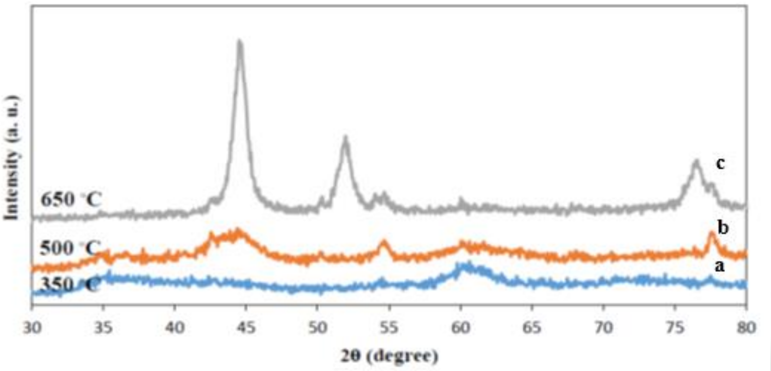

Figure 1. XRD patterns of (a) $3Ni(OH)_2 \cdot 2H_2O/rG$, (b) Ni-$3Ni(OH)_2 \cdot 2H_2O$ /rG and (c) Ni/rG

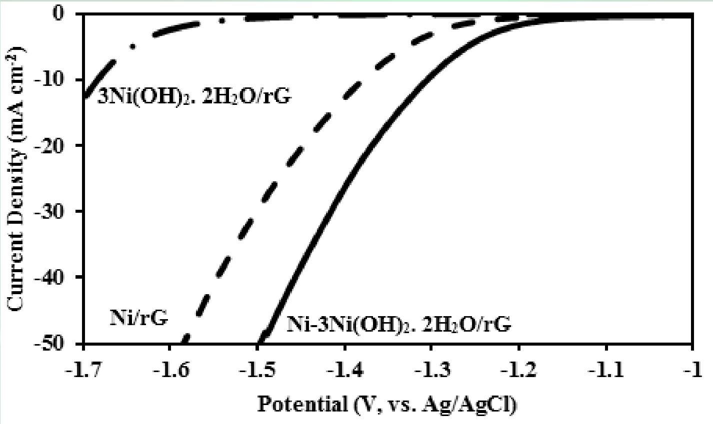

Figure 2. LSV of HER curves for the samples in 1 M KOH at 298 K with a scan rate of 5 mV s^{-1}.

Keywords: *Metal Nanoparticles, hydrogen evolution, alkaline media, synergetic effect*

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A potentiometric screen-printed biosensor for analysis of Kynurenine production to overcome immune barriers to different cancer cell progression

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Abstract

Analysis of kynurenine (Kyn) is of great importance in cancer biology. Degradation of tryptophan (Trp) to Kyn by indoleamine-2,3-dioxygenases 1 and 2 (IDO1/2) and tryptophan-2, 3-dioxygenase (TDO) in tumors and tumor-draining lymph nodes inhibits antitumor immune responses and is associated with a poor prognosis in various malignancies. Tumors increase their consumption of the amino acid tryptophan to evade immune control. Many cancers upregulate a liver enzyme, tryptophan dioxygenase, to drive tryptophan consumption. What's more, the authors find that the primary product of this process, kynurenine, is an endogenous ligand for the aryl hydrocarbon receptor, which mediates invasive tumor growth. This second finding links the fields of toxicology, immunology and cancer biology in new ways, and may help to explain how elevated tryptophan consumption helps tumors to overcome immune barriers to cancer progression. In this work, for the first time, we report on the development of biosensor based on constant current potentiometric stripping analysis (cc-PSA) for determination of Kyn in cancer cell culture media samples [1, 2].

Methods

To prepare the potentiometric biosensor, carboxylated multiwall carbon nanotubes (MWCNTs) were uniformly deposited on the gold screen printed electrode surface (MWCNT-AuSPE) and L-Kynurenine monoclonal antibody (Ab) were uniformly deposited MWCNT-AuSPE (Ab-MWCNT-AuSPE) by EDC and NHS agents. The engineered immunosensor was characterised by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS). Moreover, the parameters that affect the Kyn determination in the biological samples and cell culture were fully investigated.

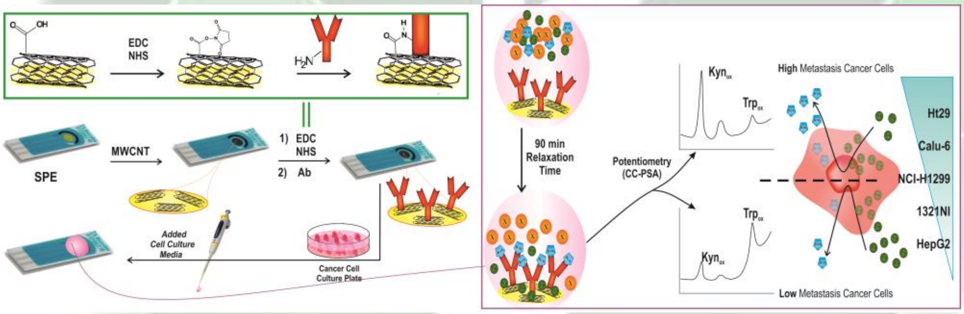
Results and Discussion

In the optimal condition limit of detection (LOD) was found to be 0.5 nM and two linear detection range (LDR) were found to be 0.001 to 1 µM and 1 to 100 µM. Based on these findings, the Kyn biosensor provides a sensitive and reproducible, yet cost-effective, tool with lower LOD for specific detection of Kyn, even in the presence of different interfering substances, in biological samples, thus suggesting the utility of this biosensor for the fast and easy determination of Kyn in clinic. Here, we determination of Kyn production in various human tumors cell culture media (HepG2 (hepatocarcinoma), 1321NI (Astrocytoma), Calu-6 (lung carcinoma), NCI-H1299 (lung carcinoma), HT29 (colorectal carcinoma)). Our results describe a mechanism of tumoral immune resistance based on Trp consumption and Kyn production. We examined the growth of human tumor cell lines which differ in their metastatic ability, in patients by determination of Kyn production.

Conclusions

HT29 cells with high Kyn production showed a greater ability to migrate to sites which favour tumor growth and to replicate to form micrometastases. These studies point to post-extravasation events (migration and growth) as being critical in metastasis formation.

***Keywords**: Immunosensor, Kynurenine, Tryptophan, Antibody, Constant current potentiometric stripping analysis, Screen-printed electrode*



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Study of organic coating/metal behavior at microscopic level

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Abstract

Organic coatings have been recognized as efficient corrosion protective layers for carbon steel substrates [1, 2]. During recent years, extensive experimental efforts demonstrated the potential applications of organic anti-corrosive files based on epoxy resins [3-5]. Here, molecular dynamics (MD) simulations were applied [6] to computationally study the ability of aminoamide-cured bisphenol A epoxy resin (Figure 1 (a)), to form coating layers above carbon steel (represented by FeO and Fe_3O_4 iron oxides, (Figure 1 (b) and (c)). By comparing the initial and final structures (visualized in Figure 2) for cured epoxy resin over each iron oxide substrate, it is seen that all epoxy resin adsorbate molecules moved toward the crystallographic plane (100) in both FeO and Fe_3O_4 adsorbents, and become localized in vicinity of surface. These observations quantitatively indicate the fact that aminoamide-modified epoxy resins have strong intermolecular interactions with the iron oxide. The adsorption affinity of epoxy coating strongly attached to surfaces of FeO and Fe_3O_4 was quantitatively investigated using binding energy parameter ($\Delta E_{binding}$). The binding energies of epoxy resin with FeO and Fe_3O_4 were -843.10 and -2539.02 kcal/mol, respectively. These negative values quantitatively confirm the interfacial interactions exist between epoxy adsorbate and oxide surface (100) in considered iron oxides. Adsorption behavior of aminoamide conjugated epoxy resin was further examined through atomic concentration profiles above surfaces before and after MD simulations. As shown in panel (iv) in Figure 2, the final time-averaged concentration profiles for oxygen and nitrogen atoms (Of and Nf) occurred at lower distances from surfaces as compared to initial concentrations (Oi and Ni), which again quantitatively describes that modified epoxy resin positioned neighboring iron oxide surfaces. All these insights firmly prove the capability of poly (aminoamide) cured epoxy resin materials to serve as effective coatings on carbon steel surfaces when exposed to corrosive electrolytes.

***Keywords**: Organic coating, Metallic substrate, Corrosion, Computation*

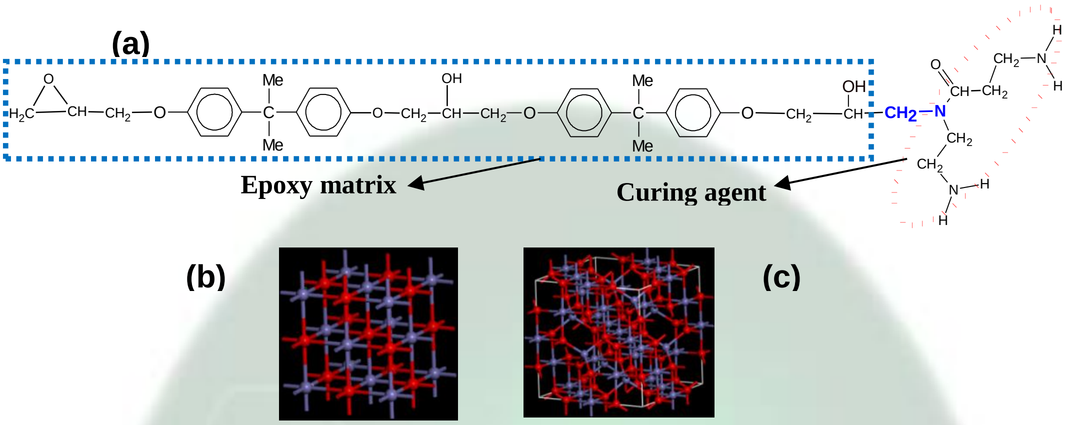

Figure 1- Molecular structures of (a) aminoamide modified bisphenol A epoxy resin, (b) unit cell of FeO, and (c) unit cell of Fe_3O_4 oxides.

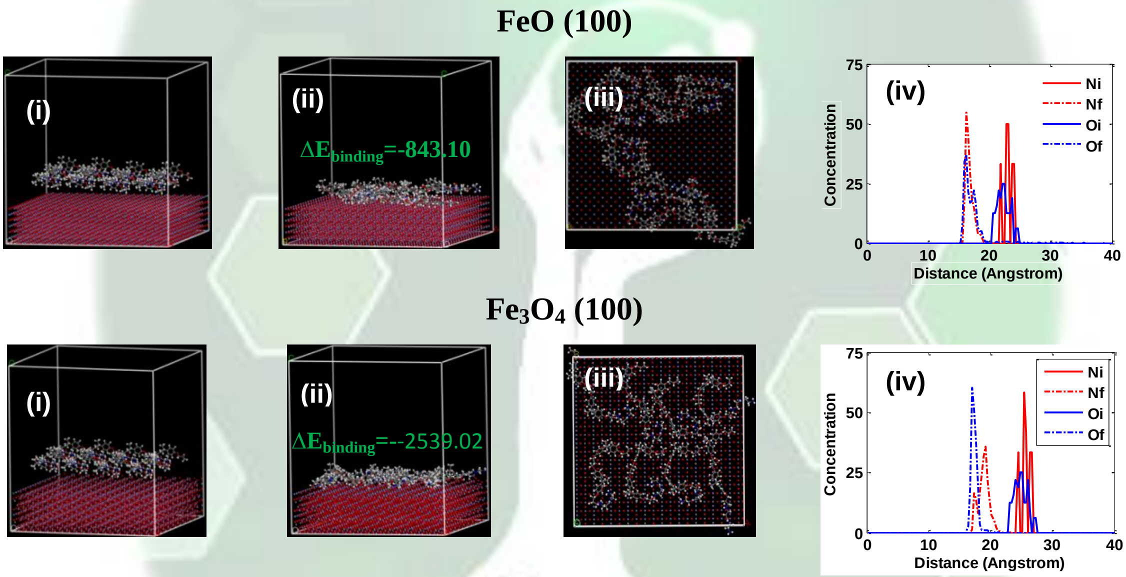

Figure 2- The initial (i) and final (side (ii) and top (iii) views) snapshots of iron oxide substrates interacting with epoxy resin; (iv) Concentration profiles above each surface before (Oi and Ni) and after (Of and Nf) MD simulations.

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How fuel permeation affects the hydrogen bond network in bio-polymeric membranes?

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Abstract

Chitosan biopolymers have been recently employed in various forms as an alternative proton-conducting membrane to Nafion due to its considerably lower methanol crossover properties or higher selectivity (i.e., the ratio of proton conductivity to methanol permeability) [1-3]. The ability of water molecules to transport the proton from anode to cathode compartments relies upon the network of hydrogen bonds emerged among them, which is influenced by the amount of methanol uptake inside the DMFC membrane [4]. In the present research, the effects associated with the methanol crossover on the water hydrogen bonding characteristics across the water/methanol solvated chitosan membrane were examined by means of molecular dynamics (MD) simulation approaches. To this purpose, a range of methanol concentrations (including 0, 10, 20, 40, 60, and 80 wt%) were taken into account. Intermolecular hydrogen bonding interactions of water with chitosan functional fragments, namely, amine (-NH_2), hydroxyl (-OH) as well as hydroxymethyl (-CH_2OH) were studied using radial distribution function (RDF), coordination number (CN), and time evolution of the number of hydrogen bonds. The obtained simulation results for RDFs and CNs (the insets in Figure 1) of water around each function group suggested that water interactions with chitosan chains weakened against an increase in methanol concentration. Such an observation was further confirmed by the reduced number of hydrogen bonds in increasingly methanol solvated chitosan membrane. These findings propose that an increase in methanol sorption (and its subsequent crossover) could significantly diminish the proton conductivity feature of DMFC membranes fabricated from chitosan biopolymers.

Keywords: *Fuel permeation, Bio-polymeric membrane, Direct methanol fuel cell, Modeling*

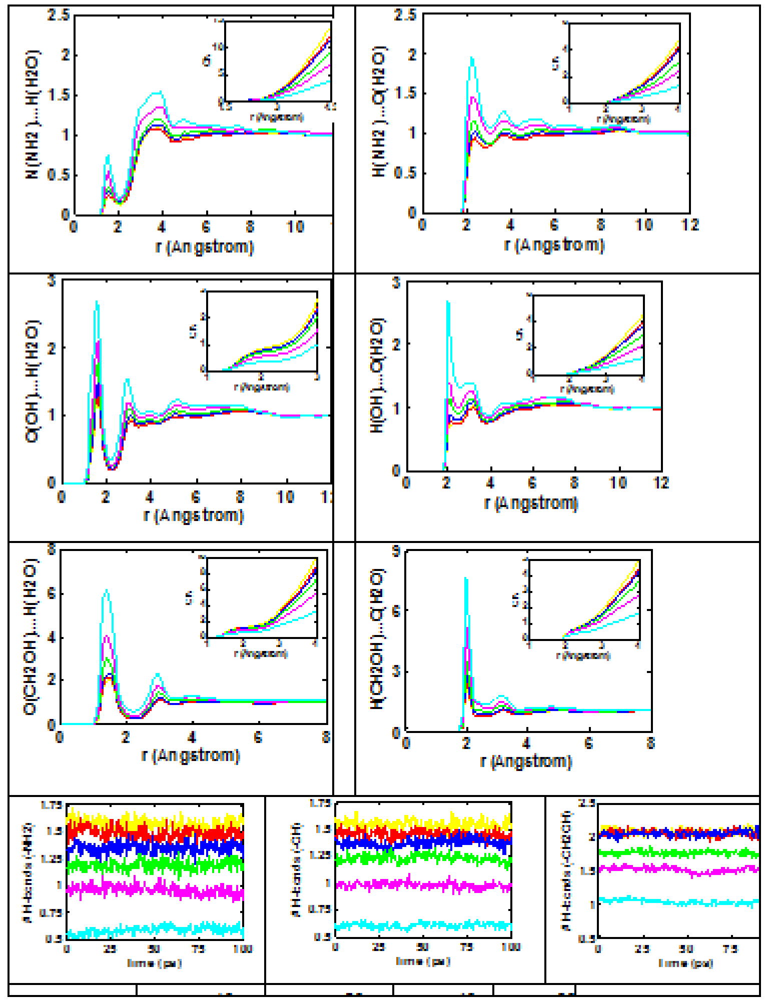

Figure 1 – RDFs, CN, and average number of H-bonds of water molecules with chitosan functional groups at different methanol concentrations.

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Gold/polypyrrole/Graphene oxide nanocomposite modified electrode for simultaneous determination of epinephrine, acetaminophen, and folic acid

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Abstract

Recently, electrochemical techniques using modified electrodes have been developed for simultaneous determination of biomolecules. Simultaneous determination of epinephrine (EP), acetaminophene (AC), and folic acid (FA) is of greater value because of their coexistence in biological systems [1]. Graphene has become one of the most exciting topics of research in the last decades, since it possesses several excellent attributes, including electronic, optical, and thermal properties, chemical and mechanical stability, and large surface area [2]. Polypyrrole (PPy), is one of the most promising Conducting polymers because of its ease of synthesis, good redox property, high conductivity, and excellent environmental stability [3].Gold nanoparticles, which are usually applied to bimolecular immobilization, have many advantages such as excellent catalytic activity, huge surface area, effective mass transport, and hospitable environment [4].

A novel biosensor graphene oxide (RGO)/ polypyrrole (PPy)/gold (Au) nanoparticles nanocomposite modified glassy carbon electrode (GCE) was prepared for simultaneous determination of epinephrine (EP), acetaminophen (AC) and folic acid (FA). Cyclic voltammetry and differential pulse voltammetry methods were used to investigate the modified electrode for the electrocatalytic oxidation of EP, AC, and FA in aqueous solutions. The separation of the oxidation peak potentials for EP-AC and AC-FA was about 210 and 270 mV, respectively. The calibration curves obtained for EP, AC, and FA were in the ranges of 0.4-260, 0.6-210, and 0.7-160 μM, respectively. The detection limits (S/N=3) were 0.071, 0.070, and 0.069 μM for EP, AC, and FA, respectively. Field emission-scanning electron microscopy (FE-SEM), Fourier transform infrared spectroscopy (FT-IR), Raman spectroscopy (Raman), X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) were employed to characterize the modified electrode.

Keywords: *Epinephrine, acetaminophen, folic acid, nanoparticles, Simultaneous determination*

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Optimization of PEM Fuel Cell Operating Conditions to Target Improved Performance

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Abstract

This paper presents a study to evaluate how a proton exchange membrane fuel cell (PEMFC) performance depends on the selected operating conditions and combination of these conditions. First, and by using the design of experiments (DoE) methodology the optimal combination of temperature, operating pressure and cathode relative humidity is studied to obtain as response the power output. A central composite design with 20 experimental runs (6 central points were used to assess the experimental error) was adopted to inspect which factors have significant effects and how they interact to each other. Second, the propagation of error (PoE) methodology is combined with DoE to determine the operating conditions where the response could be less affected by the variation transmitted from the selected operating conditions. A multi-optimization procedure is carried out considering both power and PoE to minimize the variations in the power.

Keywords: *Proton Exchange Membrane Fuel Cells, Design of Experiments, Propagation of Error.*

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Anionic surfactant modified carbon nanoparticles paste sensor for potentiometric nicotine detection in tobacco

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Abstract

Nicotine is the most important alkaloid of tobacco and its determination is very important in medicine, toxicology, human body and tobacco industry. In this work, a simple potentiometric method using modified carbon nanoparticles paste sensor is described for the rapid determination of nicotine.

The formation of carbon nanoparticles was evidenced by scanning electron microscope and energy dispersive X-ray analysis techniques. FTIR confirmed the successful coating of SDS on the surface of carbon nanoparticles. The effect of pH, response time and the composition of modified carbon paste electrode was investigated .The proposed nicotine sensor showed a Nernstian response in the wide detection range from $1x10^{-3}$ to $5x10^{-7}$ M with a low detection limit of $1x10^{-7}$ M. The electrode displayed rapid response, long-time stability (more than 6 months), and high sensitivity. Moreover, the proposed nicotine sensor was also successfully applied for determination nicotine content in tobacco products.

Keywords: *Carbon nanoparticles, Nicotine, Potentiometric sensor, Anionic surfactant.*

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New conservative numerical schemes in mass conservation in solid particles of Lithium-ion battery for efficient simulation

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Abstract

Lithium-ion batteries have been used prevalently as an energy storage system in electric and hybrid electric vehicles (HEVs) due to no memory effect, low self-discharge and high energy/power density. To design a more reliable battery with higher power/energy density, in depth understanding of phenomena occurred inside the battery is required. By using modeling and simulation, these can be handled in a low cost with less restriction against experimental methods. But simulation time is one of the most barriers to use it in applications which require huge amount of data and in battery management systems. Common methods used to solve mass transfer problem in Li-ion battery particles often require significant computational effort which makes the P2D model [1] too slow for optimization, uncertainty quantification and control purposes. Various methods have been employed to overcome these difficulties such as approximate methods including diffusion length method [2], Duhamel's superposition integral [3], polynomial approximation [4], PSS method [5], finite element method [6], finite difference method [7], and finite volume method. Some methods lose their validity under some situation such as non-constant diffusion coefficient and high rate charge/discharge. These methods show less accuracy respect to full order model and sometimes they provide nonphysical results. Since the value of Li concentration at the surface of particle determines the electrochemical reaction rate, accuracy of simulation results highly depend on its accurate value. Moreover, at the surface of particle, concentration gradient is high, so to decrease computational nodes in whole domain, non-uniform mesh spacing scheme is more convenient. To this end, the vertex based finite volume method is chosen to directly involve concentration gradient at the particle surface with variable mesh spacing. With this motivation, a new numerical discretization method is derived for spherical diffusion equation. First original PDE is integrated along spherical radius to obtain a coupled system of

ODEs, then the integrand is interpolated by second degree Lagrange polynomial which provides 3^{rd}-order approximation of integral. Despite of high order accuracy of the method, it is remained tri-diagonal. For solving system of ordinary differential equations the Crank-Nicolson method is used which is A-stable finite-difference scheme with the second order accuracy. This new numerical scheme is proposed to solve P2D mathematical model of a Li-ion battery. As shown in following figure, the results indicate good agreement as compared to Khaleghi et al. study [8] with significant time reduction.

Keywords: *Li battery, Simulation, Solid concentration, Finite volume* method.

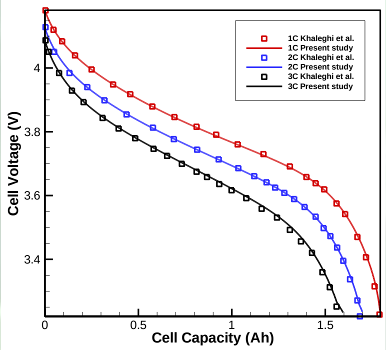

Figure 3 comparison of present study simulation with results of Khaleghi et al. case for several C rates.

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Nanomolar simultaneous determination of Ascorbic acid, Epinephrine, Acetaminophen, L-Tryptophan and L-Tyrosine on a glassy carbon electrode coated with γ-MnO_2/PPy/RGO nanocomposite

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Abstract

Ascorbic acid (AA), Epinephrine (EPI), Acetaminophen (ACT), L-Tryptophan (Trp) and L-Tyrosine (Tyr) are biochemical compounds which play important roles in various biological processes. Usually, they are co-existing substances in biological matrices. Altering the concentration of these species cause to several diseases, so their determination in human fluids such as blood plasma is much essential. These facts have encouraged chemists to develop faster, simpler, and more sensitive techniques such as electrochemistry to meet the various demands using chemically modified electrodes. This is the first report of simultaneous determination of these compounds. Graphene has been used for the sensitive determination of various drugs molecules, due to their excellent conductivity because of π-π staking and synergetic effects with other materials [1,2]. Polypyrrole has been considered as one of the most promising electrode materials to enhance the sensing sensitivity because of its low cost, easy synthesis, relatively high conductivity and good electrochemical/mechanical properties [3-5]. Among various metal oxides, manganese dioxides (MnO_2) have drawn great attention because of its high activity, non-toxicity, low cost, beneficial physicochemical property, relatively environmentally benign and good electrochemical properties [6].

The morphology and structure of the nanocomposite were characterized by the field emission scaning electron microscopy (FE-SEM), Energy-dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD) and raman spectroscopy. Among the bare (GCE), RGO/GCE, PPy/RGO/GCE and γ-MnO_2/PPy/RGO/GCE modified electrode namely γ-MnO_2/PPy/RGO/GCE exhibited much higher electrocatalytic activities toward oxidation of AA, EPI, ACT, Trp and Tyr. The measurements were carried out in pH 7.0 PBS, by Cyclic voltammetry (CV) at a scan rate of 100 mV/s, Differential pulse voltammetry (DPV) at a scan rate of 50 mV/s and Amperometry. The modified electrode gave five separated oxidation peaks

at 150 mV, 410 mV, 600 mV, 780 mV and 990 mV for AA, EPI, ACT, Trp and Tyr respectively. Under optimum conditions, DPV indicated linear relationships between oxidation peak current and AA, EPI, ACT, Trp and Tyr concentrations in the ranges of 1-360 µM, 0.5-410 µM, 0.4-470 µM, 2-190 µM and 0.2-105 µM with detection limits of 0.04 µM, 0.032 µM, 0.033 µM, 0.018 µM and 0.008 µM respectively. Under optimum conditions, amperometry indicated linear relationships between oxidation peak current and AA, EPI, ACT, Trp and Tyr concentrations in the ranges of 2-450 µM, 1-540 µM, 0.8-660 µM, 3-220 µM and 0.5-160 µM with detection limits of 0.1 µM, 0.084 µM, 0.075 µM, 0.056 µM and 0.035 µM respectively The sensor provided a good performance for the simultaneous determination of AA, EPI, ACT, Trp and Tyr by not only greatly enhanced their current responses, but also resolved the overlapping peak potentials as well as decreased the over potentials. In addition, the sensor was successfully applied for the determination of these species in human blood real samples.

Keywords: *Ascorbic acid, Epinephrine, Acetaminophen, L-Tryptophan, L-Tyrosine and* MnO_2 *nanoparticles*

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Nucleation, Growth, and Characterization of MnO2 Thin Films deposited by an Electrochemical Process on ITO

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Abstract

Recent advances in the field of solar cell have led to renewed interest thin films deposited on ITO. Types of thin films such as Cu_2ZnSnS_4[1], Zno/Zno/grapheme[2], Nis[3] and …were applied in solar cell. The metal oxide thin films are an important group of the nanostructured materials. The nano materials of thin films can be synthesized and grown by different techniques [4]. In this study, the substrates applied were ITO-coated glasses with a manganese dioxide nanostructures film were prepared by an electrochemical method. The electro deposition were performed by constant current mode with a current density of 10 mA/cm^2 at lab temperature as two electrode at 1, 2:50, 5 and 60 min. Roughness of the thin films has been characterized by Atomic force microscopy (AFM). The absorption spectra of Mno_2 films with varying thicknesses were obtained between 300 and 1100 nm at room temperature with using UV-Vis spectrophotometer. The AFM images showed that the MnO_2 nanostructures growth mode is island and also, increase in the deposition time caused a decrease in the roughness average of the films surface. The absorption spectra of deposited films were increased by increase in the deposition time.

Keywords: *MnO_2 thin film, electrochemical process, Nucleation, Growth.*

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Electrocatalytic Behavior of Nano Zeolite Modified Carbon Paste Electrode for Oxidation of Hydrazine

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Abstract

liquid fuels such as hydrazine, alcohols, alkaline borohydride and hydrazine solutions have been used in the direct liquid fuel cells [1]. several companies have started to supply power sources based on fuel cell technology to the market. The potential applications of fuel cells are broad, from mobile devices to automobiles and space ships. At present, one of the main focus of fuel cell research is portable devices, such as mobile phones, mp3 players and notebooks [2,3]. Hydrazine is commonly used in some industrial applications such as catalyst, corrosion inhibitor , reducing agent,antioxidant, emulsifier starting material in the production of some insecticides and herbicides, pesticides, dye stuffs, explosive, and the preparation of several pharmaceutical derivatives [4]. In the case of oxidation of hydrazine using electrochemical procedures, unfortunately, ordinary carbon electrodes have a number of limitations for electrochemical detection of hydrazine, such as low sensitivity and reproducibility, high overpotential for oxidation, low stability, and slow electron transfer [5]. Therefore, a main attention has been focused on the development of materials capable of the catalytic electrooxidation of hydrazine. Recently, many groups introduced several compounds to improve the anodic oxidation of hydrazine. Zeolite-modified electrodes have been developed for the determination of various compounds and the use of a mixture of a zeolite and graphite powder in various forms has been projected. Zeolite-supported electrocatalysts can be subjected to improve the performance of the Electrocatalytic responses with reduced over potentials and increased voltammetric/amperometric signals allowing low detection limits and high sensitivities. This paper intends to introduce a novel zeolite modified carbon paste electrode based on Ni modified synthesized nano ZSM-5 crystallites for the electrocatalytic oxidation of ethanol. The rate constant of the oxidation process is calculated using chronoamprometric studies.The used nano ZSM-5 zeolite was synthesized as literature [6]. All other used chemicals were purchese from Merc. The electrochemical experiments were performed on a potentiostat/galvanostat (sama 500-c Electrochemical Analysis system, sama, Iran). SCE was

used as the reference electrode, a platinum wire as the auxiliary electrode, and a home-made carbon paste electrode (ca. 3.4 mm internal diameters) as the working electrode. Appropariated ammount of synthesized nano zeolite was lightly ground and immersed to 10 ml 1 M $NiCl_2$ solution for 1 h. Then the solid was dried. The 30% (W/W) Ni^{2+}-zeolite to graphite powder paste was made by mixing the given quantity of Ni^{2+}-zeolite and graphite powder in diethyl ether and the solvent was evaporated by stirring a mixture. Then paraffin was blended by hand mixing and the resulting paste was inserted in the bottom of a glass tube. The electrical connection was implemented by a copper wire fitted into the opposite opening of the glass tube. For the comparission the unmodified carbon paste was prepared. Obtained results show that proposed modified carbon paste electrode can used for electrocatalytic oxidation of hydrazine as a fuel for fuel cell and the catalytic rate constant for this process was calculated as $9.6*10^3\ M^{-1}\ s^{-1}$ (Fig 1).

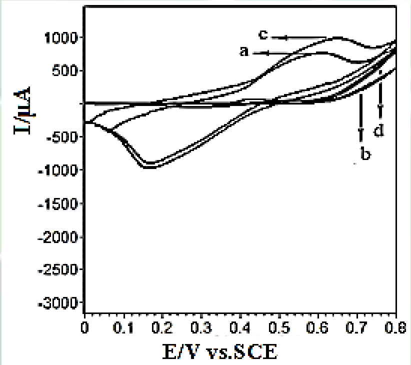

Figure1, Cyclic voltamograms for (a) Ni/Zeolite/CPE, (b) CPE in the absent and (c) Ni/Zeolite/CPE, (d) CPE in the presence of 0.11M hydrazine in the 0.1M NaOH at scan rate 20mVs^{-1} .

Keywords: *Hydrazine, Nano Zeolite, catalysis, Cyclic Voltametry, Fuel Cell*

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Electrochemical study of doxorubicin on the surface of SBA-15 modified screen -printed carbon electrode

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Abstract

Doxorubicin (DOX), has been nearly recognized as the ‘‘gold standard’’ for the treatment of various cancers including solid breast, ovarian, lung and liver tumors. However, the side effects such as systemic toxicity, cardiotoxicity and drug resistance gradually appear during the therapy. Therefore, there is an emergent need for rapid, easy and sensitive techniques for analysis of DOX .The performance of sensors can be significantly improved by using different nanomaterials. One of these materials is mesoporous silica SBA-15. SBA-15 is a promising candidate for the immobilization of various materials and can be used to create stable biosensing. Sensors based on the SBA-15 have shown high sensitivity and good detection limit through promoting electron transfer reaction and enhancing electrochemical signal. In this project, a simple and novel sensor is developed for study of clinical DOX concentration based on SBA-15 on the surface of SPE .The SBA-15 modified screen printed electrode (SPE) was fabricated to monitor the DOX in phosphate buffer solution (pH 6.0). A droplet of 9µL SBA-15 was placed on the working electrode surface, followed by air-drying for 1.0 h. The interaction of SBA-15 on the working electrode surface with DOX was investigated in the drug solution. The electrochemical behavior of DOX was observed at the surface of SBA-15-modified SPE by cyclic voltammetry (CV) and electrochemical impedance spectroscopy. The effect of pH and scan rate on the reduction current of DOX was studied using cyclic voltammetry. From the obtained results, pH 6.0 was obtained as the optimum pH. Also scan rate showed that the reduction peak current increased with increasing in scan rate from 10 to 400 mV s^{-1}. From the calculated results, the electron transfer coefficient was obtained 0.49. Under optimized condition, the measured reduction peak current of DOX by differential pulse voltammetry exhibited a good linear relationship with the increasing of the DOX concentration in the range of 0.002 µM to 2µM. The detection limit was founded to be5.4×10^{-6}µM.

Keywords: *SPE, Doxorubicin, mesoporous silica SBA-15, electrochemical impedance spectroscopy.*

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An electro amalgamation procedure for separate no carrier added Lu^{177} from Yb target for biomedical applications

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Abstract

Owing to its favorable radionuclides characteristics, such as $t_{l/2}$ = 6/73 day and $E_{\beta\ (max)}$ = 497 keV and ease of its large-scale production using medium flux research reactors, ^{177}Lu is an attractive radionuclide for various therapeutic applications. A two-step separation process for the production of no-carrier-added (NCA) ^{177}Lu from neutron irradiated Yb target through an electrochemical pathway employing mercury-pool cathode has been developed.

Methods

A two-cycle electrolysis procedure was considered for separation of ^{177}Lu from ^{177}Lu/Yb mixture in lithium citrate medium. The effects of different experimental parameters on the separation process was investigated and optimized for the quantitative deposition of Yb in presence of ^{177}Lu. The first electrolysis was performed for45 min in the ^{177}Lu/Yb feed solution at pH 7 applying a potential of 10 V using platinum electrode as anode and mercury as the cathode. The second electrolysis was performed under the same conditions using fresh electrodes. ^{177}Lu has been purified from citrate lithium electrolyte by exchange chromatography column. The suitability of ^{177}Lu for biomedical applications was ascertained by labeling tetra phenyl porphyrin (TPP) with ^{177}Lu.

Results

In this study ^{177}Lu with >99.9% radionuclide purity and an overall separation yield of 85% was obtained within 2–3 h. The Li content in the final product was determined to be <1 ppm. Radiolabeling yield of 98% was obtained with TPP under the optimized reaction conditions.

Conclusions

An efficient strategy for the separation of NCA ^{177}Lu, suitable for biomedical applications, has been developed.

Electrodeposition of Nickel on Stainless Steel Electrode and its Application for Oxygen Evolution Reaction

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Abstract

the oxygen evolution reaction (OER) is the anodic reaction that accompanies, in aqueous electrolytes, commerically important cathodic processes such as metal electrowinning and hydrogen production via alkaline water electrolysis. For the latter process, the anodic overpotential is the major factor in limting operational efficiency [1, 2]. The optimal oxygen evolution anode materials are RuO_2 and IrO_2, since these oxides exhibit the lowest overpotentials for the reaction at practical current densities. The high cost of these materials and their poor long term stability in alkaline solution, renders their widespread commercial utilization both uneconomical and impractical [3, 4]. Nickel and its alloys have therefore become the anodes of choice for water electrolysis [1, 3]. The electrodeposition method is a way to overcome the cost problem of noble metal catalysts, makes catalysts that are deposited directly on the surface of the substrate.

In this work a nickel modified stainless steel electrode was prepared using electrodeposition method in micellar solution containing Ni^{2+} ions. electrodeposition was done by two methods, containing potentiodynamic and potentiostatic methods. The OER was carried out by these modified steel electrods using linear sweep voltammetry method. Effect of some experimental parameter such as surfactant concentration, potential for Ni electrodeposition, time of Ni electrodeposition, number of potential cycling for Ni electrodeposition, on electrode response was studied. Resulting modified electrode was characterized by SEM images. The OER is significantly enhanced upon modification of the electrodes, as demonstrated by a negative shift in the LSV curves at the Ni modified electrodes compared to that obtained at the unmodified ones. The values of energy saving of oxygen gas at a current density of 10 $mAcm^{-2}$ for electrodes prepared by potentiodynamic and potentiostatic methods in optimized condition are 16.0, and 21.6 $kWh\ kg^{-1}$, respectively. These modified electrodes are very low cost and very stable even after 400 potential cycling in alkaline solution.

Keywords: *Oxygen Evolution*, *Electrodeposition*, *Nickel*, *Surfactant*

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Silver nanoparticles and polyvinylpyrrolidone-graphene quantum dots co-modified glassy carbon electrode for amperometric sensing of hydrogen peroxide

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Abstract

Graphene quantum dots (GQDs), graphene sheets with lateral sizes of less than 100 nm, are materials with characteristics derived from both graphene and carbon dots [1]. Due to their novel properties,such as fascinating optical, electronic and biocompatibility, sensors based on GQDs can achieve a high level of performance. Furthermore, GQDs increase contact area with the analyte, which could increase the electrochemical active surface area to interact with some electroactive analytes[2]. Silver nanoparticles not only have characteristics in common with noble metal nanoparticles, but also have unique properties such as the capacitance character, good electrical conductivity and high catalytic activity. Silver has the highest electrical conductivity among all metals and Ag nanostructures are considered to be instable. Moreover, Ag nanoparticles would be an ideal conductor to form electron transferring channels between the target molecules and the electrode surface [3]. In this study, Ag nanoparticles and wrapped graphene quantum dots with polyvinylpyrrolidone *were used* to *modify* the surface of a glassy carbon electrode for the detection of hydrogen peroxide. The electrocatalytic activity of the film was investigated by cyclic voltammetry and amperometric techniques for developing an electrochemical sensor. The synergist cooperation between Ag nanoparticles and graphene quantum dots could increase specific surface area and enhance electronic and catalytic properties of glassy carbon electrode. The response to H_2O_2 at a working potential of −0.3 V (vs. Ag/AgCl) was linear in 200 µM to 9 mM concentration range at pH 7.2. The detection limit of hydrogen peroxide was 52.3 µM, demonstrating the superior detection efficiency of the Ag nanoparticles and graphene quantum dots co-modified glassy carbon electrode as a new sensing platform.

***Keywords**: Silver nanoparticles, Graphene quantum dots, Polyvinylpyrrolidone, Hydrogen peroxide, Amperometric sensing*

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A glassy carbon electrode modified with a new simple nanocomposite film based on multiwall carbon nanotubes and zein nanoparticle for simultaneous determination of ascorbic acid, dopamine and uric acid

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Abstract

Zein is the major storage protein in corn or maize, has attracted attention because of its potential applications as an industrial biopolymer. Zein protein can form composites or conjugates with other compounds such as nanomaterials and also in encapsulation processes. Therefore, in recent years, several research groups have reported the use of nanoparticles in different research areas such as drug delivery, food science, pharmaceutics, and biomedicine [1]. Carbon nanotubes (CNTs) have been considered as an important class of nanomaterials with excellent mechanical, electrical and chemical properties since they have been discovered. These unique properties make them extremely attractive for fabricating electrochemical sensors because of the ability of CNTs to facilitatethe electron transfer reactions [2]. However, no works have been reported about the use of zein/multiwall carbon nanotubes nanocomposite for glassy carbon electrode modification for electroanalytical applications. For a mixture containing ascorbic acid (AA), dopamine (DA) and uric acid (UA), the three compounds can well separate from each other at the scan rate of 100 mV s^{-1} with a potential difference of 250 mV and 160 mV for the oxidation peak potentials of AA–DA and DA–UA, respectively, which was large enough to simultaneous determine AA, DA and UA. The catalytic peak current linearly depended on the AA, DA and UA concentrations in the range of 8.55–812 µM, 7.85–824 µM and 0.33–73.3 µM, respectively. The detection limits for AA, DA and UA were 2.11, 2.05 and 0.056, respectively. The analytical performance of this sensor has been evaluated for simultaneous detection of AA, DA, and UA in human serum and urine samples.

***Keywords**: Multiwall carbon nanotubes, Zein nanoparticle, , Ascorbic acid, Dopamine, Uric acid*

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Development of electrochemical DNA biosensor for “DG74 primer” using modern FFT voltammetry

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Abstract

“DG74 primer” is a universal bacterial primer to amplify and detect DNAs from phylogenetically divergent bacteria by targeting conserved regions of the 16S rRNA gene [1, 2]. In this study, a simple and rapid fast Fourier transform square-wave voltammetry (FFT-SWV) method for development of an electrochemical DNA biosensor for “DG74 primer”, using a gold electrode as transducer and methylene blue (MB) as electroactive label is described. The sensor relies on covalent attachment of the 19-mer thiolated DNA probe on the gold electrode. Covalently self-assembled probe could selectively hybridize with a complementary sequence (DG74 primer) in solution to form double-stranded DNA on the surface [3]. The hybridization between the probe and its complementary sequence as the target was studied by modern FFT-SWV signal of MB accumulated on the modified electrode by scanning the electrode potential between 0.1 and -0.5 V. In this approach the extent of hybridization is evaluated on the basis of the difference between FFT-SWV signals of MB accumulated on the probe modified Au electrode before and after hybridization. Some hybridization experiments with noncomplementary oligonucleotides were carried out to assess whether the suggested DNA sensor responds selectively to the target. Furthermore, signal-to-noise ratio was significantly increased by application of discrete fast Fourier transform (FFT) method [4]. Some experimental variables affecting the performance of the biosensor including: MB accumulation time, probe SAM formation time and concentration of probe and method and required time for hybridazition were investigated. Furthermore effects of square-wave frequency, step potential and pulse amplitude were examined for the optimization of instrumental conditions. Diagnostic performance of the biosensor is described and the calibration graph is linear between 0.1 and 3 nM. The detection limit was found to be 33 pM and the relative standard deviation over five independently probe-modified electrodes measured at 1 nM Target, was 1.7%, indicating a remarkable reproducibility of the detection method.

Keywords: *Fast Fourier transformation, Square wave voltammetry, DNA biosensor, DG74 primer, Gold electrode*

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Synthesis of Nano Composite TiO_2Nanotube/Fe_2O_3/Ni as Anode Materials for Li Ion Batteries

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Abstract

TNT/Fe_2O_3/Ni composite as anode materials was synthesized by iron oxide nanoparticles that embedding on high cycleable nanotube titanium oxide substrate and improving its electrical conductivity with Ni doping. Electrode performance was tested by charge/discharge galvanostatic and cyclic voltammetry experiments. The structure of composite will be studied by XRD and scanning electron microscope (SEM).

Keywords**:** Li ion battery, Anode, iron oxide, nanotube titanium oxide, Electro deposition

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Electro oxidation of Ethanol and Acetaldehyde on carbon supported PtSnO2 for application in passive direct ethanol fuel cell

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Abstract

Direct ethanol fuel cells (DEFCs) are very promising as they are capable of giving high-power density at low and intermediate temperatures. It has concerned a great deal of interest as a power source in plentiful applications because ethanol is a nontoxic, safe, and high density energy carrier, which is commonly available from the reformation of numerous kinds of biomass [1,2]. Several researches have been done on the using of metal oxide to improve Pt catalytic EOR activity. PtSnO2 and PtSn alloy catalyst were synthesized and the investigation of the products demonstrated that the addition of SnO2 improved the total oxidation to CO2. SnO2 is recognized for being potentially able to provide OH-species to oxidize toughly bound intermediates such as CO [3].In the present work, an experimental study on the performance of a passive DEFC is described. The PtSnO2/C (3:1) and Pt/C are used for anode and commercial Pt/C is used for anode material. A maximum power density of 1.78 mW cm-2, was obtained using a Nafion 115 membrane, 4 mg cm-2 of PtSnO2 and 3 mg cm-2 of Pt on the anode and cathode catalyst layer.

Keywords: DEFC, SnO_2

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DFT Study of Acetaldehyde Oxidation on Pt5/SnO_2 (110) as a New PEM Catalyst

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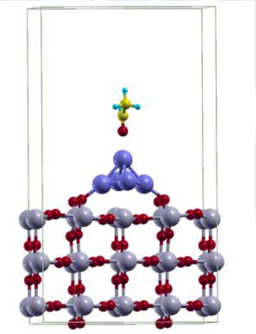
Abstract

Owing to higher reactive lattice oxygen sites and low cost, Pt5/SnO2(110) is introduced as a proper substitute to the classic SnO2 catalyst that is used for improving the ethanol oxidation reaction in direct ethanol fuel cells[1-2]. The detailed adsorption of Acetaldehyde as one of the most important intermediates of the ethanol oxidation procedure into carbon dioxide and water on the Pristine SnO2(110) and Pt5/SnO2(110) surfaces was investigated by Density Functional Theory calculations with the Quantum Espresso Pakage. In order to go further and gain insight into the binding features of Pt5/SnO2(110) with acetaldehyde, the structural and electronic parameters such as adsorption energy of each constituent, band structures and density of states (DOS) properties were scrutinized. Based on the results, It is found that composition of Pt5/SnO2 structure play a significant role in the acetaldehyde Oxidation. The interaction of Acetaldehyde with the surface of catalyst leads to the notable differences in catalyst structure and conductivity (Figure1.). These findings may provide insights into the structural and electronic properties of acetaldehyde intermediate on Pt5/SnO2 and will help us to enhance our knowledge about manipulating effects on physical and chemical properties of SnO2 and its derivatives.

Keywords: *SnO_2, Pt5, Acetaldehyde, Oxidation procedure*



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Hydrogen Production by Silver compounds loaded Titania Photoandoes via Photo electrochemical Measurements

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Abstract

A thin silver compound layer deposited on a conducting support of TiO_2, photocatalyzes the oxidation and reduction of water to O_2 and H_2.To test its photoelectrochemical capability, the coated-TiO_2 photoanode was employed in the anodic part of a setup for photoelectrochemical measurements for hydrogen production. This setup is consisting of platinum plate for cathode and Ag/AgCl as a reference electrode. Illumination of the photoanode by a Xenon arc lamp led to photoelectrochemical production of H_2. Silver composund coated- TiO_2 photoanode showed more enhanced and increased photocurrent density than the pure TiO_2 in both I_V curve and transient photocurrent measurements.

***Keywords*:** Photoelectrochemical Hydrogen Production, TiO_2 photoanodes, Silver compound coating, H_2 production

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Synthesized and Use the Metal organic framework (MOF) as catalyst for Oxygen reduction reaction (ORR)in alkaline media for fuel cell

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Abstract

Metal organic frameworks (MOF) electrocatalysts for the oxygen reduction reaction (ORR) were synthesized by a hydrothermal process using cobalt salts as the metal ion precursors.The bifunctional catalytic activities of metal organic framework (MOF) toward the oxygen reduction reaction(ORR) in alkaline electrolyte were investigated by cyclic voltammetry (CV) and linear sweep voltammetry (LSV).The results demonstrate that the as-prepared MOF has a good crystalline structure with abundant micropores, a high specific surface area and a high thermal stability. MOFs exhibit excellent bifunctional catalytic activities for ORR. The high specific surface area and abundant micropores are beneficial for oxygen diffusion and catalytic sites utilization in the catalyst, which is favorable for the ORR. The electrochemical measurements were carried out in alkaline medium. The synthesized MOF/CNT composite showed a comparable activity with Pt/C.

Keywords: MOF, Oxygen reduction reaction

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Electrochemical polymerization of sunset yellow on carbon ceramic electrode and electrocatalytic activity for oxidation of tryptophan

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Abstract

The compounds which provide chromophore azo group (-N=N-) form a piece of conjugate system together with two or more aromatic ring in their structure and combination of these rings are called azo dye matrial [1]. Sunset yellow (E-110, sy) is one of the synthetic dyes that contain the azo group as chromophore in its molecular structure, have during several years widely use as food coloring agent in many countries[2-3]. In the present work, sunset yellow as a food dye, has been polymerized on ceramic carbon electrodes using cyclic voltammetry and the formation of polysunset yellow nano films has been confirmed. The characteristics and morphology of polysunset yellow synthesized on carbon cermic electrode were characterized by SEM and FT-IR, NMR and TGA. The electrochemical behavior of polysunset yellow modified carbon ceramic electrode showed a pair of symmetrical redox peaks at a formal redox potential, $E^{`0}$=-0.03V vs. Ag/AgCl. The carbon ceramic electrode modified with polysunset yellow showed eletrocatalytic activity towards oxidaization of tryptophan. Under optimal experimental conditions, the carbon ceramic electrode modified with polysunset yellow exhibited a EC´ mechanism for the selective electrooxidation of tryptophan in the presence of other amino acids (pH= 5, phosphate buffer solution).

Keywords: *Azo dyes, Sunset yellow, Nano polymeric films, Electrocatalytic activity, Tryptophan, Carbon ceramic electrode*

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Electrochemical determination of glutathione in hemolysed erythrocyte by modified glassy carbon electrode

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Abstract

Glutathione (GSH) is a biological compound widely distributed in living cells from microbes to higher organisms. It is found mainly in its reduced form being the most abundant nonprotein sulfhydryl compound in cells [1].

The role of glutathione in the human metabolism includes protection against oxidative stress and detoxification of xenobiotics. Its viability in the reduced form may be a key factor in the health maintenance. It has been well established that a decrease in (GSH) concentration may be correlated with aging and pathogenesis of several diseases, including rheumatoid arthritis, muscular dystrophy, amyotrophic lateral sclerosis, AIDS, Alzheimer disease, and Werner syndrome [2–5]. The level of glutathione in blood may reflect glutathione status in less accessible tissues. Thus, measurement of (GSH) in blood is essential for whole-body glutathione status and can be used as an indicator of disease risks in humans [6]. In this paper, we selected electrochemical strategy to determination of glutathione by multiwall carbon nanotubes ($MCNT_S$) -modified glassy carbon electrode. (2Z,4E) -3-(3,4- dihydroxy phenyl) -1,5-bis(2,4- dinitrophenyl) formazon acted as a mediator between the analyte and electrode surface. The electrocatalytic oxidation of (GSH) is individually investigated at the surface of modified electrode using cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Initially, cyclic voltammetry was used to investigate the redox properties of this modified electrode at various scan rates. Next, the mediated oxidation of (GSH) at the modified electrode was described. Based on differential pulse voltammetry, the oxidation of (GSH) exhibited a dynamic range between 0.05 and 100.00 µM. The influence of some (GSH) metabolites and structurally related substances of common blood components on the assay were also examined, since this electrode is to be applied in erythrocyte samples. The results showed that l-ascorbic acid produced a slight increase in the sensor response. A slight interference from cysteine was also observed, due to the structural similarity between this compound and the (GSH) molecule. Although both l-ascorbic acid and cysteine showed slight interferences, they are normally not present at a significant levels in erythrocyte samples [7]. The other interfering

compounds (glutamic acid, glucose, glycine,glutamic acid, …) did not show significant interferences on the sensor response. DPV was used for determination of (GSH) at the modified electrode, and quantitation of (GSH) in three different hemolysed erythrocyte samples by the standard addition method. The modified electrode showed good stability and repeatability.

***Keywords**: Glutathione, Multiwall carbon nanotube, Electrocatalysis, Modified electrode, Voltammetric determination.*

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Determination of dopamine and uric acid in presence ascorbic acid by means a carbon paste electrode modified with nanoclay- ionic liquid

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Abstract

Dopamine (DP) is one of the catecholamine which distributed in the brain tissues and acts as an important neurotransmitters in mammalian brain tissues and fluids [1-2].Uric acid (UA) is the primary produced of purine in human body [3].Ascorbic acid (AA) is an important antioxidant which is used for the prevention and treatment of cancer and common cold [4].

The aim of this study was to develop a new sensitive method for simultaneously the determination of DP, UA in presence AA in serum samples. Using the cyclic voltammetry and differential pulse voltammetry as diagnostic methods, this study describes the electrochemical behavior of drugs, at the NC-IL-CPE electrode. The response currents are is linear in DP concentration range of 20.0µM to 200.0 µM,and 200.0µM to 600.0 µM , the UA concentrations from 5.0 to 600.0 µM,and the AA from 100.0-2000.0 µM concentrations the detection limits for DP and UA are estimated to be about, 2.25 µM and 3.72 µM (S/N = 3), respectively. Repeatability was examined for 7 replicate measurements of 50 µM DP, 85µM UA in presence 100µM AA the relative standard deviation, RSD of 3.1% for DP and 2.8% for UA, respectively, was obtained, indicating a high degree of reproducibility.

Keywords: *Determination, Nanoclay, Ionic Liquid, Electrode Modified*

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Hot corrosion behavior of cobalt coated AISI 430 ferritic stainless steel

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Abstract

AISI 430 ferritic stainless steel was coated with cobalt by pack cementation method to investigate the hot corrosion behavior. Coated and uncoated samples were subjected to hot corrosion at 800 °C for 100 hours with a salt mixture consisting of 80 wt.% Na_2SO_4+20 wt.% NaCl. Coated substrates hot corrosion behavior as a function of corrosion time showed that the formation of spinels containing cobalt ($MnCo_2O_4$, $CoCr_2O_4$ and $CoFe_2O_4$) improves hot corrosion resistance by limiting the inward diffusion destructive ions of oxygen, sulfur and chloride. The weight gain obtained 2.43 mg.cm^{-2} for uncoated substrates and 1.15 mg.cm^{-2} for coated substrates after 100 h of hot corrosion at 800 ºC.

Keywords: *Hot corrosion, AISI 430 steel, Pack cementation, cobalt.*

Introduction

Metals depending on their chemical nature and that of the environment exhibit different corrosion resistances. Stainless steel is a family of iron-based alloys containing at least 11% Cr and other elements such as C, Mn, Si, Ni, Mo, Ti, a nd N. The high degree of chromium activity is actually the principal basis for utilizing it as an alloying element in corrosion resisting alloys. Not all the stainless steels are equally resistant in most environments but some have been developed through alloy additions to resist the aggression from anions in certain environment containing oxygen, sulfur and chloride [1]. One approach to improve the corrosion resistance of these alloys is to employ a protective coating [2]. In the present study, cobalt was pack cemented on AISI 430 ferritic stainless steel and hot corrosion behavior was investigated.

Methods

The substrate materials used in this study was AISI 430 ferritic stainless steel that contains 17.4% Cr, 0.92% Mn, 0.85% Si, 0.12% C, 0.02% S, 0.03% P whit Fe as remaining. Samples of AISI 430 stainless steel measuring 10 mm × 5 mm × 2 mm were used as substrates. The samples were coated with cobalt by pack cementation method, which was described in the previous study [2]. After the pack cementation treatment, the samples were weighed using an electronic balance. Prior to hot corrosion tests, samples were subjected to oxidation at 800 °C to form Co spinels ($MnCo_2O_4$, $CoCr_2O_4$ and $CoFe_2O_4$) [2]. Hot corrosion was done at 800 ºC for 100 hours with a salt mixture consisting of 80 wt.% Na_2SO_4+20 wt.% NaCl (melting point ~700 °C). After hot corrosion test the coated and uncoated samples were weighed and weight changes was calculated.

Result and discussion

Hot corrosion resistance of cobalt coated and uncoated AISI 430 steel was studied at 800 ºC for 100 h. Fig. 1 illustrates the specific weight gain as a function of hot corrosion time for uncoated and coated steel coupons. For the uncoated samples, the initial corrosion rate is higher compared to the uncoated ones. This is due to the bare substrate in uncoated samples that corrode and oxidize freely in primary times. In both of samples the weight gain increase parabolically with time, satisfying the parabolic kinetics low. Parabolic behavior in Fig. 1 is because of chromia scale growth which obeys the parabolic rate low according to Eq. (1) [3]. All the coated samples exhibited smaller mass gain compared with the bare substrates in all the times. The bare substrate had weight change of 2.43 mg cm^{-2} after 100 h hot corrosion, while the coated samples had the weight change of 1.15 mg cm^{-2}. Cobalt coating restricted the inward diffusion of destructive ions of oxygen, sulfur and chloride. Therefore the nucleation and growth of iron sulfide and chromium sulfide is restarted and stress corrosion cracking is decreased. Cracks create diffusion paths for oxygen, sulfur and chloride anions. Therefore, the simple migration of ions results to the higher corrosion rate [4]. Fig.2 shows the SEM micrograph of the uncoated surface sample after 100 h of hot corrosion. The uncoated specimen surfaces shows cracks and pits (Fig. 2a) while the coated sample surface exhibited better resistance against cracking and pitting (Fig. 2b). Pitting and cracking are the result of the thermal expansion coefficient mismatching of the oxide, or coating layer, with the substrate. Another reason is the formation of iron sulfide and chromium sulfide in bare samples. The formation of $MnCo_2O_4$, $CoCr_2O_4$ and $CoFe_2O_4$ spinels in coated samples improved sulfidation resistance.

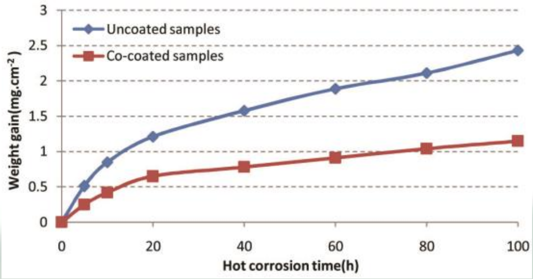

Fig. 1. Specific weight gain for samples as a function of time after 100 of hot corrosion.

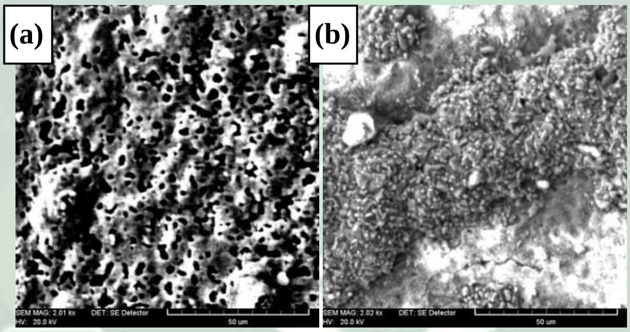

Fig. 2. SEM micrographs of (a) uncoated and (b) Co-coated sample after 100 of hot corrosion.

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Voltammetric Determination of Cysteine by Means of 4 4'- biphenol as a Homogeneous Mediator

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Abstract

Cysteine (2-amino-3-mercaptopropanoic acid, **CySH**) is a type of the important amino acids which is widespread used in the medicine and food additives. It is important in collagen production, as well as skin elasticity and texture [1]. In recent years, several analytical approaches have been reported for electrocatalytic oxidation of 4,4'-biphenol toward the determination of thiols in the literature[2,3]. In this research 4,4'-biphenol was used as a homogeneous mediator for determination of cysteine, on glassy carbon. Cyclic voltammetry and liner sweep voltammetry were applied for describing the electrochemical properties of 4,4'-biphenol and to investigate its electrocatalytic effect on the cysteine oxidation. The results indicated that 4,4'-biphenol remarkably accelerate the electron transfer reactions of cysteine.The diffusion coefficient of cysteine and the catalytic rate constant of the reaction of 4,4'-diphenoquinone with cysteine was also estimated using chronoamperometry method. The proposed method was successfully used for the determination of cysteine in serum samples.

Keywords: *Homogeneous Mediator, Determination, Cysteine, Cyclic voltammetry, Chronoamperometry*

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Hot corrosion resistance activation energy of manganese-cobalt coated Crofer 22 APU steel

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Abstract

In this study, the pack cementation method was employed to coat manganese and cobalt onto Crofer 22 APU steel. Hot corrosion at 800°C and hot corrosion at different temperatures were applied to evaluate the activation energy. In each test, the coated samples demonstrated lower $k_{p,}$ indicating that the coating layer had acted as a mass barrier against the outward diffusion of cations (Cr) and inward diffusion of anions (Cl, S, O). The formation of $MnCo_2O_4$, $CoFe_2O_4$, $CoCr_2O_4$ and Co_3O_4 spinels, improved the hot corrosion resistance of Crofer 22 APU steel and it resulted to the lower hot corrosion activation energy of cobalt coated samples in comparison with the coated ones.

Keywords: *Hot corrosion, Pack cementation, Manganese, Cobalt, Activation energy.*

Introduction

Spinel ferrites with general formula MFe_2O_4 have interesting physical properties and are of technological importance. In particular, $CoFe_2O_4$ spinel is of increased interest as this material, in the form of bulk, powder, film, or nanoparticles, finds or promises numerous applications in microwave devices, magnetic drug delivery and solid oxide fuel cells [1]. In addition, it has been found that $CoFe_2O_4$ spinel is a highly reproducible material for humidity and gas sensing. Apart from its technological importance in these fields, $CoFe_2O_4$ has attracted considerable attention because of its potential for high temperature structural applications due to its low density, high strength at elevated temperature, good resistance to hot corrosion and high electrical conductivity [2]. Few researches have focused on the hot corrosion resistance of $CoFe_2O_4$ coating. In the present study, manganese and cobalt were pack cemented on Crofer 22 APU ferritic stainless steel and hot corrosion resistance behavior and hot corrosion resistance activation energy was investigated.

Methods

Coupons of Crofer 22 APU stainless steel, measuring 10 mm × 5 mm × 2 mm with chemical composition of 22.7% Cr, 0.38% Mn, 0.02% Si, 0.01% C, 0.02% Ni, 0.02% Al, 0.07% Ti, 0.06%

La with Fe as remaining were used as substrates. Specimens were polished from 320-grit sic paper up to 1200-grit, ultrasonically cleaned in ethanol and dried. The samples were coated with cobalt and manganese by pack cementation method, which was described in the previous study [3]. After the pack cementation treatment, the samples were weighed using an electronic balance. Prior to hot corrosion tests, samples were subjected to oxidation at 800 °C to form Mn-Co spinels. The isothermal hot corrosion was done at 800 ºC for 100 hours with a salt mixture consisting of 80 wt.% Na_2SO_4+20 wt.% NaCl (melting point ∼700 °C). The samples were also subjected to hot corrosion at different temperatures (700-1000 ºC). After each test the coated and uncoated samples were weighed and weight changes was calculated.

Result and discussion

Hot corrosion resistance of manganese-cobalt coated and uncoated samples was studied at 800 ºC for 100 h. The corrosion resistance was remarkably reduced by the application of coating layer. The bare substrate had a weight change of 1.853 $mg.cm^{-2}$ after 100 h of hot corrosion, while the coated samples had a weight change of 0.658 $mg.cm^{-2}$. The coating effectively protected the substrate from the corrosion at high temperatures. In order to measure the hot corrosion resistance activation energy of Mn-Co coating, uncoated and coated samples were subjected to hot corrosion at 800 °C, 900 °C and 1000 °C for 20 h. By increasing the temperature, the kp increased. This is because of the lower activation energy for the diffusion of the corrosion rate limiting species at higher temperatures [4].

The parabolic rate constants (*k*p), can be fit into an Arrhenius expression to determine the activation energies for the oxide formation process on each of the samples (Fig. 1). Activation energies were calculated 126 and 73 $kJ\ mol^{-1}h$ for uncoated and coated specimens, respectively. The lower activation energy for the Mn-Co-coated samples would imply that oxide formation is easier during hot corrosion. This is an interesting result, considering the fact that the oxides on the coated samples are thinner than the oxides on the uncoated Crofer 22 APU samples. The activation energy for hot corrosion of the coated samples is relatively close to that for the uncoated samples. It is, thus, possible that hot corrosion of the coated samples, at these temperatures in air, is essentially controlled by the same mechanism that control the hot corrosion of the uncoated samples.

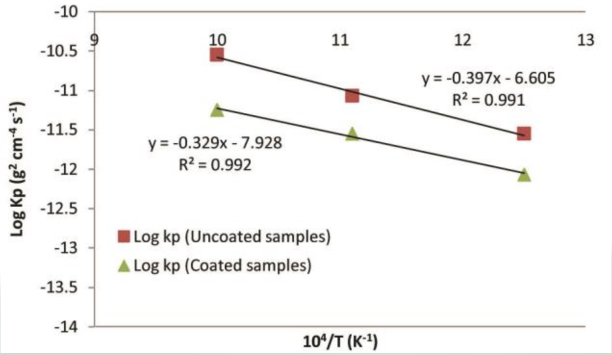

Fig. 1. Plots of log(kp) vs. 1/T for uncoated and Mn-Co-coated Crofer 22 APU steel.

Conclusions

Crofer 22 APU ferritic stainless stainless was pack cemented with manganese and cobalt. The formation of $MnCo_2O_4$, $CoFe_2O_4$, $CoCr_2O_4$ and Co_3O_4 in coated samples improved hot corrosion resistance. The activation energy of Mn-Co-coated samples was lower than the uncoated ones which indicated that during hot corrosion the oxide formation in coated samples is easier.

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Effect of deposition time on the microstructure of Mn–Co thin films and cathodic current efficiency

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Abstract

Manganese-Cobalt coatings are promising candidates for SOFC interconnect applications because of their high conductivity and good oxidation resistance. In the present study, manganese and cobalt were electrodeposited on Crofer 22 APU ferritic stainless steel. The effect of deposition time on the microstructure and cathodic efficiency was investigated. Results showed that the increase of deposition time caused to the decrease of current efficiency.

Keywords: *Electrodepositon, Mn-Co coatings, Microstructure, Current efficiency, Deposition time.*

Introduction

The formation of oxide scales is one of the critical issues for applying Fe–Cr alloys in solid oxide fuel cells (SOFCs) operated at 773 K–1073 K (intermediate operation temperature SOFCs) [1-2]. The growth of oxide scale is dominated by the diffusion of elements (cations and oxygen) in the scales and the microstructures of scales [3]. One of the most effective approaches to improve the interconnect properties is to apply surface coatings to provide better conductivity, reduced scale growth and Cr volatility. Manganese-Cobalt coatings are promising candidates for SOFC interconnect applications because of their high conductivity and good oxidation resistance. In the present study, manganese and cobalt were electrodeposited on Crofer 22 APU ferritic stainless steel and the effect of deposition time on microstructure was investigated.

Methods

For the direct current (DC) electrodeposition process, a one-compartment cell was used. Platinum foil was used as the anode and it was placed in the same compartment as the working electrode. All experiments were carried out in 100 ml electrolytes prepared with deionized water. Ammonia hydroxide or 20 vol% H_2SO_4 was used to adjust the electrolyte pH. Bath electroplating with composition of 0.5 M $MnSO_4$ + 0.10M $CoSO_4$ + 1 M H_3BO_3 + 0.7 M $NaC_6H_{11}O_7$ + 0.1 M $(NH_4)SO_4$ at pH 2.5 and current density of 250 $mA.cm^{-2}$ was used to electrodeposition of Mn-Co coating. The effect of deposition time on the microstructure and cathodic efficiency were characterized by means of scanning electron microscopy (SEM), weight gain measurements, and energy dispersive X-ray spectrometry (EDS), respectively.

Result and discussion

Surface morphologies of coating obtained at different times (10, 20 and 30 min) are illustrated in Fig. 1. The deposited layer after 10 minutes is not uniform and continues (Fig. 1a). After 20 minutes electrodeposition, a uniform thin film with no cracks was developed (Fig. 1b). The coating achieved after 30 minutes electrodeposition is relatively uniform, but some cracks are observed in the surface of coating (Fig. 1c). Also the solution was dark and unclear after 30 minutes of electroplating. At lower times, the deposition time is no sufficient to coat all parts of the substrate, therefore some areas remain bare. At higher times the coating gets thicker, and the residual stresses in the coating causes to the cracking of coating. Also by increase of time in a constant solution, unwanted reactions will occurs (perhaps the formation of hydroxides or oxides) which result to the dark and unclear solution [4]. Current efficiency as a function of deposition time was also studied. Results showed that the increase of deposition time, caused to the decrease of current efficiency. It refers to the deposition time and faraday slow. At higher times the weight gain of deposition should be higher in relation to the theoretical weight gain based on the faraday slow. So in a constant solution this relation (experimental weight gain/theoretical weight gain) decreases by increase of deposition time [4]. Also in a constant solution, by increase of time, the concentration of Co^{+2}/Mn^{+2} in the solution will decreases and therefore it results to the lower current efficiency. The reduction of cation in the solution also reduces the deposition rate.

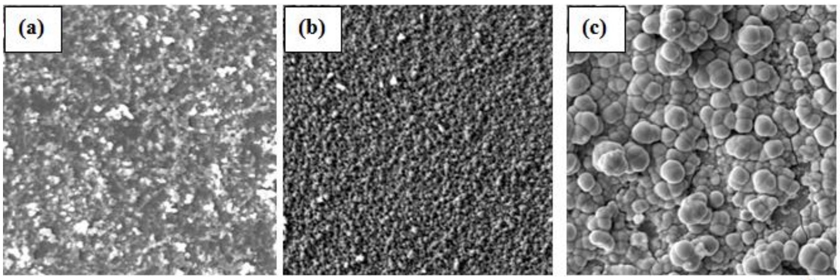

Fig. 1. Effect of electrodeposition time on current efficiency at pH 2.5 and current density of 250 mA.cm^{-2} for bath containing 0.5 M $MnSO_4$ + 0.1 M $CoSO_4$ + 1 M H_3BO_3 + 0.7 M $NaC_6H_{11}O_7$ + 0.1 M $(NH_4)_2SO_4$; (a) 10 min ; (b) 20 min ; (c) 10 min.

Conclusions

Crofer 22 APU ferritic stainless stainless was electrodeposited with manganese and cobalt simultaneously. The effect of deposition time (10, 20 and 30 min) on the microstructure of Mn-Co thin film was studied. Results showed that the best coating was obtained after 20 min electrodeposition. Also deposition time caused to the decrease of cathodic current efficiency.

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Influence of $CoSO_4$ concentration on the microstructure and cathodic current efficiency of Mn–Co electrodeposition

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Abstract

Spinels containing cobalt and manganese are the best candidates for the coating of interconnects. In the peresent study, the effect of cobalt sulfate consentration on the microstructure and cathodic efficiency was investigated. . Results showed that the increase of cobalt sulfate concentration caused to the increase of current efficiency.

Keywords: *Electrodepositon, Mn-Co coatings, Microstructure, Current efficiency, Cobalt sulfate.*

Introduction

The reduction in the operating temperature of SOFC from 1000 °C to 600–800 °C leads to the potential for using lower cost metallic interconnects materials such as stainless steel. Almost all of the candidate alloys being considered for this application are chromia forming alloys due to the acceptable electrical conductivity and stability of Cr_2O_3. However, excessive growth of chromia and chromium evaporation can lead to cathode poisoning, and thus shorten the required service life for the SOFC stack. In order to solve the mentioned problems, protective and conductive coatings can be employed. Manganese-cobalt coatings are promising candidates for SOFC interconnect applications because of their high conductivity and good oxidation resistance [1-3]. In the present study, manganese and cobalt were electrodeposited on Crofer 22 APU ferritic stainless steel.

Methods

One-compartment cell was used for DC electrodeposition process. Platinum foil was used as anode and was placed in the same compartment of working electrode. During the deposition, the solution was remained unchanged, and no inert gas was used to purge the electrolyte. All experiments were carried out in 100 ml electrolytes prepared with deionized water. The pH of electrolytes was adjusted using either ammonia hydroxide or 20 vol.% H_2SO_4. Bath electroplating with composition of 0.5 M $MnSO_4$ + 1 M H_3BO_3 + 0.7 M $NaC_6H_{11}O_7$ + 0.1 M $(NH_4)SO_4$ at pH 2.5 and current density of 250 $mA.cm^{-2}$ was used to electrodeposition of Mn-Co coating. The effect of cobalt sulfate concentration ($CoSO_4$) on the microstructure and cathodic efficiency were characterized by means of scanning electron microscopy (SEM), weight gain measurements, and energy dispersive X-ray spectrometry (EDS), respectively.

Result and discussion

In order to investigate the effect of cobalt sulphate in the solution, different amounts of $CoSO_4$ (0.01 M, 0.05 M, 0.1 M and 0.2 M $CoSO_4$) in the electrolyte solution were studied. SEM surface morphologies of coatings achieved based on the introduced conditions bath illustrated in Fig 1. The coating obtained in 0.01 M (Fig. 1a) and 0.05 M (Fig. 1b) cobalt sulfate solution is not uniform and continues. Also some parts of the substrate are bare. This is because of low amount of cobalt sulfate in the solution which causes to the low amount of Co^{+2} [4]. With increase of sulfate cobalt content to 0.1 M the coating grows uniformly and it is continues (Fig. 1d). At higher amount of cobalt sulfate (0.2 M) the deposition rate is such high that a coarse layer is produced (Fig. 1c). Also the grain size is larger than the coatings obtained in lower amounts of cobalt sulfate in the solution. In addition the high deposition rate produces some stress in the coating that results to the cracking of the coating. Also based on the EDX observations the amount of cobalt in the coating is high and the manganese content is low. For the formation of Mn-Co spinels during the oxidation, a higher amount of manganese is needed. Also such coarse coating with large grains will result to the lower oxidation resistance in compare of the coating with smaller grains [5]. Current efficiency as a function of $CoSO_4$ was also studied. Results demonstrated that by the increase of cobalt sulfate the current efficiency enhanced. By increase of cobalt sulfate the deposition rate increased and in a constant time of 20 min it results to the thicker coating. Therefore the experimental weight gain of coating increases and it causes to the higher current efficiencies, which is consistent with SEM surface morphologies (Fig. 1).

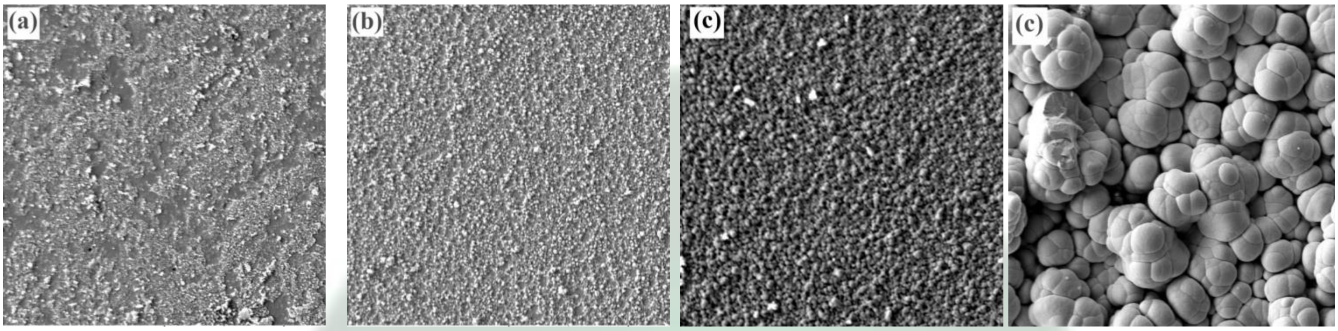

Fig. 1. SEM surface morphology of coatings after 20 min electrodeposition with different cobalt sulfate content in solution of 0.5 M $MnSO_4$ + 1 M H_3BO_3 + 0.7 M $NaC_6H_{11}O_7$ + 0.1 M $(NH_4)_2SO_4$ with pH 2.5 at current density of 250 $mA.cm^{-2}$; (a) 0.01 M $CoSO_4$; (b) 0.05 M $CoSO_4$; (c) 0.1 M $CoSO_4$; (d) 0.2 M $CoSO_4$.

Conclusions

Crofer 22 APU ferritic stainless stainless was electrodeposited with manganese and cobalt simultaneously. The effect of cobalt sulfate concentration (0.01 M, 0.05 M, 0.1 M, 0.2 M) on the electrodeposition of Mn-Co was studied. Results showed that the increase of cobalt sulfate concentration caused to the increase of cathodic current efficiency. Also results demonstrated that the variation of cobalt sulfate concentration ($CoSO_4$) had significant effect on the grain size, uniformity and adherence of the coating.

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An indirect electrochemical determination of thioacetamide by using of $Ag@Fe_3O_4$ nanoparticle modified carbon paste electrode

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Abstract

Tahiocetamide (TAA), is a widely used sulfur-containing compound both in the laboratory and in various technical applications and can also be present in the environment as organic sulfur compounds. TAA is used as a replacement for hydrogen sulfide in qualitative analyses and in hospital practice, as an accelerator in rubber vulcanization, as a reductant additive in the leather, textile and paper industries, generally having a similar role to thiourea. The widespread uses of TAA are unavoidably accompanied by its toxicity and a number of ecotoxic effects in environmental pollution can result from TAA manipulation and its consequent presence in waste waters. These aspects become increasingly important due to high degree of hepatic and neurotoxic injury, and carcinogenity, of TAA, which has been demonstrated under various experimental conditions. Thus, in these circumstances the detection of thioacetamide in real time has become more and more important [1]. Electrochemical methods are simple and versatile due to their advantages such as cheap instrumentation, quick response time, high sensitivity and wide linearity. In this work an electrochemical sensor was proposed for the determination of thioacetamide. For this propose $Ag@Fe_3O_4$ nanoparticles [2] were applied as an effective modifier for the modification of carbon past electrode. TAA can form the self-assembled monolayers (SAMs) on the surface nanoparticles and decrease the peak current of the modified electrode. Under the optimized condition, the linear range and detection limit were obtained as 50-100 nM and 32.58 nM, respectively.

The obtained results for the determination of TAA by this method, showed, excellent analytical performance for the determination of thioacetamide in terms of an appropriate detection limit, high sensitivity, very good accuracy, repeatability and reproducibility.

Keywords: $Ag@Fe_3O_4$ nanoparticles, Electrodhemical Indirect determination, Self –assembled monolayer, Thioacetamide.

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A Sensitive Electrochemical Immunosensor for the Determination of Prostate Specific Antigen

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Abstract

Clinical analysis of a cancer biomarker leads to early cancer diagnosis which in turn, is followed by increase the chances of successful treatment [1]. Prostate specific antigen (PSA) has been demonstrated to be the most validated serum marker for prostate and breast cancers [2,3]. Blood PSA concentrations above 4 ng/ml are often related to prostate cancer [4]. So, sensitive and accurate quantification of PSA is critical to early detection of prostate cancer, increase the expectancy of complete patient recovery and monitor for disease recurrence after treatment [5]. Herein, an electrochemical immunosensor for the quantification of PSA is presented. For the preparation of the sensor, at first streptavidin was covalently immobilized on the surface of a nano TiO2-modified carbon paste electrode using glutaraldehyde as crosslinking agent. Then anti-PSA antibody functionalized with biotin was linked to the electrode surface after specific interaction between streptavidin and biotin. After sandwich-type immunoreaction, thionine-conjugated polycolonal antibody was bound to PSA and the reduction current of the thionine was recorded with differential pulse voltammetry. This electrochemical signal was directly correlated to the concentration of PSA. All experimental parameters affecting the sensor response including those involved in the construction of the sensor and in the electrochemical transduction, were optimized. The immunosensor exhibited a linear concentration range of 0.10-100 ng/ml under the optimized conditions. The proposed sensor was successfully applied to the determination of PSA in health and cancerous human serum samples. In addition, the designed immunosensor minimized the issue of nonspecific protein adsorption using streptavidin-biotin specific interaction.

***Keywords**: Prostate cancer antigen, Immunosensor, HRP, Electrochemistry*

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Temperature dependence of CO desorption and oxidation from cathodic electrochemically treated carbon paper supported Pt electrodes

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Abstract

The Proton Exchange Membrane Fuel Cells (PEMFCs) are considered good alternatives as power generation systems for different kinds of applications because of their high efficiency in energy conversion and suitability. One of the problems appears when using hydrogen obtained from reforming, because it contains CO, which can strongly compete with H_2 for adsorption on Pt surface .This contamination lead to the metal poisoning and decreases the anode performance[1]. Three mechanisms have been suggested to explain improved CO tolerance of Pt based catalyst compared to pure Pt: the bifunctional mechanism, the ligand effect mechanism, and the “detoxification” mechanism [2].Whereas the bifunctional and ligand effect mechanisms explain the improved CO tolerance by a favoured electrochemical oxidation of CO, the “detoxification” mechanism proposes a lower equilibrium CO coverage at the surface, simply via the CO adsorption/desorption process. Therefore, both the electrochemical CO oxidation and the equilibrium attained through the adsorption/desorption process should be considered as physicochemical processes affecting the CO tolerance [3].Studies have shown that particle size, exposed crystal faces and oxidation state of carbon supports are important factors which have influence on specific activity of the Pt electrocatalyst for CO and methanol oxidation [4] Studies show the effect of electrochemical treatment of GC support [5] and oxidation of the HOPG substrate [4] on CO and methanol oxidation, because a large influence on the particle size and better distribution of platinum on the substrate. But, as we know, these supports are not real support for fuel cells. The study of the electrooxidation mechanisms of CO_{ad} on Pt based catalysts is very important for designing more effective CO-tolerant electrocatalysts for fuel cell.To the best of the authors’ knowledge, there is no study about the effect of temperature on cathodic oxidation of carbon paper as a support for Pt electrodeposition on CO electrooxidation . The goal of this study is to investigate the effect of temperature on CO tolerancefor cathodic electrochemically treated carbon paper supported Pt with considering two approaches: electrochemical CO oxidation and the

equilibrium coverage attained through the adsorption/desorption process.0.25 cm^2 carbon paper (TGPH-090;Toray) was used as the support for electrochemical catalyst preparation. Oxidation on carbon papers were performed by applying -2 V for cathodic oxidation for 5 min in 0.5M H_2SO_4 solution. Pt was electrodeposited onto the carbon paper by electrodeposition in an electrolyte solution of 0.2M H_2SO_4 +2mM $H_2PtCl_6.6H_2O$. Single-pulse chronoamperometry electrodepsition by adjusting potential profile of 0V (1 s) and 1.15 V (600 s) (vs.Ag/AgCl(sat)) was done. All chemicals used in this investigation were of analytical grade (Merck).

The oxidized CPs were characterized by micro-ATR-FTIR. Primary alcohol, ether, phenol, carboxylic, quinne and conjugated ketone, Phenol oraal tertiary alcohol and lactone functional group peaks can be observed. The effect of the temperature on CO electrochemical oxidation at different temperatures was analyzed by CO stripping voltammetry in the range of 25–85 ^{0}C. Figure 1 and figure 2 show the results obtained from CO stripping voltogramms for non-treated and cathodic electrodes, respectively. At elevated temperatures, a small current from upd-H oxidation was observed before CO removal. This current increases with the temperature, indicating the decrease of CO_{ad} coverage at higher temperatures, as is clearly demonstrated in the θ_{CO}-temperature plot in Figure 3. It seems that the presence of oxygen functionalized groups on the surface of carbon paper support may make weaken the strength band between the CO and the Pt catalyst. As it has shown (Fig.3) the CO coverage is lower for treated electrode at room temperature. Indeed, the changes of CO coverage with temperature on cathodic electrode is higher than non-treated one (Fig.3).

Figure 2: CV results of clean at 25°C and CO-saturated Cathodic electrode at different temperatures in 1M H2SO4 and Scan rate of 50 mV/s.

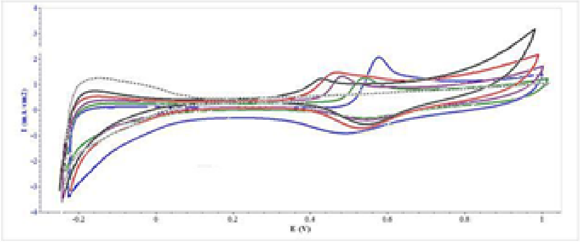
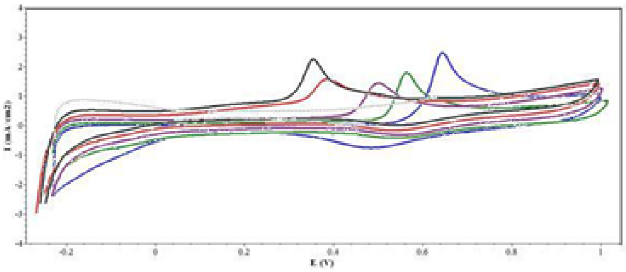


Figure 1: CV results of clean at 25°C and CO-saturated Non-treated electrode at different temperatures in 1M H2SO4 and Scan rate of 50 mV/s.



🟦 **Ambient**
🟩 **313K**
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⬛ **358K**

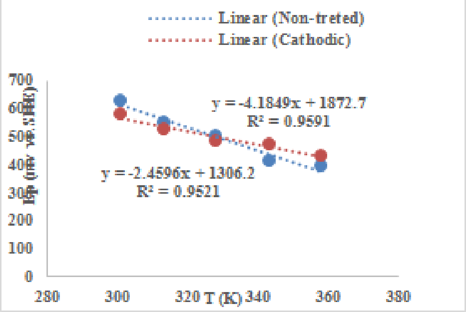

Figure 4: Ep changes with temperature

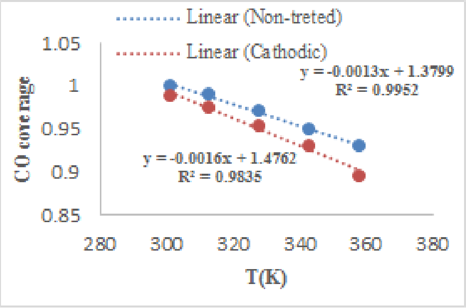

Figure 3: Co coverage changes with temperature

Increasing the temperature may have synergetic effect on lowering the equilibrium coverage attained through the adsorption/desorption process for cathodic electrode in compare with non-treated one. As it has shown in figure 1and figure 2 effect of the temperature was similar for both electrodes, the anodic current (onset and peak potential) related to the CO oxidation reaction shifts towards more negative potentials as the temperature increases. This is related to an increment of the water dissociation reaction as well as to a faster surface CO diffusion toward the most active site with the rise of the temperature. The activation energy for the CO oxidation reaction can be calculated using the temperature-depending Nernst equation (Eq.1), which was suggested by Herrero et al. [6]:

$$E_p - E^0 = \frac{RT}{F} ln \frac{j_p A_{-1} a_{H^+}}{Q_p A_1 A_2 \theta_{CO,p} \theta_{H2O,p}} + \frac{E_{act}}{F} \qquad \text{(Eq.1)}$$

The plot of the peak potential of CO electrooxidation vs. the absolute temperature for CO-stripping is given in Fig 4. From Fig. 4 and employing the Eq.1, activation energies for CO oxidation reaction were determined from the value of the potential at 0 K [7]. Consequently, different activation energies for Pt catalysts on cathodic and non-treated carbon paper are achieved. The obtained activation energy for cathodic and non-treated electrode was 125 kJ mol^{-1} and 180 kJ mol^{-1}, respectively. Results show that the presence of oxygen containing groups on carbon paper were likely contributing to CO electrooxidations similar to bifunctional mechanism. Indeed, more desorption of adsorbed carbon monoxide and consequently lower coverage were shown for cathodic electrode because of the synergetic effect between treated electrode and increasing the temperature. We can conclude that in addition to bifunctional mechanism, detoxification can contribute for CO tolerance on cathodic electrochemically treated carbon paper supported Pt electrodes, especially on elevated temperature.

Keywords: *CO oxidation, carbon paper, cathodic oxidation, coverage, desorption, Temperature effect*

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Investigation of the electrical field effect on silver nanoparticles synthesized using sodium citrate and pvp stabilizers

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Abstract

The behavior of silver nanoparticles (AgNPs) under applied electric field depends primarily on their stabilizing agent. This research is aimed at investigating the behavior of AgNPs and their stabilizers under electrochemical (EC) process. Silver nitrate and hydrazine hydrate were used as the sources of silver ion and reducing agent, respectively. In separate experiments, sodium citrate and polyvinylpyrrolidone (PVP) were used as nanoparticle stabilizers. Stability of the particles was studies when electrical current was applied. The efficiency of the EC process was investigated for different of AgNP sols. With sodium citrate for different voltages, after using the electric field for 90 min, the plasmon resonance peak of the sample disappeared, reflecting the removal of the AgNPs in the sol by 99.91%. With PVP, after applying electric field for 10 min, the absorbance peaks disappeared, and removal efficiency of the AgNPs reached 99.98%. Based on these results, it can be recognized that the AgNPs stabilized by citrate, are slightly more stable, whereas AgNPs solutions prepared by PVP showed better results on floc formation and, therefore, agglomerated more easily. The UV/Vis spectroscopy analysis was used for characterization of all samples. Also, the Field Emission Scanning Electron Microscopy (FESEM) was used for floc characterization.

Keywords: *AgNPs, Sodium Citrate, PVP, Stabilizer, Electrochemical Process*

Carbon monoxide and methanol oxidations on electrochemically treated carbon paper supported Pt electrodes

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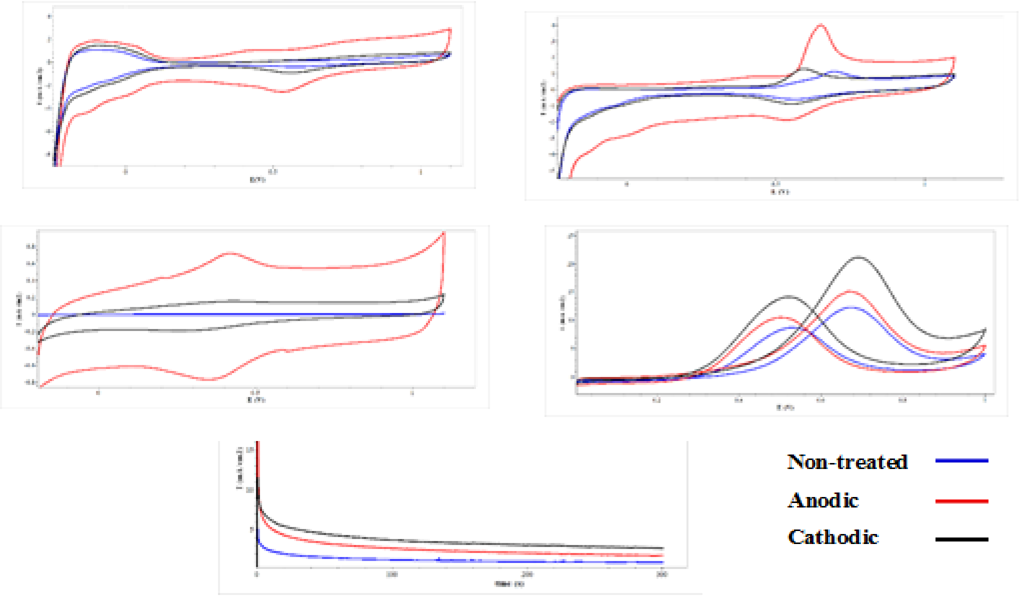
Abstract

The Proton Exchange Membrane Fuel Cells (PEMFCs) and Direct Methanol Fuel Cells (DMFCs) are considered good alternatives as power generation systems for different kinds of applications because of their high efficiency in energy conversion and suitability. One of the PEMFC's problems appears when using hydrogen obtained from reforming, because it contains CO, which can strongly compete with H_2 for adsorption on Pt surface. This contamination lead to the metal poisoning and decreases the anode performance. On the other hand the oxidation of methanol produces CO-type intermediates in the anode of DMFC, which also lead to the Pt metal poisoning [1]Studies have shown that particle size, exposed crystal faces and oxidation state of carbon supports are important factors which have influence on specific activity of the Pt electrocatalyst for CO and methanol oxidation[2]. Unfortunately, the non-treated carbon is often hydrophobic, so there is particular interest to carry out treatments on the carbon surface to activate it by additional functional groups. Studies show the effect of electrochemical treatment of GC support [3] and oxidation of the HOPG substrate on CO and methanol oxidation [4]. But, as we know, these supports are not real support for fuel cells. In this study, the carbon paper (CP), as electrode support, is activated by applying anodic and cathodic potential to introduce oxygenated surface compounds. The Pt was electrodeposited on treated and non-treated electrode and the effect of treatment for CO tolerance was investigated. To the best of the authors' knowledge, studies about the effect of anodic oxidation for CP as a support on Pt electrodeposition is scarcely found in the literature [5] and there is no research for these oxidation of CP as catalyst support for enhancing the Pt activity for CO tolerance in fuel cells electrode. 0.25 cm2 CP (TGPH-090;Toray) was used as the support for electrochemical catalyst preparation. Oxidation on carbon papers were performed by applying +2V for anodic oxidation and -2 V for cathodic oxidation for 5 min in 0.5M H2SO4 solution. Pt was electrodeposited onto the CP by electrodeposition in an electrolyte solution of

0.2M H_2SO_4 +2mM $H_2PtCl_6.6H_2O$. Single-pulse chronoamperometry electrodepsition by adjusting potential profile of 0V (1 s) and 1.15 V (600 s) (vs.Ag/AgCl(sat)) was done. Oxidation of carbon leads to a formation and growth of oxide layer, causing the surface of individual fibers becomes roughened and more defects appear on the surface which is in accordance with the SEM pictures. The surface of the cathodic electrode has more defect than anodic electrode that shows the changes in surface functional groups is different for cathodic and anodic electrooxidation. The oxidized CPs were characterized by micro-ATR-FTIR for both oxidized electrodes. Primary alcohol, ether, phenol, carboxylic, quinne and conjugated ketone functional group peaks can be observed. The strength of these peaks is weaker for anodic electrode which may result from the higher oxidation of carbon paper during the cathodic oxidation. Indeed, Phenol oraal tertiary alcohol and lactone peaks only appear after cathodic treatment which shows additional oxygen functional groups on CP which is prepared by cathodic oxidation. Cyclic voltammetry diagrams of the oxidized CPs (Fig.1) show the magnitude of the background current is highly sensitive to the electrochemical treatment and it is small for non-treated CP in compare with oxidized ones, but in the case of the anodic a high capacitive-like background current is observed. The CV of anodic shows evidence of surface oxidation due to the presence of one anodic and cathodic peak current is assigned to the hydroquinone–quinone redox couple (in the ranges0.3–0.4 V) [6] In cathodic electrode the weak reduction peak at 0.3–0.4 V together with the results of FTIR and SEM analyses, indicate that higher oxidation states of carbon were produced. [1]



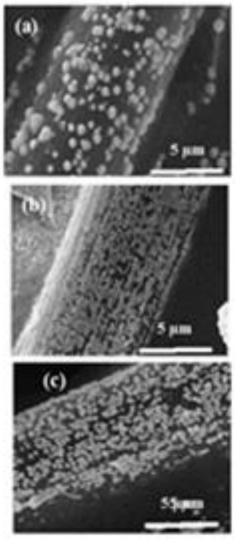


Figure 2 : SEM images of Pt particles deposited directly on (a) non-treated, (b) anodic and (c) cathodic carbon paper

On the other hand, more small particles are noticeable when the deposition is performed on anodic CP(Fig.2). Further, although the metal particles seems bigger on cathodic electrode, uniformly dispersion of Pt with low agglomeration is visible (Fig.2.c). It seems that it is because of the different type of oxygen groups and amount of them, which have influence on nucleation and agglomeration of the particles on treated supports. The higher coulombic charge of the hydrogen adsorption/desorption zone for oxidized electrodes in Fig.3 is related to an increase in ECSA of the catalyst due to lower particle size. [1]. The CO oxidation abilities of the electrodes were evaluated by CO-stripping experiment (Fig.4). The cathodic electrode has lower onset potential of CO electro-oxidation (0.44V) and peak potential of CO electro-oxidation (0.59V) than that of anodic (0.65V) and non-treated electrode (0.70V). These negative shifts show that cathodic electrode has more effective for CO oxidation in compare with anodic and non-treated electrode. The CV curves of methanol electrooxidation for electrodes (Fig.5) were consisted of two well-defined peaks at the forward and backward scans which were related to oxidation of methanol molecules and oxidation of intermediates, respectively. The ratio of the forward anodic peak current (If) to the backward anodic peak current (Ib) which can be used to gauge the tolerance exhibit larger ratios of If/Ib(1.50,1.41) for cathodic and anodic electrodes in compare with non-oxidized electrode. The onset potential of methanol oxidation occurs at 0.135 V, which is relatively 100 mV negative than non-treated electrode. Results show that cathodic electrode has more tolerance for intermediate species in compare with anodic and non-treated electrode. The stability of the electrodes in methanol was also evaluated by amperometric measurements.(Fig.6).Treated electrodes are more stable than non-treated one and cathodic electrode was able to maintain the highest current density and higher stability among all electrodes. We have revealed how the treatment of carbon with cathodic and anodic oxidizing improves the activity of the electrocatalyst in methanol and CO electrooxidations on Pt surface. Our results show that in addition to the size of the catalyst the type of the oxidation and the amount of functional groups and type of them has great effect on the activity of the electrodes on CO tolerance when the carbon support is oxidizing and oxygenated functional groups has two ways to effect on catalytic activity: first, by changing the size and metal dispersion in electrodeposition of Pt on carbon paper. Second, these groups were likely contributing to methanol and CO electro-oxidations similar to bifunctional mechanism .These additional oxygen functional groups on cathodic oxidized CP make this electrode more tolerant in compare with other electrodes in this study.

Keywords: *Carbon paper, Oxidation, CO tolerance, Fuel cell*

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Synthesis of SiNWs Array by Metal-Assisted Chemical Etching

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Introduction

According to special feature of Silicon nanostructures, they have also used in some new devices such as sensors[1], solar cells[2] and lithium-ion batteries. Among the silicon nanostructure silicon nanowires have been identified as one of well-known nanostructures in the semiconductors application [3]. Also, among the methods that used to synthesis of SiNWs, the MACH has been applied because of low cost, controllability and fast synthesis.

Methods

The silicon wafer (p-type, 8-12 Ω.cm and <111> direction) was cut to 1*1 cm^2 square and washed with H_2SO_4:H_2O_2 in ratio of 3:1 (v: v) for 10 minutes. Then it was immersed into solution of 5% HF for 3. The samples were placed into these solutions mixture of $AgNO_3$=0.005 M and HF=4.8 M for one minute. In last step, the sample was placed in solution mixture of H_2O_2=0.8 M and HF=4.8 M. in order to remove silver particles the sample was placed in solution of HNO_3:H_2O_2 by ratio of (1:1, v: v) and washed with deionized water and dried by N_2. The sample was characterized by FE-SEM (MIRA3 TESCAN) equipped with EDX.

Result and discussion

The figure 1-a shows the FE-SEM cross section of SiNWs array. As shown in figure 1-a, the silicon nanowires have been synthesized by the length of 8.5 µm. Also the figure 1-b shows the SiNWs has been formed by diameter of 40 nm. On the other hand, holes were completely injected beneath of silver particles and the silver particles are sunk and localized etching has happened. The uniform silver particles layer is necessary to form the SiNWs array. On the other hand, in the second step the silver particles play catalysis role and help to transfer of holes to silicon valance band.

Conclusion

In summary, we have successfully synthesized of SiNWs array by MACE. Also, the holes injection plays the most important role in MACE. Therefor the SiNWs whit diameter of 30nm was formed. As a result, the uniform of silver particles layer is necessary to form the SiNWs array.

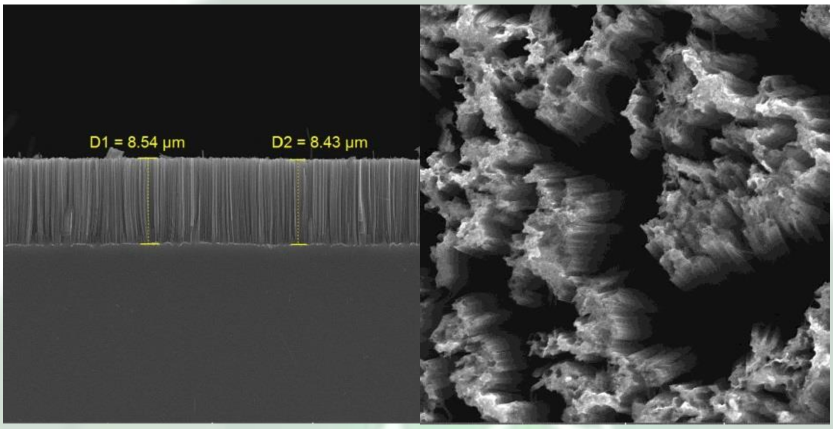

Figure 5 the FE-SEM images of SiNWs array in solution mixture of HF=4.8 M and H_2O_2= 0.8 M.

Keywords: *SiNWs array, Metal assisted chemical etch, Electroless reactions, Silver plating*

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Fabrication of an electrochemical molecularly imprinted polymer sensor for determination of ketorolac trometamin using multivariate optimization using multi-walled carbon nanotubes

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Abstract

Ketorolac trometamin (KT) is used for the short-term treatment of moderate to severe pain in adults. It is usually used before or after medical procedures or after surgery. One of the most promising separation techniques that have emerged during the last decade is based on the use of molecularly imprinted polymers (MIPs). Recently, MIPs have attracted a broad interest from researchers engaged in sensor development (2013, 2014). The general principal of molecular imprinting is based on such a process where functional monomers are copolymerized in the presence of a target analyte (the imprint molecule) which acts as a molecular template (2012). A novel electrochemical sensor using molecularly imprinted polymer (MIP) technique for the detection of KT was developed. The sensitive MIP sensor for KT was electrochemically synthesized onto multi-walled carbon nanotubes (MWCNTs) immobilized pencil graphite electrode (MWCNTs/PGE) surface. The multivariate methods were used to optimize the voltammetric response of modified electrode for determination of KT (2014). A Plackett–Burman design (PBD) was chosen as a screening method to estimate the relative influence of the factors that could have an influence on the analytical response (current). The significant variables including MWCNTs (A), deposition time (B), pyrrol concentration (C), KT concentration (D), number of cycles (E), pH (F), scan rate (G), loading time (H) and stirring rate (I) were optimized using central composite design (CCD). The optimum values of significant parameters i.e. A, C, D, F and I were obtained 0.36g.L^{-1}, 421s, 0.07mol.L^{-1}, .002 mol.L^{-1}, 10, 4, 103mV.s^{-1}, 14min and 400r.p.m, respectively. The equation for sensor response based on the optimized parameters was obtained as :

$$\text{MIP} = -200.7 + 0.1081\text{B} + 2.619\text{G} + 9.74\ \text{H}$$

Under the optimal conditions, the sensor showed a high selectivity and excellent stability toward KT and used to detect the analyte in real samples successfully. This work discusses an

electrochemical sensor, which combines the advantages of the use of MIPs with those of employing electrode surface modification and multivariate optimization techniques.

Keywords: *Molecularly imprinted polymer, Multivariate optimization, ketorolac, Electrochemical sensor*

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Perturbation Factors on Titania Nanotubes Anodization Process

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Abstract

Titania nanotubes are one of the most promised materials which apply in numerous applications due to its unique properties. In order to obtain highly ordered and well aligned Titania nanotubes, well modified titanium sheets and appropriate junction are desirable. In this research we are aiming to demonstrate the small perturbations and their results in morphological and structure properties. In the end, highly ordered Titania nanotubes were synthesized successfully.

***Keywords**: Perturbation factors, Anodizing procedure, Titania nanotubes, morphology optimization*

Introduction

Titania nanotubes are the most promised materials which applied in dye synthesized solar cells[1] lithium ion batteries [2]and drug delivery systems[3] .Various advantages of titania nanotubes including low cost, non-toxicity and chemical stability [2].

There are a lot of methods which can be used to prepare titania nanotubes including hydrothermal[4], template assisted [5]and anodizing method. Nanotubes which were synthesized by anodizing method are more aligned and has high length to diameter ratio[6].

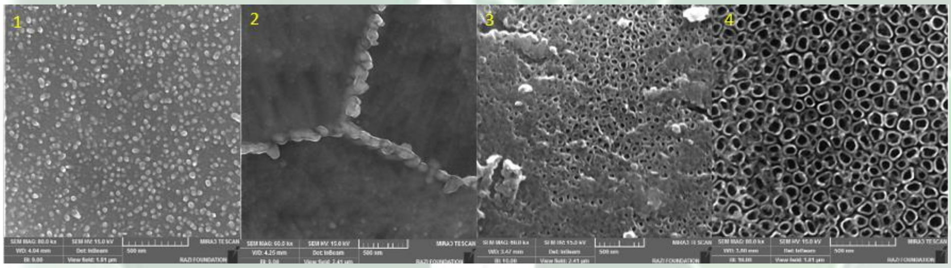
In this research, we presume that well junction and fine polishing are major determinants of desired Titania nanotubes. By fixing these issues, highly ordered Titania nanotubes were obtained successfully.

Experimental

Titanium sheets were polished mechanically cleaned in ethanol and deionized water. The electrolyte is a 1wt% HF solution. Titanium sheet was used as anode and Pt used as cathode. Anodizing process were carried out at 20 volt. Meanwhile the procedure, magnetic stirring were used continuously in order to have a homogeneous solution. The anodizing procedure were performed at room temperature.

Results and discussion

Formation of Titania nanotubes can be influenced by different conditions. To obtain well aligned Titania nanotubes, it is necessary to ensure junctions and surface modification. Figure 1 show a sample which cannot be anodized well due to the contact of solution and anode/cathode -wire junctions. it is demonstrated that the contact with solution make a huge perturbation on electronic contact which result in creation some small pits and in the other case, figure 2, the sample etched completely which is indicated that the electric field does not have any effect on titanium sheet. Similar observations were obtained when the surface modified in an inappropriate way. The scratches may results in perturbation in local electric field so the formation and uniformity of Titania nanotubes will be affected. Figure 3 is illustrated that poor polishing results in low uniformity. Figure 4 shows a well modified titania sheets that the junction were well defined, so the titania nanotubes were well aligned and highly uniform.



Conclusions

Titania nanotubes were synthesized successfully. The perturbation factors were defined and analyzed carefully. Morphological and structural properties were characterized by field emission scanning electron microscopy.

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Effect of etching current density on photoluminescence properties Of porous silicon

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Abstract

Due to the excellent properties such as efficient visible room-temperature photoluminescence (PL) and extremely large surface-to-volume ratio, porous silicon (PS) is material of interest in many applications such as photodetectors [1]. In this research, effect of etching current density (J) on optical properties of photo-electrochemically synthesized PS samples was characterized in order to achieve a porous morphology with maximum PL properties. PS samples were synthesized by photo-assisted electrochemical etching (PECE) of (100) oriented phosphorus doped crystalline silicon (c-Si) substrates with specific resistance of $0.05\ \Omega.cm$ and thickness of $680\ \mu m$. A thin film of silver (Ag) with the thickness of $\sim 150\ nm$ was deposited on the back side of c-Si substrates in order to facilitate anodization process. The metallization was taken place in a vacuum chamber of a sputtering system and an ultra-pure Ag plate was used as a target. This process decreased the surface resistivity to $0.001\ \Omega.cm$ after 15 min of annealing in tube furnace at a temperature of $430\ ℃$ under nitrogen gas flow [2]. The chemical solution used here was containing a mixture of hydrofluoric acid (HF 38-40%) and ethanol (C_2H_5OH 96%) in a volumetric ratio of 1:4. Current densities as critical experimental parameters were fixed at 10, 20, 40, 60 and 80 $mA.cm^{-2}$ for sample a, b, c and d respectively using DC source meter (Keitlly 2400, USA) throughout the etching time (20 min). A platinum mesh was used as a counter electrode (cathode) in PECE cell and it was located approximately $10\ mm$ directly above the surface of c-Si sample (anode). To create the required holes for occurrence of dissolution reaction on the surface layer of working electrode (anode) and PS formation, front side of the c-Si was irradiated by means of one 100 W tungsten lamp at a distance of $20\ cm$ above it during the etching process. Fig. 1 shows SEM micrograph of synthesized porous substrate. SEM view reveals that while the applied J increases from $20 mA.cm^{-2}$to $80 mA.cm^{-2}$, pore diameter of the PS samples increases and total volume of

Si nanocrystallites on the surface decreases. Also, the decrease in pore density N_p(the number of pores per unit area) was observed on PS surfaces by increasing J for sample c and d. The logical reason for the evolution in the morphological characteristics of the pores of these PS samples is influence of the electric field on carrier's movement and hence on dissolution [3]. The effect of J on the band gap structure (E_g) and emission properties of the PS samples was identify using PL spectra. In this experiment, in order to record S-band transition, excitation wavelength of PL was 405 nm. Fig. 2 shows the PL spectra of PS samples. A remarkable increase in intensities of the emitted photon from porous samples was observed with initial increase in J from $10mA.cm^{-2}$ to $20mA.cm^{-2}$. Then a slight decrease in PL intensity was shown by increasing J from 20 $mA.cm^{-2}$ to 80 $mA.cm^{-2}$. Maximum intensity was detected in sample b with J = 20 $mA.cm^{-2}$, at a wavelength of ~658.2 nm that can be due to the total amount of nanocrystallites on the surface of this sample compared to sample a. Applying higher current densities (more than 20 $mA.cm^{-2}$) will increase dissolution of silicon material on the surface (as shown in Fig. 1) and thus will reduce PL intensities in samples c and d compare to sample b. The larger macro-cavity pores reduce the amount of nanocrystallite and result in light trapping. Therefore, the specific surface area of PS will reduce by increasing macro-cavities which lead to decrease in PL peak in samples c and d.

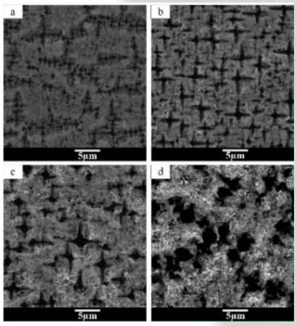

Fig. 1. SEM image of porous samples a, b, c and d

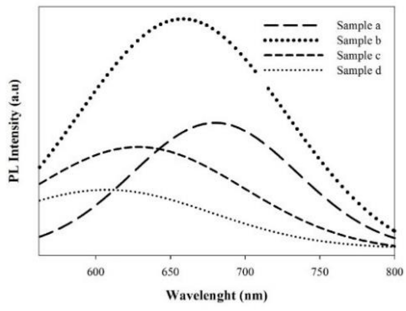

Fig. 2. Photoluminescence (PL) spectra of porous samples a, b, c and d.

Consequently, our PL analysis reveals that applied J has a significant effect on structural properties such as size of pores and crystalline properties of PS. Therefore, etching current density can be assumed as an outstanding parameter to optimized electronic structure of PS (e.g. band gap) and it has an important role in its light emitting properties. In the current report, it was shown that the porosity of PS is not the only parameter which affects the optical properties. The morphology of pores acts an important role to determine PS properties.

Keywords: *Porous silicon, Photo-electrochemical etching, Etching current density, Photoluminescence.*

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Synthesis of Commercial Li($Ni_{0.33}Co_{0.33}Mn_{0.33}$)$O_2$ Cathodic material via Sol-Gel Method

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Introduction

To date, batteries play an important role in storage energy industry. Cathodic materials due to existence lithium ions in own structures for lithiation/delithiation should be have high specific capacity, high current rate capability and long life time [1]. Commercial NCM with $Li(Ni_{0.33}Co_{0.33}Mn_{0.33})O_2$ chemical formulae due to high specific capacity of 170 mAh/g in comparison to 165 mAh/g for LFP and 145 mAh/g for LCO as a popular cathodic material attracts many researches attention. Moreover, intercalation of lithium ions into NCM layered structure cause to prevent induced stress due to lithiation and delithiation [2].

Experiment

In order to NCM-111 synthesis via sol-gel method, acetate precursors of Ni, Co and Mn were weighted to stoichiometry ratio, and were vigorously stirred after adding to 100 mL deionized water. Afterward, lithium precursor and 1 M complexing citric acid were added to solution to form NCM complex. Finally, fixed pH solution was drying at 80 ˚C and was calcined at 450 ˚C and 700 ˚C respectively for 5 h and 10 h for phase stability and removal polymeric impurities.

Results and discussion

In this study, the effect of calcination temperature to synthesize pure $Li(Ni_{0.33}Co_{0.33}Mn_{0.33})O_2$ was investigated. The achieved XRD patterns of sample well shows to form NCM compound with $Li(Ni_{0.33}Co_{0.33}Mn_{0.33})O_2$ stoichiometry that completely consistent with 98-011-06256 reference code. Comparison of both pattern together clearly shows that increasing calcination temperature caused to decline of peaks width and rising of peaks intensity, which showing grain growth and dislocation formation. FESEM micrograph of sample after 10 h calcination at 700 ˚C was shown in figure 2. The existence of porosity into 20 µm particle makes it possible for lithium ion insertion/extraction with high rate capability. Moreover, figure 2-b demonstrate 20 µm particles involve lower particles, which ranging of 300 nm to 1 µm.

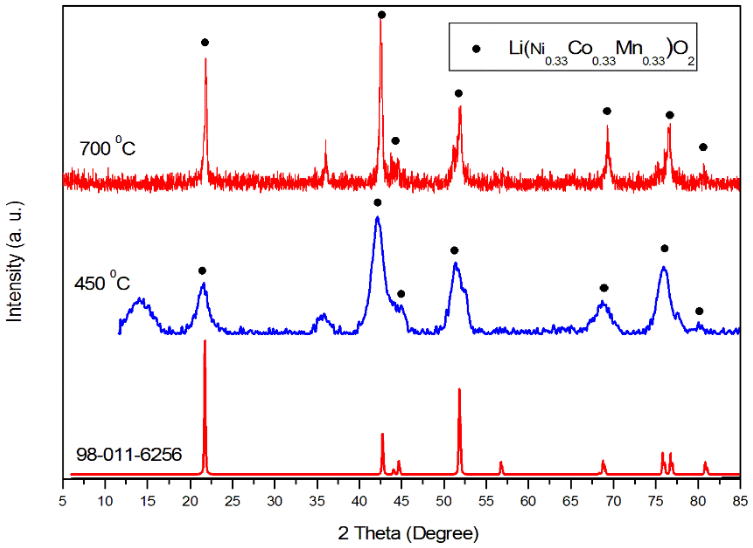

Figure 1. XRD pattern of sample after calcination at 450 ˚C for 5 h and 700 ˚C for 10 h.

Conclusion

In summary, we have shown that Li($Ni_{0.33}Co_{0.33}Mn_{0.33}$)$O_2$ successfully synthesized via sol-gel method and the existence of porosity in its microstructure makes it possible for lithium ion insertion/extraction with high rate capability.

Keywords: *NCM, cathode materials, sol-gel.*

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Implementing Potentiostat for Electrochemical Capacitance Voltage Dopant Profiling

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Abstract

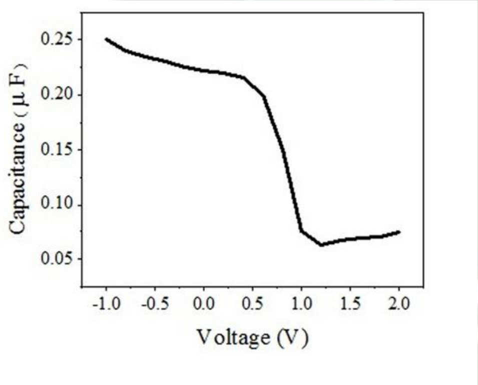
In this work, we have developed an algorithm to use potentiosatat for acquiring data required for ECV calculations. The results have been compared with the results of ECV instrument in the literature. Dopant distribution characterization of semiconductor devices is critical for obtaining optimum performance [1]. Conventional methods for obtaining depth profile are spreading resistance profiling(SRP), secondary ion mass spectroscopy (SIMS), capacitance-voltage (CV), electrochemical capacitance voltage (ECV) [2]. The SIMS method is expensive in comparison to the other methods and are limited to measuring chemical doping concentration[3]. In addition SIMS has difficulty in characterizing textured wafers. SRP method required that the junctions be less than 100 nm deep. Moreover SRP accuracy depends on the proper probe conditioning[3]. Conventional CV technique is useful in the measurements of the carrier concentration profiles. In this technique a metal Schottky contact is formed on the sample and a stepped reverse bias is applied to slowly depleting thin regions of the semiconductor. Using differential capacitance-voltage the carrier profile can be deduced. Main limitation in this method occurs during applying a high field to low-doped regions which will be create an electrical breakdown. Electrochemical capacitance voltage (ECV) method overcomes on this limitation by using an electrolyte solution instead of a metal for creating a schottky contact. By frequently etching the sample and measuring the capacitance at every etch step, one can calculate concentration in any depth without the need of applying high bias voltages [4]. While secondary ion mass spectroscopy (SIMS) has difficulty in characterizing textured wafers, ECV can practically measure them by assuming the area factor ([surface area] / [projected area]). Another advantage of ECV method over other methods is that this method provides only the electrically active dopants and has a depth resolution in the sub-nm range, which makes it a very powerful measurement tool for the use in device simulations and for device optimization in the PV industry. Unfortunately ECV instrument is expensive instrument and is not a conventional analysis instrument in laboratories, but potentiostat is commonly available in

labs. This method can be used for obtaining concentration profile for variety of semiconductors such as p and n-type silicon, GaAs, InSb by using appropriate electrolyte[5]. Developed algorithm began by differentiating C-V and using formula 1 and 2 to obtain carrier concentration and depletion regions depth. Where q is charge of electron, ε_0 is permittivity of vacuum, ε_r is relative permittivity and A is the measurement area[2]. (1)

$$N(W) = \frac{c^3}{q\varepsilon_0\varepsilon_r A^2(\frac{dc}{dv})} \qquad (2)\ \ W = \frac{\varepsilon_0\varepsilon_r A}{c}$$

By step by step etching the wafer and calculating the etch thickness by integrating Current–time, and adding etched thickness to W the accurate profile to any depth can be calculated.

Figure 1 shows C-V curve measured at 20KHz[6]. Implementing the algorithm for the C-V, we have calculated dopant profile as shown in figure 2. As it can be seen in figure 2 at width 19nm a dopant profile smoothly decreases and will be fixed in width 46nm which reached to p-n junction. Our result is different from the reported values by about 10% which could be improved by using correction factors in the algorithm and implementing repeated etching we will obtain more accurate profile.



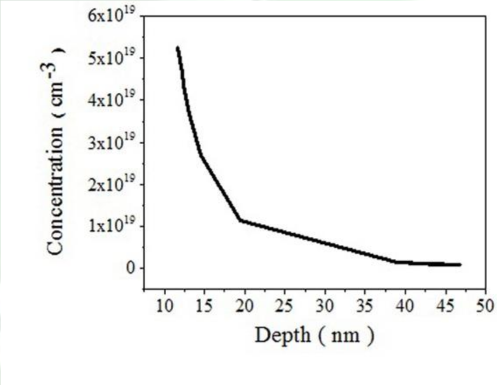


Fig.1. Capacitance-voltage curve (reference [6])

Fig.2. Concentration dopant by ECV method

***Keywords**: ECV, Depth profile, Carrie concentration*

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Preparation and Evaluation of Nanocomposite Membranes Based on Sulfonated Graphene Oxide and Carbon Nanotube for Aluminum Air Batteries

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Abstract

The procedure of membrane synthesis and evaluation plays an important role in development of new energy related technologies such as fuel cells, batteries and electrolyzer. The main challenge of membrane technology is the synthesis of high efficient, environmental friendly and cost effective membranes. In this work, a series of proton exchange membranes based on multi-functionalized graphene oxide (GO) and multi walled carbon nanotube (MWCNT) were synthesized via a solution casting procedure. The structure and morphology of the samples were investigated by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and optical polarizing microscopy. Finally, the synthesized membranes were evaluated for proton conductivity from the point of measured current versus time at a constant potential in a homemade aluminum air battery cell setup and compared with the commercial nafion 112 membrane. For the synthesis of membranes, at first GO was synthesized through modified hummer method [1], MWCNT purchased from US research nanomaterials Inc. (OD: 20-30 nm) and purified via reflux treatment in HCl: HNO_3 solution at 90 °C for 30 min, Then they were sulfonated via chlorosulfonic acid [2] and labeled as GO-SO_3H and MWCNT-SO3H respectively. The membranes were prepared by casting the polymer solution of polyacrylonitrile/dimethylformamide With GO, GO-SO3H and MWCNT-SO3H to get modified membranes with the labels of GO-AN, GO-SO_3H-AN and MWCNT-SO_3H-AN. Fig. 1 shows the FT-IR spectra of GO, GO-SO_3H and MWCNT-SO_3H. As it can be seen in the figure, all of the characteristic peaks of C-O, C=C, C=O and C-OH are obvious in all samples spectra. But GO-SO_3H and MWCNT-SO_3H spectra showed the additional O=S=O stretching vibration, -SO_3- symmetrical stretching vibration and S-OH stretching vibration which can enhance the proton conductivity of membrane.

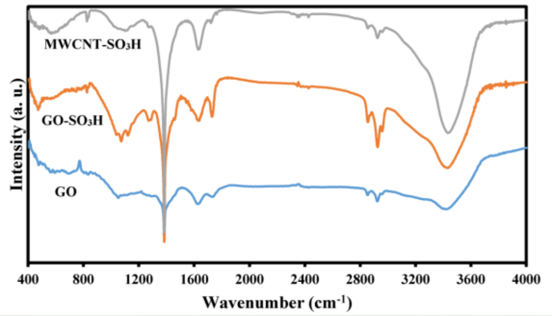

Figure 6. FT-IR spectra of GO, of GO-SO_3H and MWCNT-SO_3H

Fig. 2 shows the optical polarizing microscopy of GO-SO_3H. It confirms the transparity and presence of sulfonated GO in the nanocomposite membrane. The average currents of GO-SO_3H-AN, MWCNT-SO_3H-AN and GO-AN were 705, 653 and 608 mA at 2.3 V whereas the measured current for nafion 112 was 1200 mA at this voltage. It appears that of GO-SO_3H-AN and MWCNT-SO_3H-AN nanocomposite membranes can be good candidates for future battery applications

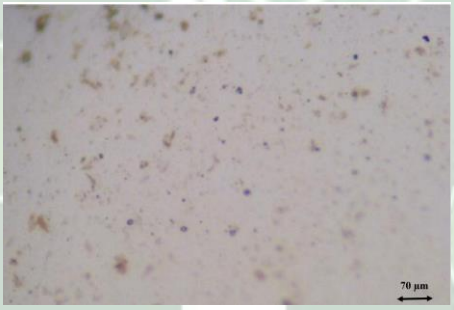

Figure 7. Typical optical polarizing microscopy of GO-SO_3H

Keywords: *graphene oxide, multi walled carbon nanotube, solution casting procedure, nanocomposite membrane, aluminum air battery*

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Preparation and electrochemical performance of Pt black-carbon nanotube composite for methanol oxidation reaction

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Abstract

Fuels cells are actively investigated as an attractive alternative to conventional fossil fuel combustion engines for cleaner power generations [1]. Direct methanol fuel cells (DMFCs) have attracted much attention of researchers due to their high energy density, non-pollution and other great advantages [2]. The excellent catalytic activity of platinum for the electrooxidation of methanol makes this metal preferable to be used as electrocatalysts both at anode and cathode of DMFCs [3]. This work reports the preparation, characterization, and electrocatalytic characteristics of a new metallic nanocatalyst. The catalyst, Pt black–carbon nanotube (Pt-CNT), was prepared by ultrasonication method and characterized by scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS), and voltammetry. The electrocatalytic properties of the Pt-CNT composite modified carbon paste electrode (Pt-CNT/CPE) for methanol (CH_3OH) oxidation have been investigated by cyclic voltammetry (CV); high electrocatalytic activity of the Pt-CNT/CPE can be observed. This may be attributed to the high dispersion of Pt catalyst and the particular properties of CNT support. The long-term stability of Pt-CNT composite was investigated in 0.05 M CH_3OH in 0.1 M H_2SO_4 solution. The results imply that the Pt-CNT composite has good potential applications in fuel cells.

Keywords: *Pt black, Carbon nanotubes, Methanol oxidation reaction, Electrocatalyst*

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Synthesis of Potassium Exchange Membrane by Clindamycin Antibiotic

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Abstract

Ionophores are moderate molecular weight compounds that are mobile ion carriers. Because ionophores are highly lipophilic, they rapidly dissolve into bacterial cell membranes. Ionophores bind ions, shield the ionic charges and translocate ions across the bacterial membrane, disrupting crucial ion gradients [1]. The first neutral ionophores used in ISE membranes were antibiotics. They were followed by a large number of natural and synthetic, mainly uncharged carriers for cations and a series of charged and uncharged ones for anions [2]. The structure of clindamycin raises additional possibilities for its mode of transport. This antibiotic is composed of an amino acid (hygrinic acid) linked to an amino sugar [3]. In this research, we aimed to analysis the amounts of the Clindamycin membrane selectivity with the base of acrylonitrile polymer and the current transition is tested by an aluminium Air battery. The results show a notable current transition. The effect of this method has been examined by FT-IR and XRD analysis.

First dissolve poly acrylonitrile with some DMF solution on a magnetic stirrer. Then add some Clindamycin powder. In order to slick the solution, put them into an ultrasonic bath for some minutes. After that pour the solution on a flat glass and put it into an oven with 90C$^{\circ}$ to be dried. FT-IR spectra of Clindamycin is shown in Fig. 1 In this spectra there are two peaks in 3376cm^{-1} and 3373cm^{-1} that are related to the OH connected to cyclohexane ring in the structure of Clindamycin. Besides that, there is a peak around 1456cm^{-1} and one other in 1683cm^{-1}. These are respectively related to the functional group of C-O-H and NH.

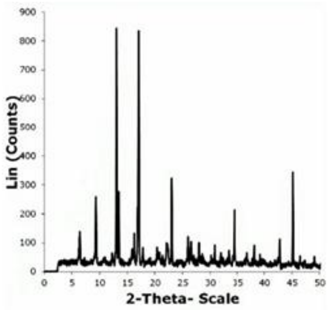

Fig. 1 FTIR Spectrum of Clindamycin

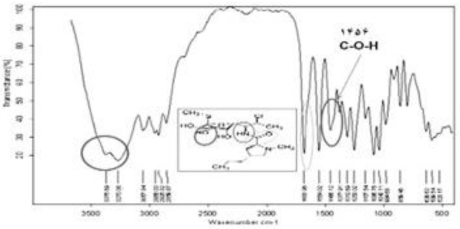

Fig.2 XRD pattern of Clindamycin

Fig. 2 shows the XRD spectra of Clindamycin powder. This chart explains intensity of X-Ray reflected from clindamycin particles as a function of angle. As shown in Fig. 2, Clindamycin powder has different peaks in different angles. Each peak is related to a special particle. The angle between Source-Sample and Detector-Sample is shown by 2Ө which is equal to 17.0545, in this method. Ө is the angle among X-Ray and sample particle. The average current transition tested by the Aluminium Air battery was 600mA with the voltage of 2.1v. Its shows that the current transition through this membrane is notable

Keywords: Potassium exchange membrane, Clindamycin, ionophore, poly acrylonitrile

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A hydrothermal-electrochemical synthesis of MnO_2 nanostructures for Zn-Air applications

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Abstract

In recent years, metal-air batteries that are receiving attention for both fundamental and industrial viewpoints, because they exhibit high specific energy density compared to other energy storage devices, in particular the Li-ion systems. Among metal–air batteries, the zinc–air batteries represents a safe, environmentally friendly and potentially cheap and simple way to store and deliver electrical energy for both portable and stationary devices as well as for electric vehicles [1]. In the development of zinc-air batteries, the high performance electrocatalysts for air cathode is an important issue [2]. MnO_2 has attracted great attention due to its favorable Oxygen Reduction Reaction activity, redox stability, low-cost and abundance [3].

In this work, manganese dioxide nanostructures were prepared by a hydrothermal-electrochemical method. The syntheses were performed in a closed, Teflon-lined stainless steel reaction vessel as a two-electrode system by constant current mode with a current density of 10 mA/cm^2 at 80 and 110 °C. Prepared samples have been characterized using X-ray diffraction (XRD), morphology of the samples has been characterized by field-emission scanning electron microscopy (FESEM). The pore structures of the prepared samples were tested by N_2 adsorption-desorption measurements. The electrochemical behaviors of prepared samples were investigated by electrochemical techniques including polarization curve and galvanostatic discharge.

The XRD patterns of the as-prepared samples indicating that purely crystalline □-MnO_2 were successfully synthesized. The FESEM images showed that the nanoclusters of MnO_2 were composed. The size of nanoparticles were about 1–20 nm that reduced by increasing the synthesis temperature. The N_2 adsorption-desorption measurements results showed that isotherms of these samples were of typical IV classification and exhibited clear hysteresis loops which were characteristic of mesoporous materials. The results of electrochemical tests revealed that the peak power density of Zn-Air batteries were 80 mW/cm^2 which increased to 120 mW/cm^2 when

temperature of MnO_2 synthesis was raised from 80 to 110℃. The cells galvanostatic discharge showed maximum discharge current density of 150 and 300 mA/cm^2 for cells, respectively.

Keywords: *MnO_2 nanostructure, hydrothermal-electrochemical synthesis, Zinc-air battery.*

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Electrochemical Study Of 4-(2- amino-1-hydroxyethyl)benzene-1,2-diol in the Presence of Triethyl phosphite

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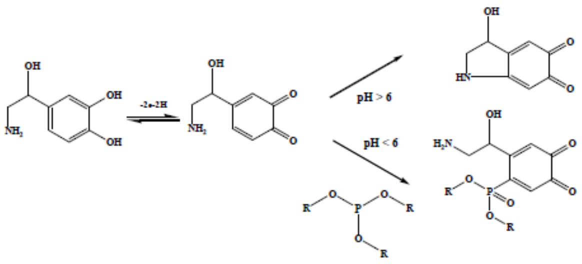
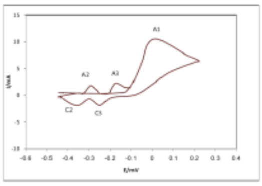
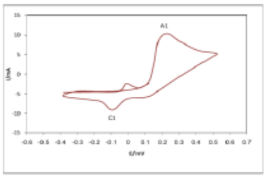
Abstract

4-(2-amino-1-hydroxyethyl)benzene-1,2-diol also called Norepinephrine (NEP) is a catecholamine with multiple roles including those as a hormone and a neurotransmitter.[1] It is the hormone and neurotransmitter most responsible for vigilant concentration in contrast to its most chemically similar hormone, dopamine, which is most responsible for cognitive alertness.[2] The mechanism of electrochemical oxidation of NEP, in the presence of triethyl phosphite as a nucleophile has been studied in an aqueous solution using cyclic voltammetry and controlled potential coulometry. Cyclic voltammetry was performed using a Behpajoh Model BHP 2061-C potentiostat/galvanostat. In the voltammetry experiments, a glassy carbon disc (2 mm diameter) and a platinum wire were used as working and counter electrodes, respectively. The working electrode potentials were measured versus Ag/AgCl (KCl 3.0 M). All electrodes were purchased from AZAR electrode. Alumina powder (0.3 M) was used for mechanical polishing of the working electrode. This treatment was followed by ultrasonic cleaning for 30 s. Figure show the CVs of 1.0 mM solution of NEP in the pH 6.0 and 7.0. The CV in the pH=6 show one anodic peak (A1) related to the conversion of the catechol moiety of NEP to *o*-quinone and one cathodic peak (C1) related to the reduction of the produced *o*-quinone under mild acidic conditions. At pH =7.0, the CV show one anodic peak in the positive-going scan and two cathodic peaks (C2 and C3) in the negative-going scan. In the second cycle, the CV show another anodic peak, A2, as the counterpart of C2. The appearance of these new anodic and cathodic peaks indicates the formation of an electroactive species at this condition. The most probable reaction for the formation of this product is the intramolecular Michael addition of amine group to electrochemically generated *o*-quinone. More voltammetric studies were performed at various scan rates and the normalized voltammograms of NEP. a Normalized CVs are obtaind by dividing the current of CVs by the square root of the scan rate. They can be simply overlaid for obtaining more useful information. [3]





pH=7



pH=6

The reaction mechanism is an ECE mechanism and the products of reaction are believed to be triethyl phosphite derivatives of NEP. The whole characteristics of a typical ECE mechanism are observed for this electrode reaction in which E represents an electron transfer at the electrode surface and C represents a homogeneous chemical reaction. The observed homogeneous rate constants (k_{obs}) for reactions were estimated by comparing the experimental voltammetric responses with the digitally simulated results based on the proposed mechanism. The simulated cyclic voltammograms show good agreement with those obtained experimentally. A quantitative relation between half-wave potentials of NEP and the reactivities of their corresponding *o*-Quinone were derived.

Keywords: *Cyclic voltammetry, ECE mechanism, Catechol, Norepinephrine*

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Graphene for corrosion protection of stainless steel bipolar plates for polymer electrolyte membrane fuel cell

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Abstract

In this study, stainless steel with a nickel layer (Ni/SS) and composite of RGO and Ni coated on SS (G/Ni/SS). The Ni and graphene film, synthesized by electrochemical method in watts bath. The morphology of coated surfaces are studied by field emission scanning electron microscopy (FE-SEM) and Atomic-force microscopy (AFM). Here, we employ electrochemical measurements such as linear polarization and electrochemical impedance spectroscopy measurements in 3.5% NaCl solution to study the corrosion inhibition of the sample. Finally, we use Tafel analysis to quantify the corrosion rates of samples with and without coatings. Our results show that even non-perfect multilayer graphene films can considerably increase the life time of future-generation bipolar plates for fuel cells.

Keywords: *Linear polarization, electrochemical impedance spectroscopy, Graphene, corrosion rates*

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Synthesis of Nanostructured ZrC Coating by Electrolysis

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Abstract

Zirconium alloy due to low thermal expansion coefficient and neutron absorption coefficient is used as clad of fuel in nuclear fission reactors. Coating can be used to extend efficiency of the Zr cladding and also reduce its corrosion. One of the applications of transition metal carbide is use of zirconium carbide in nuclear fuel cladding (1). In this study nanostructured zirconium carbide (ZrC) coating was synthesized on the zirconium by electrolysis of molten salts. For the synthesis of zirconium carbide, NaF (99%, Merck), KF (99%, Merck), ZrO_2 (99.5%, Made in China), $Na_2B_4O_7.10H_2O$ (99.5%, Merck) and $Na_2CO_3.H_2O$ (99.5%, Merck) were used with (18/44، 13/54 ،1/58، 32/59، 33/84) wt%, respectively (2). ZrO_2 as a source of zirconium and Na_2CO_3 were used as a carbon source. The mentions salts were poured into platinum crucible and inserted inside outdoor furnace in 772 °C temperature. Zirconium cladding as the cathode and platinum crucible as the anode for electrolysis was used. Using the power supply DC, electrolysis operation was done with current density150 mA /cm^2. In the presence of argon gas at the time 180 minutes. The coating was characterized by scanning electron microscopy (ZEISS, EV018 model) and X-ray diffraction (H2E-STOE-Germany, STIDY-MP model).

X-ray diffraction patterns ZrC coated on the zirconium shown in Figure 1. Zirconium carbide peak in positions $2\theta \approx 32.6, 38.5, 55.5, 65.8, 69.1^o$ be seen in this sample is to show the formation of ZrC crystal plates (3-4). Using the Scherrer equation, the crystallite size was calculated below 60 nm that indicates a nanostructure coating is synthesized. Other peaks observed in XRD is related to zirconia. SEM image of ZrC coating in current density150 mA/cm^2 was shown (Fig. 2). The average particle size of ZrC was 71 nm. The coating was formed from agglomerates of nanoparticles of zirconium carbide. The average thickness of the coating was 98 μm.

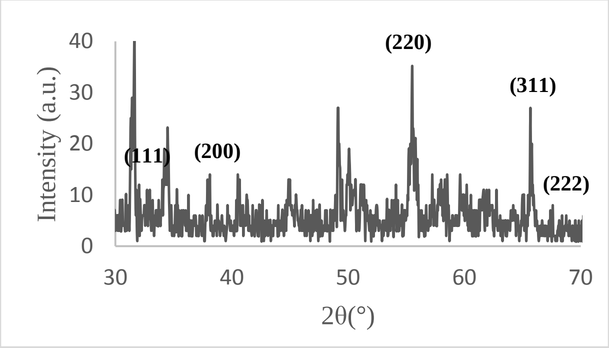

Fig. 1 XRD pattern of ZrC coating

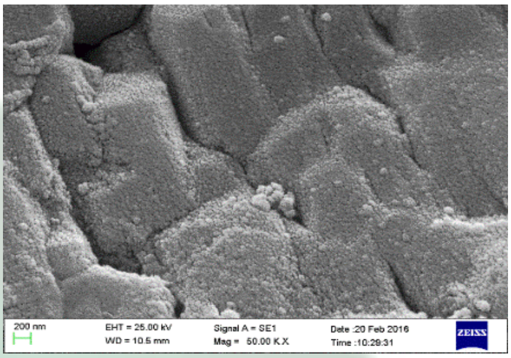

Fig. 2 SEM image of ZrC coating

In this study nanostructured zirconium carbide (ZrC) coating was synthesized on the zirconium cladding by electrolysis of molten salts. Coating characterization was performed using XRD and SEM. Formation of zirconium carbide coatings with nano-structure confirmed by using XRD. The results were shown that the average crystallite size and the average thickness of the coating, 71 nm and 98 µm, respectively.

Keywords: *Electrolysis, Nanostructured, ZrC, XRD, SEM*

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The Corrosion Study of Nanostructured ZrC Coating

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Abstract

In this study nanostructured zirconium carbide (ZrC) coating was synthesized by electrolysis of molten salts, and its corrosion resistance was investigated by polarization method. The results show that the coating increased the corrosion resistance of zirconium and the passivation range. This behavior is influenced by nanometric structure of zirconium carbide because of coherence and lack of cracks in the coating.

Keywords: *Nanostructure, ZrC, Corrosion, Polarization*

Introduction:

Coating on the Zr cladding can be used to extend its efficiency and also reduce corrosion. Transition metal carbides for high hardness, high melting point and chemical stability is considered in the industry (1-2). One of the applications of transition metal carbide is use of zirconium carbide in nuclear fuel cladding. In this study, corrosion behavior of nanostructure zirconium carbide coating was investigated.

Method

Nanostructured zirconium carbide (ZrC) coating was synthesized on the zirconium by electrolysis of molten salts (3). Corrosion studies of samples were performed using potentiodynamic polarization. Corrosion tests were done in a solution similar to the nuclear reactor coolant containing boric acid (H_3BO_3), lithium hydroxide (LiOH) at pH = 6.85. The range of potential was -1.7-2.6 V *vs* Ag/AgCl electrode. The scanning speed 1mV/s were used for samples coated and uncoated by the galvanostat-potentiostat Auto Lab.

Results and Discussion:

Polarization curves for Zr and ZrC was shown in Figure 1. Information related to corrosion, including the polarization resistance (Rp) and corrosion rate (CR) of polarization curves extracted and presented in Table 1. ZrC has higher polarization resistance and lower corrosion rate compared to zirconium. The curve shows that both samples have the range of passivation (4). But by formation ZrC coating on the surface of Zr, the current of passivation transferred to smaller amounts and the range of passivation potential severely spread. Both behaviors (in the presence of ZrC coating, corrosion rate decreases and the wider region of passivation) shows the behavior of ZrC as a protective layer against corrosion for zirconium in solution similar to the reactor coolant.

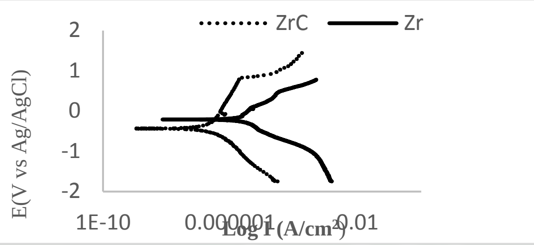

Fig. 1 Polarization curves of Zr and ZrC

Table 1

sample	ZrC	Zr
R_p(ohm)	2.75E+05	6.62E+04
CR (mm/year)	2.11E-4	1.63E-03

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Electrochemical deposition of porous Cu and Cu-Zn and investigation of hydrogen evolution reaction about them

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Abstract

Nano porous metals with nano porosity because of a very high specific surface area of them, low density and good catalytic activity have unique chemical, physical and mechanical properties. Due to these advantages they can be used as an electrocatalyst in several reactions. In this work we used them for investigation of hydrogen evolution reaction.

During that, at first we deposited Cu and Cu-Zn by electrochemical method and investigated by scanning electron microscopy. After that we used mentioned electrodes as cathode in hydrogen evolution reaction and compared with each other by linear sweep voltammetry and chronoamperometry. Results showed that electrochemical performance of porous Cu-Zn electrode is better than porous Cu. Also porous Cu showed porosity has an important effect on electrochemical properties of metals.

Keywords: *Hydrogen Evolution, Electro-deposition, porosity, Nano-porous*

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Improving the performance of vanadium redox flow batteries for large - scale energy storage

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Abstract

Recently, vanadium redox flow batteries (VRFBs) have received significant attention due to their potential as large-scale electric energy storage devices. Indeed, they have been trialed or adopted commercially for load levelling and related applications worldwide. The VRB employs vanadium ions, V (II)/V (III) and V (IV)/V (V) redox couples, to store energy in negative and positive electrolytes, respectively. Electrical balance is achieved by the migration of proton across a membrane separating the electrolytes. VRBs use only one element (vanadium) in both tanks, exploiting vanadium's ability to exist in several states. By using one element in both tanks, VRBs can overcome cross-contamination degradation, a significant issue with other RFB chemistries that use more than one element. The performance of VRFBs still needs to be improved in terms of their voltage efficiency (VE) and energy efficiency (EE) to afford long-term and low-cost operation of the cells. In this work, the importance of operational variables on the performance of a unit VRB cell is investigated. Therefore, in order to optimize the operating conditions which can reduce the crossover and maintain the long-term stability of the electrolyte, it is necessary to evaluate the electrolyte, for instance optimum electrolyte can hold more than 70% more vanadium ions or by using graphen-modified-graphite (GMG) electrode, electrochemical activity of the VRBs can be increased about 30% compare to those of pristine graphite. In addition in order to optimize the operating condition which can reduce the crossover and maintain the long-term stability of the electrolyte, it is necessary to evaluate the ion exchange membrane for VRB system.

Keywords: *Flow Battery ،Optimize, Voltage efficiency ، Modified Electrode*

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An indirect electrochemical determination of thioacetamide by using of $Ag@Fe_3O_4$ nanoparticle modified carbon paste electrode.

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Abstract

Tahiocetamide (TAA), is a widely used sulfur-containing compound both in the laboratory and in various technical applications and can also be present in the environment as organic sulfur compounds. TAA is used as a replacement for hydrogen sulfide in qualitative analyses and in hospital practice, as an accelerator in rubber vulcanization, as a reductant additive in the leather, textile and paper industries, generally having a similar role to thiourea. The widespread uses of TAA are unavoidably accompanied by its toxicity and a number of ecotoxic effects in environmental pollution can result from TAA manipulation and its consequent presence in waste waters. These aspects become increasingly important due to high degree of hepatic and neurotoxic injury, and carcinogenity, of TAA, which has been demonstrated under various experimental conditions. Thus, in these circumstances the detection of thioacetamide in real time has become more and more important [1]. Electrochemical methods are simple and versatile due to their advantages such as cheap instrumentation, quick response time, high sensitivity and wide linearity. In this work an electrochemical sensor was proposed for the determination of thioacetamide. For this propose $Ag@Fe_3O_4$ nanoparticles [2] were applied as an effective modifier for the modification of carbon past electrode. TAA can form the self-assembled monolayers (SAMs) on the surface nanoparticles and decrease the peak current of the modified electrode. Under the optimized condition, the linear range and detection limit were obtained as 50-100 nM and 32.58 nM, respectively.

The obtained results for the determination of TAA by this method, showed excellent analytical performance for the determination of thioacetamide in terms of an appropriate detection limit, high sensitivity, very good accuracy, repeatability and reproducibility.

Keywords: *$Ag@Fe_3O_4$ nanoparticles, Electrochemical Indirect determination, Self –assembled monolayer, Thioacetamide.*

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Hot corrosion resistance activation energy of manganese-cobalt coated Crofer 22 APU steel

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Abstract

In this study, the pack cementation method was employed to coat manganese and cobalt onto Crofer 22 APU steel. Hot corrosion at 800°C and hot corrosion at different temperatures were applied to evaluate the activation energy. In each test, the coated samples demonstrated lower $k_{p,}$ indicating that the coating layer had acted as a mass barrier against the outward diffusion of cations (Cr) and inward diffusion of anions (Cl, S, O). The formation of $MnCo_2O_4$, $CoFe_2O_4$, $CoCr_2O_4$ and Co_3O_4 spinels, improved the hot corrosion resistance of Crofer 22 APU steel and it resulted to the lower hot corrosion activation energy of cobalt coated samples in comparison with the coated ones.

Keywords: *Hot corrosion, Pack cementation, Manganese, Cobalt, Activation energy.*

Introduction

Spinel ferrites with general formula MFe_2O_4 have interesting physical properties and are of technological importance. In particular, $CoFe_2O_4$ spinel is of increased interest as this material, in the form of bulk, powder, film, or nanoparticles, finds or promises numerous applications in microwave devices, magnetic drug delivery and solid oxide fuel cells [1]. In addition, it has been found that $CoFe_2O_4$ spinel is a highly reproducible material for humidity and gas sensing. Apart from its technological importance in these fields, $CoFe_2O_4$ has attracted considerable attention because of its potential for high temperature structural applications due to its low density, high strength at elevated temperature, good resistance to hot corrosion and high electrical conductivity [2]. Few researches have focused on the hot corrosion resistance of $CoFe_2O_4$ coating. In the present study, manganese and cobalt were pack cemented on Crofer 22 APU ferritic stainless steel and hot corrosion resistance behavior and hot corrosion resistance activation energy was investigated.

Methods

Coupons of Crofer 22 APU stainless steel, measuring 10 mm × 5 mm × 2 mm with chemical composition of 22.7% Cr, 0.38% Mn, 0.02% Si, 0.01% C, 0.02% Ni, 0.02% Al, 0.07% Ti, 0.06%

La with Fe as remaining were used as substrates. Specimens were polished from 320-grit sic paper up to 1200-grit, ultrasonically cleaned in ethanol and dried. The samples were coated with cobalt and manganese by pack cementation method, which was described in the previous study [3]. After the pack cementation treatment, the samples were weighed using an electronic balance. Prior to hot corrosion tests, samples were subjected to oxidation at 800 °C to form Mn-Co spinels. The isothermal hot corrosion was done at 800 ºC for 100 hours with a salt mixture consisting of 80 wt.% Na_2SO_4+20 wt.% NaCl (melting point ∼700 °C). The samples were also subjected to hot corrosion at different temperatures (700-1000 ºC). After each test the coated and uncoated samples were weighed and weight changes was calculated.

Result and discussion

Hot corrosion resistance of manganese-cobalt coated and uncoated samples was studied at 800 ºC for 100 h. The corrosion resistance was remarkably reduced by the application of coating layer. The bare substrate had a weight change of 1.853 $mg.cm^{-2}$ after 100 h of hot corrosion, while the coated samples had a weight change of 0.658 $mg.cm^{-2}$. The coating effectively protected the substrate from the corrosion at high temperatures. In order to measure the hot corrosion resistance activation energy of Mn-Co coating, uncoated and coated samples were subjected to hot corrosion at 800 °C, 900 °C and 1000 °C for 20 h. By increasing the temperature, the kp increased. This is because of the lower activation energy for the diffusion of the corrosion rate limiting species at higher temperatures [4].

The parabolic rate constants (*k*p), can be fit into an Arrhenius expression to determine the activation energies for the oxide formation process on each of the samples (Fig. 1). Activation energies were calculated 126 and 73 kJ $mol^{-1}h$ for uncoated and coated specimens, respectively. The lower activation energy for the Mn-Co-coated samples would imply that oxide formation is easier during hot corrosion. This is an interesting result, considering the fact that the oxides on the coated samples are thinner than the oxides on the uncoated Crofer 22 APU samples. The activation energy for hot corrosion of the coated samples is relatively close to that for the uncoated samples. It is, thus, possible that hot corrosion of the coated samples, at these temperatures in air, is essentially controlled by the same mechanism that control the hot corrosion of the uncoated samples.

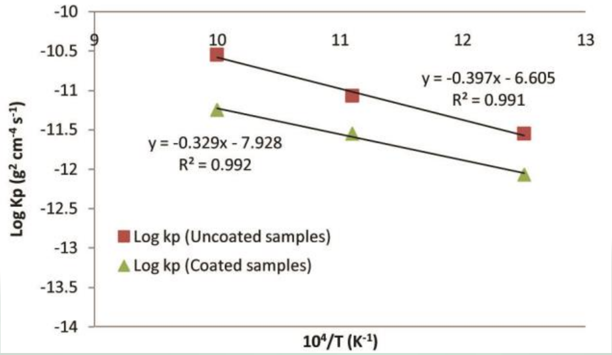

Fig. 1. Plots of log(kp) vs. 1/T for uncoated and Mn-Co-coated Crofer 22 APU steel.

Conclusions

Crofer 22 APU ferritic stainless stainless was pack cemented with manganese and cobalt. The formation of $MnCo_2O_4$, $CoFe_2O_4$, $CoCr_2O_4$ and Co_3O_4 in coated samples improved hot corrosion resistance. The activation energy of Mn-Co-coated samples was lower than the uncoated ones which indicated that during hot corrosion the oxide formation in coated samples is easier.

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Electrochemical study of doxorubicin on the surface of SBA-15 modified screen -printed carbon electrode

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Abstract

Doxorubicin (DOX), has been nearly recognized as the ‘‘gold standard’’ for the treatment of various cancers including solid breast, ovarian, lung and liver tumors. However, the side effects such as systemic toxicity, cardiotoxicity and drug resistance gradually appear during the therapy. Therefore, there is an emergent need for rapid, easy and sensitive techniques for analysis of DOX .The performance of sensors can be significantly improved by using different nanomaterials. One of these materials is mesoporous silica SBA-15. SBA-15 is a promising candidate for the immobilization of various materials and can be used to create stable biosensing. Sensors based on the SBA-15 have shown high sensitivity and good detection limit through promoting electron transfer reaction and enhancing electrochemical signal. In this project, a simple and novel sensor is developed for study of clinical DOX concentration based on SBA-15 on the surface of SPE .The SBA-15 modified screen printed electrode (SPE) was fabricated to monitor the DOX in phosphate buffer solution (pH 6.0). A droplet of 9μL SBA-15 was placed on the working electrode surface, followed by air-drying for 1.0 h. The interaction of SBA-15 on the working electrode surface with DOX was investigated in the drug solution. The electrochemical behavior of DOX was observed at the surface of SBA-15-modified SPE by cyclic voltammetry (CV) and electrochemical impedance spectroscopy. The effect of pH and scan rate on the reduction current of DOX was studied using cyclic voltammetry. From the obtained results, pH 6.0 was obtained as the optimum pH. Also scan rate showed that the reduction peak current increased with increasing in scan rate from 10 to 400 mV s^{-1}. From the calculated results, the electron transfer coefficient was obtained 0.49. Under optimized condition, the measured reduction peak current of DOX by differential pulse voltammetry exhibited a good linear relationship with the increasing of the DOX concentration in the range of 0.002 μM to 2μM. The detection limit was founded to be5.4×10^{-6}μM.

Keywords: *SPE, Doxorubicin, mesoporous silica SBA-15, electrochemical impedance spectroscopy.*

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Protection of 316L Stainless Steel by $Mn_{0.5}Mg_{0.5}Fe_2O_4$/Chitosane in HCl and H_2SO_4 Media

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Abstract

The use of corrosion inhibitors is one of the most economical and simplest method for overcoming the corrosion problems [1-3]. From the standpoint of safety, the expansion of non-toxic and effective inhibitors is required. Chitosan is a natural polycationic copolymer and is one of the important biopolymers that extensively used in pharmaceutical applications, such as in tissue engineering materials, drug carriers [4]. Chitosan is rich in hydroxyl and amino groups, so it is a good potential inhibitor. Umoren et al. were estimated the inhibition action of chitosan on the corrosion of mild steel in 0.1 M HCl solution. They found that chitosan inhibit corrosion of mild steel even at a very low concentration and inhibition efficiency increases with a rise in temperature up to 96 %at 60°C and then drops to 93 % at 70 °C, while it slightly increases with an increase in chitosan concentration [5]. The inhibition action of 2-N,N-diethylbenzene ammonium chloride N-oxoethyl chitosan and 12-ammonium chloride N-oxododecan chitosan on the corrosion of carbon steel in 1 M HCl has been evaluated. The results illustrate that the inhibition efficiency of 2-N,N-diethylbenzene ammonium chloride N-oxoethyl chitosan in 1 M HCl at varying temperature is higher than for chitosan and 12-ammonium chloride N-oxododecan chitosan [1]. The main aim of this study is investigation of inhibition action of $Mg_{0.5}Mn_{0.5}Fe_2O_4$/chitosan nanocomposite on the corrosion of 316L stainless steel in 2 M HCl and 1 M H_2SO_4 solutions. The synthesized nanocomposite was evaluated using X-ray diffraction (XRD) and field emission scanning electron micrographs (FESEM). The corrosion behavior of 316L stainless steel was estimated by using electrochemical methods including potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) methods in both acidic media in the absence and presence of various concentration of chitosan, $Mg_{0.5}Mn_{0.5}Fe_2O_4$ and $Mg_{0.5}Mn_{0.5}Fe_2O_4$/chitosan nanocomposite. In order to designed the effect of temperature on the behavior of nanocomposite, polarization measurements in the temperature range of 25-65 °C was carried out for different concentration of three mentioned inhibitor. Comparing the results indicated that, for both acidic media, the inhibition efficiency of

$Mg_{0.5}Mn_{0.5}Fe_2O_4$/chitosan nanocomposite at all investigated temperature is higher than chitosan and $Mg_{0.5}Mn_{0.5}Fe_2O_4$. The nanocomposite was found to inhibit corrosion even at a very low concentration (0.1 g/L) and high temperature (99 % at 65°C). Because of these features and non-toxic properties of nanocomposite, we think this inhibitor can be introduced for use in the oil and gas industry.

Keywords: *Corrosion; Chitosan; Spinel; Potentiodynamic polarization; electrochemical impedance spectroscopy (EIS)*

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Application of Graphene Modified Carbon Paste Electrode for Simultaneous Determination of Acetaminophen, Dopamine and Ascorbic acid

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Abstract

Graphene is a family of carbon nanoscaled materials that is of great interest for pH sensors, biosensor and chemical sensor applications due to its intrinsic unique mechanical and electronic properties [1, 2]. Paracetamol (N-acetyl-p-amino-phenol) or acetaminophen (AC), is non-carcinogenic and an effective substitute for aspirin to be used for the patients who are sensitive to aspirin, and it is safe up to therapeutic doses.However, overdoses will cause liver and kidney damage and finally lead to death [3, 4]. Dopamine [4-(2-aminoethyl) benzene-1, 2-diol (DA)] plays an important role in the function of the central nervous, cardiovascular, renal and hormonal systems [5]. Insufficient DA concentration due to the loss of DA-producing cells may lead to a disease called Parkinson’s disease [6]. Ascorbic acid (AA) due to its characteristics such as, essential to the skin, immune system and connective tissues is important in health care of human beings [7]. In the present research, application of modified carbon paste electrode (CPE) with graphene was examined in determination of AC, DA and AA and their mixtures by electrochemical methods. The modified electrode exhibited strong function for resolving the overlapping voltammetric responses of AC, DA and AA into three well-defined voltammetric peaks. Differential pulse voltammetry peak currents of AC, DA and AA increased linearly with their concentrations at the ranges of 6.3×10^{-8}-20.5×10^{-4} M, 7.0×10^{-8}-7.8×10^{-4} M and 3.8×10^{-7}-9.6×10^{-4} M respectively with a detection limits 0.43×10^{-8} M for AC, 0.65×10^{-8} M for DA and 0.25×10^{-7} M for AA. High sensitivity and selectivity, very low detection limit, the ease of preparation and surface regeneration of the modified electrode and reproducibility of the voltammetric responses suggest that this electrode very useful for accurate determination of AC, DA and AA in real samples.

Keywords: *Modified carbon paste electrode, Dopamine, Acetaminophen, Ascorbic acid, Graphene.*

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Determination of Ceftizoxime Using Reduced Graphene Oxide Hollow Gold Nanosphers (RGO-HGNs) Electrode by Differential Pulse Voltammetry

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Abstract

At first Graphene Oxide (GO) was reduced on the surface of electrode by electrochemical method then reduced graphene oxide-hollow gold Nanosphers (RGO-HGNs) were generated onto pencil graphite electrode (PGE). HGNS was produced by electrodeposition and subsequent displacement reaction between the cobalt nanoparticle and Au^{3+} ions (1). Differential pulse voltammetry was used for determination of ceftizoxime (CFX). CFX is a third-generation cephalosporin available for parenteral administration CFX that is used to reduce the infection caused by both gram-negative and gram positive bacteria, by interfering with the formation of the bacterial cell wall so that the wall ruptures, resulting in the death of bacteria. The design experiment was a central composite design (CCD) methodology was developed as experimental strategies for modeling and optimization of the influence of some variables on the performance of modified electrode (2). The dynamic range was 1nM to 100 nM. The present method has good selectivity and sensitivity. It has been applied to the determination of CFX in real sample.

Keywords: *Ceftizoxime, RGO-HGNs, Differential pulse voltammetry (DPV), Minitab (CCD)*

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Development of a New Method for Determination of Hydrazine Based on Modified Screen Printed Electrode

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Abstract

Introduction

Hydrazine is a toxic agent numerated as a pollutant of environment and biologic systems and in another hand is one of the most used compound in industries which is used to remove oxygen in cycle, create passive layer and also increase the alkalinity of vapor phase so, determination of this reagent is very important due to its effects on human body and environment. This reagent absorbed by skin and lung which cause irritation, liver disease and neurotic damages [1]. Therefore introducing a selective and sensitive method for accurate determination of hydrazine is crucial. Recently, electrochemical techniques have been applied to determine hydrazine because they offer an opportunity for portable, rapid and cheap methodologies [2,3].

Purpose of research

The aim of this work is development of people health and enhancement of the determination precision of hydrazine based on new a method using electrochemical reaction on the surface of multiwall carbon nanotube screen printed electrode modified with an imidazole derivative 5(1H-benzo[d]imidazol-2-ylthio)-3-methoxybenzene-1,2-diol(Im/MWCNT-SPE).

The electrocatalytic oxidation of hydrazine on a (Im/MWCNT-SPE) has been studied. The (Im/MWCNT-SPE) shows highly catalytic activity toward hydrazine electrooxidation. The results indicated that hydrazine peak potential at (Im/MWCNT−SPE) shifted for 172 mV and 127 mV to negative values as compared with activated and multiwall carbon nanotube modified screen printed electrode surface. Fig.1 shows the electrocatalytic effect of (Im/MWCNT-SPE) toward oxidation of hydrazine. The kinetic parameters, such as the electron transfer coefficient, α, and the standard heterogeneous rate constant, k', for oxidation of hydrazine at the (Im/MWCNT-SPE) were determined as 0.29 and 1.07×10^{-3} cms^{-1}. The differential pulse voltammetric detection of hydrazine was carried out in a 0.1 mol L^{-1} phosphate buffer solution (pH 7.0) resulting in tree linear response ranges of 1.8 to 45.6 nM and 45.6 to 148.1 nM and 148.1 to 2285.7 nm and the detection limit of 0.55 nM.

Conclusion

The (Im/MWCNT−SPE) can decrease the oxidation peak potentials of Hydrazine for about 172 mV and 127 mV on the surface of (Im/MWCNT-SPE) toward activated and modified electrode with multiwall carbon nanotube therefore, determination of the analyte (Hydrazine) is possible without any interference. Moreover, the (Im/MWCNT−SPE) was used to determine hydrazine in real samples with satisfactory results.

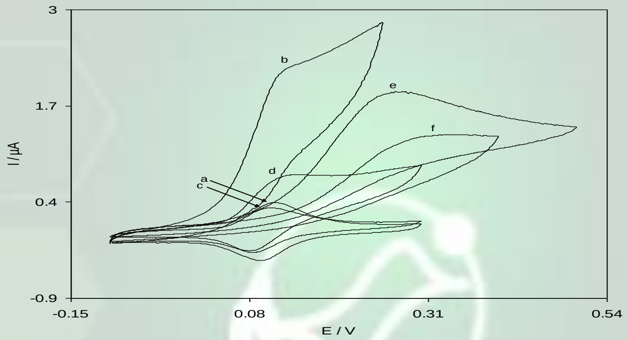

Fig. 1 Cyclic voltammograms of the GOBSNPs-SPE, in the 0.1 M phosphate buffer (pH 7.0) at scan rate 20 mV s^{-1} in absence (a) and (b) presence of 0.2 mM hydrazine (c) like (a) and (d) like (b) for modified electrode with imidazole derivative (e) and (f) like (b) for modified electrode with multiwall carbon nanotube and activated electrode consequently.

Keywords: *Multiwall Carbon Nano Tube, Imidazole Derivative, Hydrazine, Screen printed electrode*

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Polyaniline-based Symmetric solid-State supercapacitor

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Abstract

Supercapacitors, also known as ultracapacitors, are energy storage devices that can often be charged and discharged in seconds with extremely long cycle life [1, 2]. Supercapacitors are divided into two types: electrochemical double-layer capacitors (EDLCs) based on carbon electrodes that store and release energy by electrostatic charge separation at the electrode/electrolyte interface and pseudo-capacitors with certain metal oxides or conducting polymers as the active electrode materials that associate with adsorption and surface redox processes of the electroactive species [3]. Recently solid-state supercapacitors using a Nafion membrane as an electrolyte separator with the conductive composite electrodes have been studied [4]. In the present work, Nafion-based ionic polymer free metal nanocomposite (IPFMC) supercapacitor was fabricated. The suspension of graphene oxide/multiwalled carbon nanotube/PANI (GMP) was sprayed onto both sides of the Nafion membrane to complete the fabrication of the solid-state symmetric supercapacitor. Performance of the symmetric supercapacitor was investigated by Field emission scanning electron microscopy (FE-SEM) and X-ray photoelectron spectroscopy (XPS). The electrochemical properties of symmetric solid-state supercapacitor were investigated by cyclic voltammetry (CV), galvanostatic charge–discharge (CD) and electrochemical impedance spectroscopy (EIS) techniques in 0.5M Na_2SO_4. The specific capacitance of 383.25 $F.g^{-1}$ (326 $mF.cm^{-2}$) was obtained for the GMP in solid-state supercapacitor cell at a scan rate of 10 $mV.s^{-1}$, respectively.

Keywords: *Supercapacitor, Polyaniline, Nafion, Grapheme oxide*

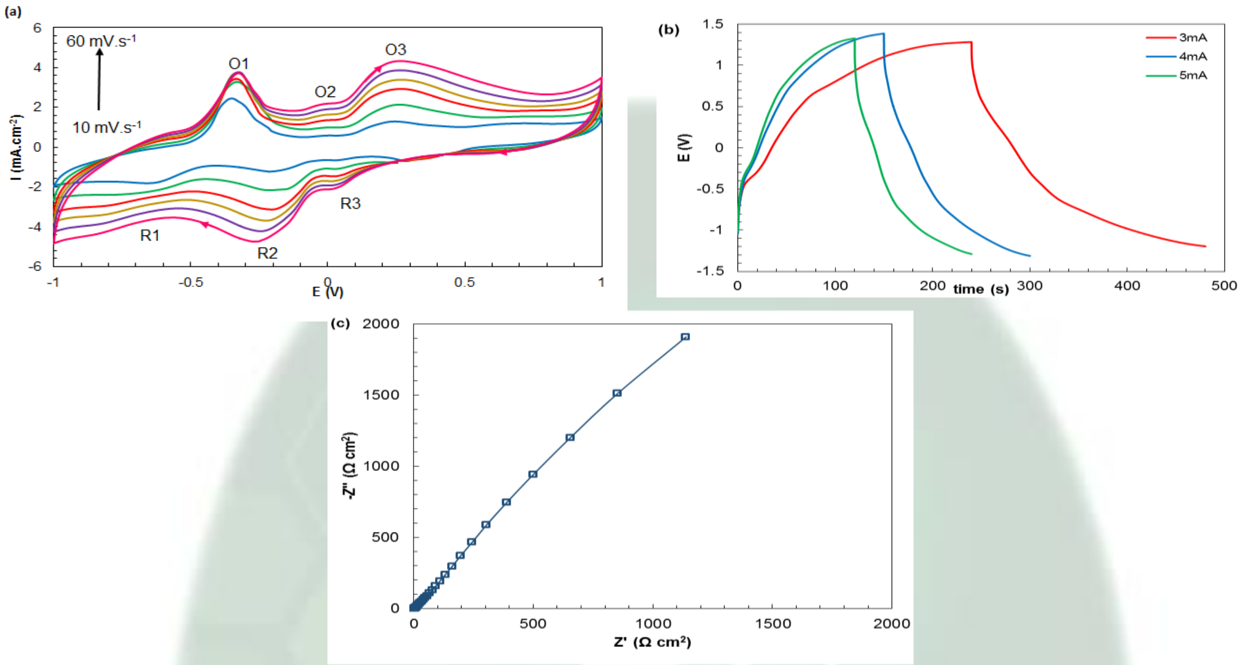

Fig. 1. a) Cyclic voltammetry of GMP at 10-60 mV.s^{-1} at 0.5M Na_2SO_4, b) charge-discharge, and c) nyquist plots of the GMP-based symmetric supercapacitor

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Disposable NiO/Graphene Nanocomposite Modified-Graphite Screen Printed Electrode for the Rapid Voltammetric Assay of Isoproterenol

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Abstract

Isoproterenol (ISO) is a medication used for the treatment of hypertension, allergic emergencies, bronchitis, cardiac shock, heart attack and rarely for asthma. It is a sympathomimetic. It works by relaxing blood vessels and helping the heart pump blood more efficiently. It helps to relax the airway during anesthesia to help patients breathe more easily [1]. Recently the development of graphite screen printed electrodes (SPEs) has become a major revolution in the construction of electrochemical biosensors. The suitability of SPE, which has been demonstrated in multiple applications, is consequence of low cost, high possibilities of modification, versatility of its miniaturized size and possibility of connecting them to portable instrumentation [2]. As one of the special structures of carbon, graphene (GR) exhibiting many attractive advantages, such as extraordinary electronic transport properties, large surface area (~2630 m^2g^{-1}), strong mechanical strength and long cycling life stability [3]. In this study, a NiO/graphene oxide nanocomposite was fabricated on the graphite screen printed electrode (NiO/GR/SPE), and used for determination of isoproterenol. The plot of catalytic current versus isoproterenol concentration showed linear segment in the concentration range 0.5–400.0 µM with a regression coefficient of 0.999. The NiO/GR/SPE electrode has been successfully applied and validated by analyzing isoproterenol in urine and pharmaceutical samples.

Keywords: *Isoproterenol, NiO nanoparticle, Graphene, Nanocomposite, Graphite screen printed electrode*

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Voltammetric Determination of Bisphenol A Using a Modified Screen-Printed Carbon Electrode Modified With Nanocomposite

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Abstract

Bisphenol A (BPA) is one of a number of potential endocrine disruptors. BPA could potentially interfere with the endocrine system of both the wild animals and humans, reduce immune function, cause cancer and impair reproduction even at concentrations as low as the 10–25 nM level. BPA is used as a monomer in synthesis of polycarbonate plastics, epoxy resins, flame retardants, polystyrene resins and other specialty products which are widely used for inner coating of dental composites, food cans and drug delivery systems. [1]. Screen-printed carbon electrodes (SPCEs) are acknowledged to be very effective devices for the determination of different kinds of analytes in biomedical, environmental, and industrial samples [2]. Electrode modification using nanoparticles (NPs) has grown exponentially. In particular, nanoparticles have been studied extensively for the design and fabrication of catalysts, an enhancement of catalytic activity or selectivity, the large surface area-to-volume ratios, and good conductivity [3]. The relevance of Bisphenol A (BPA) in human health is well-known. For this reason we designed and developed a biosensor based on a nanocomposite modified screen printed carbon electrode. Nanocomposite modified electrode shows a higher catalytic response and lower overpotential for BPA. The lowest limit of detection (LOD) of 0.57 µM is able to be achieved using NPs/SPCE electrode. The sensor showed very good sensitivity along with an excellent operational stability.

Keywords*: Bisphenol A, Modified electrode, Voltammetry, Nanocomposite, Graphite screen printed electrode*

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Synthesis of Polyaniline Nanofibers for Non-enzymatic Glucose Sensor

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Abstract

Considering the intrinsic flaws of insufficient stability and fair repeatability for enzyme based biosensors, one moves interest to develop new electrochemical glucose sensors without using any bio-enzyme, namely non-enzymatic sensors. In this study, copper oxide particles modified polyaniline nanofibers (PANI-NF) were deposited on FTO electrode and used as a non-enzymatic sensor for glucose. PANI-NFs were polymerized by a chemical method and through membrane cellulose ester. These fibers were dip coated on FTO and then copper oxide cubic particles was deposited on PANI-NFs by electrodeposition method. The morphology and structure of CuO/PANI-NF composite was characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDS) and Fourier transform infrared (FT-IR). The electrochemical response of the proposed electrode in presence of glucose was investigated in various pHs, which the best result was obtained in 0.1 M NaOH. Also the performance of this electrode for glucose detection was compared with bare FTO and PANI-NF/FTO, which its performance was very better. The linear range of the proposed sensor was studied by chronoamperometry, which was between 0.7 µM to 2.17 mM. The interference effect of some important species (uric acid, ascorbic acid, dopamine, sodium and chloride ions) was examined, which no considerable interfering effect was observed. The repeatability and reproducibility of the electrode were 4.9 and 3.6%, respectively. Finally, the electrode stability was investigated and after 10 days the electrode showed ~90% of the its initial efficiency. According to simplicity, ease of preparation, wide linear rang, good selectivity and stability the proposed electrode can be used as a non-enzymatic glucose sensor.

Keywords: *Polyaniline Nanofiber, Copper Oxide, Glucose sensor, Non-enzymatic*

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Electrochemical Investigation of Adsorption potential of Benzothiophene on Pt electrode at acidic and basic electrolytes

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Abstract

Determining adsorption potential is important for oxidation/reduction of Benzothiophene to be occurred. In this paper Electrochemical Investigation of Adsorption potential of Benzothiophene on Pt electrode at acidic and basic electrolytes has been performed. All experiment was done at three electrolytes (0.5 M H_2SO_4, 0.5 M $HClO_4$, 1 M KOH). Investigation conducted using CV and CA methods. The results of this study showed that adsorption of Benzothiophene in acidic electrolyte is proper than basic electrolyte. The optimum benzothiophene adsorption potential for H_2SO_4, $HClO_4$ and KOH is 0.1, 0.1 and -0.52, respectively. The best electrolyte for electro-adsorption of BT on Pt is H_2SO_4 with optimum adsorption potential of 0.1 V.

Keywords: *Pt electrode, Adsorption potential, Benzothiophene, Electrochemical*

Introduction

Among Sulfur-containing compounds that are typically present in hydrocarbon-based fuels, aromatic sulfur molecules, such as thiophene (T), benzothiophene (BT), dibenzothiophene (DBT), are relatively hard to remove using a conventional hydrodesulfurization (HDS), i.e., up to 60 bar and 500K, because of steric hindrance. Electrochemical desulfurization is a promising method for removing thiophenic compound from aqueous/organic solution. despite of electrode/electrocatalyst and electrochemical method (static/dynamic), electrolytes are needed due to the low ionic conductivity of fossil fuels [1].

In systems where ionic conductivity is required, a proper electrolyte is required. For electroreductive desulfurization, acidic electrolyte media are used [2], while for electrooxidative desulfurization, basic electrolyte media are preferred [3]; however acidic electrolyte can also be used, whose function might be different from that of a basic electrolyte. Generally, a redox reaction occurs on the surface of electrode and subsequently the related reaction was started [4]. So exploring the Proper adsorption potential to control the desired reaction is important. In this paper effect of two acidic and a basic electrolyte on electro-adsorption of benzothiophene on Pt electrode has been investigated using CV and CA method and optimum adsorption potential on each electrolyte was indicated.

Experimental

Material, Cell, Electrodes

The analytical grade chemicals used in this work (i.e., Benzothiophene, potassium hydroxide, H_2SO_4, $HClO_4$) were supplied by the Merck Company. All measurements were controlled using the SP-150 Potentiostat with EC-Lab software, (Bio-Logic.). A three-electrode setup was used in all experiments: reference electrode (Ag/AgCl, KCl saturated, a counter electrode (platinum plate, 2×3 cm), and the working electrode (platinum disk polycrystalline 1 mm in diameter, before each experiment, the electrolyte was degassed with nitrogen gas. All experiments were performed at room temperature (25°C).

Electrochemical measurements

Before each experiment the electrodes surfaces were polished using a silicon carbide 3000 mesh sand-paper and electro-polished (i.e. CA at -0.7V) for 2 min. For investigation of the electro-adsorption of Benzothiophene on the platinum electrode surface, a three-stage using two methods (i.e., chronoamperometry (CA) and cyclic voltammetry (CV)) was utilized. In each experiment, Initially, the working electrode was placed in a solution of a specified aqueous electrolyte (e.x. 0.5 M H_2SO_4, 0.5 M $HClO_4$, 1 M KOH). Reference voltagram using CV on the Pt electrode in each electrolyte were performed in suitable potential window. The potential windows were selected based on inhibiting from Hydrogen and Oxygen evolution. Then, this solution was exhausted and the cell was filled with specified aqueous electrolyte including 1.0 mM Benzothiophene (C.a. 85 ppm) solution and the CA technique (electro-adsorption stage) was applied for 5 min under several fixed-potential (in double layer region) to find the optimum adsorption potential. Next, Solution containing Benzothiophene was then rinsed out from the working electrode compartment and replaced with Benzothiophene-free solution. The voltammogram of the Benzothiophene-dosed platinum electrode was recorded in Benzothiophene-free solution (desorption stage). In the CV studies the potential scan rate was 50 mV/s.

Result and Disscution

To determine adsorption potential for each electrode, oxidation charge quantity of benzothiophen-dosed Pt electrode on every electrolyte was determined. Fig. (1) shows the reference voltammogram of Pt electrode in each electrolyte. Oxidation charge quantity of benzothiophene in each electrolyte is depicted on Fig. (2). Table (1) show CV potential range, adsorption potentials, oxidation charge quantity and optimum adsoption potential for three electrolytes. Result showed that optimum Benzothiophene adsorption potential for H_2SO_4, $HClO_4$ and KOH is 0.1, 0.1 and -0.52, respectively.

Conclusion

The results of this study showed that adsorption of Benzothiophene in acidic electrolyte is proper than basic electrolyte. The optimum benzothiophene adsorption potential for H_2SO_4, $HClO_4$ and KOH is 0.1, 0.1 and -0.52, respectively. The best electrolyte for electro-adsorption of BT on Pt is H_2SO_4 with optimum adsorption potential of 0.1 V.

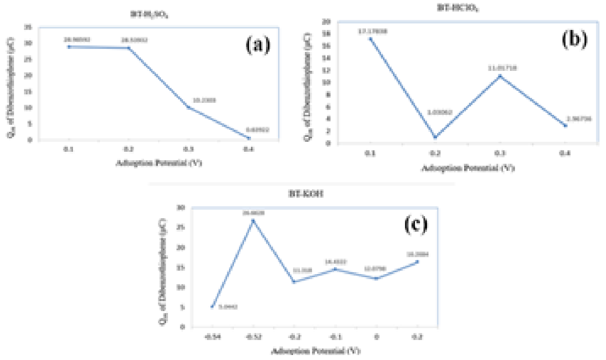

Fig. (1): The Charg quantity of Benzothiophene on a Pt electrode vs. the potential at which thiophene was adsorbed. Benzothiophene adsorption was carried out potentiostatically in **a)** 0.5 M H_2SO_4 + 1.0×10^{-3} M benzothiophene, b) 0.5 M $HClO_4$ + 1.0×10^{-3} M benzothiophene, c) 1 M KOH + 1.0×10^{-3} M

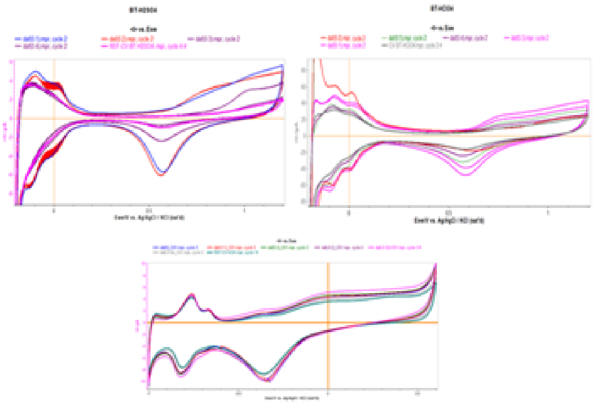

Fig. (2): The reference voltagaram of Benzothiophene on a Pt electrode for **a)** 0.5 M H_2SO_4 + 1.0×10^{-3} M benzothiophene, b) 0.5 M $HClO_4$ + 1.0×10^{-3} M benzothiophene, c) 1 M KOH + 1.0×10^{-3} M benzothiophene.

Table (1) Result of electrochemical adsorption for three electrolyte.

Type of Electrodes	Adsorption Potential measured	Reference Voltagram range	Optimum adsorption potential	Oxidation Charge
H_2SO_4	0.1, 0.2, 0.3, 0.4	-0.2 to 1.2	0.1	28.98
$HClO_4$	0.1, 0.2, 0.3, 0.4, 0.5	-0.2 to 1.2	0.1	17.18
KOH	-0.54, -0.52, -0.2, -0.1, 0, 0.2	-1 to 0.6	-0.52	5.04

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Investigation of the Thiophene adsorption on Pt electrode in different electrolytes

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Abstract

In this paper Investigation of the Thiophene adsorption on Pt electrode in different electrolytes has been performed. All experiment was done at three electrolytes (0.5 M H_2SO_4, 0.5 M $HClO_4$, 1 M KOH). Electrochemical measurement was done using CV and CA methods. The results of this study showed that adsorption of thiophene in acidic electrolyte is proper than basic electrolyte. The optimum benzothiophene adsorption potential for 0.5 M H_2SO_4, 0.5 M $HClO_4$, 1 M KOH is 0.2, 0.1 and -0.54, respectively. The best electrolyte for electro-adsorption of BT on Pt is H_2SO_4 with optimum adsorption potential of 0.2 V.

***Keywords**: Pt electrode, Electrochemical desulfurization, Thiophene adsorption, Electrolyte.*

Introduction

The combustion of high sulfur content fossil fuels can release harmful sulfur oxides into the air, which are causing numerous environmental problems. Thus, great efforts have been made to decrease the sulfur content in fossil fuels[1]. To achieve these goals with the conventional hydrodesulphurization (HDS) technology, higher temperature, higher pressure, larger reactor volume, and more active catalysts are unavoidable [2]. Unfortunately, required investment and operating costs of HDS units are too high and also HDS units possess some operational difficulties [3]. Due to high efficiency, low capital investment, mild operating conditions, environmental protection, etc., electrochemical desulfurization has been attracted more and more attention [4]. Hourani [5],Wang et al. [2] , Schucker et al.[6] and Alipoor et al.[3] reported that thiophene could be removed by electrochemical oxidation. Several methods have been employed for electrochemical desulfurization, which can be generally grouped into two categories. The methods that facilitate electrochemical desulfurization by applying a fixed potential or drawing a fixed current can be categorized as static methods. Other methods where the applied potential changes over time, such as linear or square wave voltammetry can be categorized as dynamic methods. In static methods, electrochemical desulfurization is conducted at a fixed potential (oxidative or reductive potential (potentiostatic) or a fixed current (galvanostatic)). dynamic methods offer the flexibility of controlling the applied potential or applied current. By changing the electrode potential over time, we can subject the feed to both oxidizing and reducing conditions, or subject the feed to varying degrees of electrooxidative/electroreductive conditions. Hourani [5] investigated the desulfurization of thiophene by electrochemical perturbation using square wave voltammetry on a Pt working electrode in 0.5M H_2SO_4. It was found that thiophene adsorption on Pt competed with hydrogen adsorption starting at 0.2 V vs SHE (standard hydrogen electrode) in 0.5 M H_2SO_4 and electrooxidized independently in the Pt oxidation region starting at 0.5 V vs SHE [1] in this research is studied effect of electrolyte on thiophene adsorption potential.

Experimental

Cell, materials and electrodes

A SP-150 Potentiostat was used for electronic control and data acquisition. A conventional, three electrode cell was used equipped with a multiple-inlet system for purging and blanketing the solution with oxygen-free nitrogen. The reference electrode was Ag/AgCl/l.0 M Cl^- and all the potentials reported in this paper are referenced to this electrode. The working electrode used for voltammetric measurements of thiophene adsorption on platinum electrodes was a 2 mm diameter platinum rod. all the reagents used were highly pure (Merck Millipore)

Experimental procedures

The electrode was initially cleaned in a freshly prepared sulfuric acid solution. For investigation of the adsorption of thiophene on platinum electrodes, the working electrode was allowed into contact with a electrolyte + 1.0 $*10^{-3}$ M thiophene solution for 5 min under potential control. Thiophene solution was then rinsed out from the working electrode compartment with thiophene-free 0.5 M H_2SO_4 solution. The voltammogram of the thiophene-dosed platinum electrode was recorded in thiophene-free 0.5 M H_2SO_4.

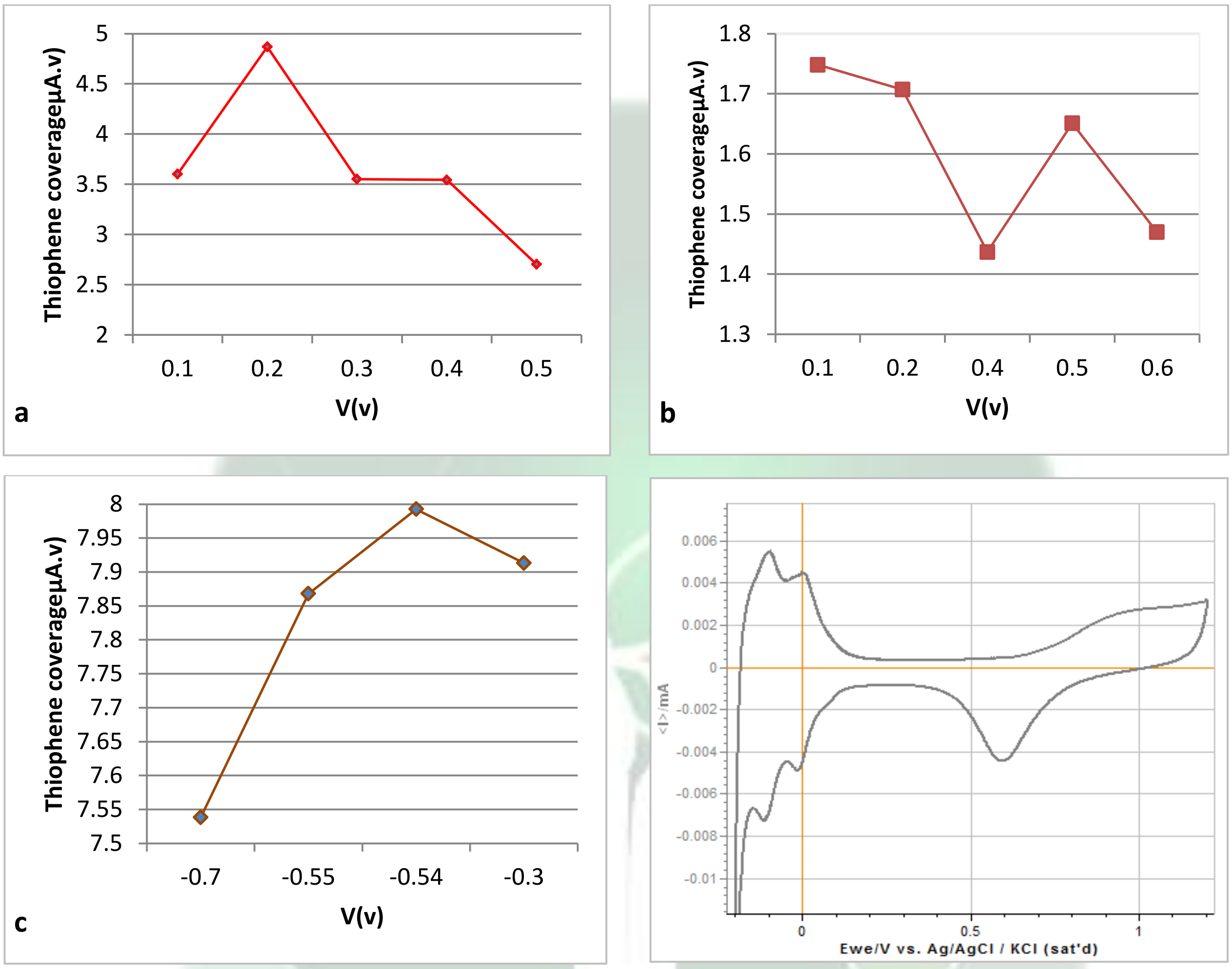

Fig. 1. The coverage of thiophene on a Pt electrode vs. the potential at which thiophene was adsorbed. Thiophene adsorption was carried out potentiostatically in **a)** 0.5 M H_2SO_4 + 1.0×10^{-3} M thiophene, b) 0.5 M $HClO_4$ + 1.0×10^{-3} M thiophene, c) 0.5 M KOH + 1.0×10^{-3} M thiophene. d) 0.5 M H_2SO_4 free-thiophene

Results and discussion

Figure 1:d shows the voltammogram was recorded in thiophene-free 0.5 M H_2SO_4. hydrogen under potential deposition data of thiophene adsorption in H_2SO_4, $HClO_4$ and KOH shown in fig 1:a, b and c, respectively. The results of this study showed that the best thiophene adsorption potential for H_2SO_4, $HClO_4$ and KOH is 0.2, 0.1 and -0.54, respectively.

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Determination of carmoisine in food samples using nanostructure based electrochemical sensor

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Abstract

Carmoisine is a synthetic azo food dye in the red to maroon colour range. In the US, this color was listed in 1939 as D&C Red No. 10 for use in externally applied drugs and cosmetics. It was delisted in 1963 because no party was interested in supporting the studies needed to establish safety. It was never used in food in the US [1]. In this work, we describe synthesis of NiO/CNTs nanocomposite by chemical precipitation method. The synthesized nanocomposite identified by XRD, SEM, and TEM methods. In continuous, a carbon paste electrode modified with NiO/CNTs nanocomposite and ionic liquid (NiO/CNTs/IL/CPE) had been fabricated as a voltammeric sensor for determination of carmoisine. Electrochemical behavior of carmoisine at the NiO/CNTs/IL/CPE had been investigated in phosphate buffer solution (PBS) by cyclic voltammetry (CV), chronoamperometry (CA) and square wave voltammetry (SWV). The experimental results suggested that the modified electrode exhibited an electrocatalytic activity toward the redox of carmoisine. Detection limit of carmoisine was found to be 0.04 μM. The proposed sensor was successfully applied for the determination of carmoisine in food samples.

Keywords*: Carmoisine analysis, Voltammetric sensor, Food samples, Modified electrode*

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Surface Modification of Superelastic NiTi Alloys by Electrochemical Dealloying Method

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Abstract

Superelastic NiTi alloys are extensively used in biomedical field especially in orthodontics and orthopedics applications due to their desirable properties [1]. These alloys are susceptible to surface corrosion and serious problem might be raised due to release of toxic nickel ions from surface to tissues and body fluids. Therefore, optimizing the surface and electrochemical and biocompatibility investigations of the NiTi SMA alloys are required [2]. In this survey, it is tried to improve surface characteristics of NiTi specimens by electrochemical dealloying methd.

Superelastic Ti-50.8 at.% Ni alloy has been produced by powder metallurgy was used in this study. After polishing and cleaning, the specimens surface were treated by electrochemical method in a two component electrolyte of nitric acid and methanol with a volume ratio of 25:75 at 5.5 V for 30, 60, 120 and 180s at room temperature. After electrochemical dealloying, surface structure of the specimens was investigated by SEM coupled with EDX analysis. Also, corrosion behavior of the specimens is examined by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) tests in Ringer solution at 37°C.

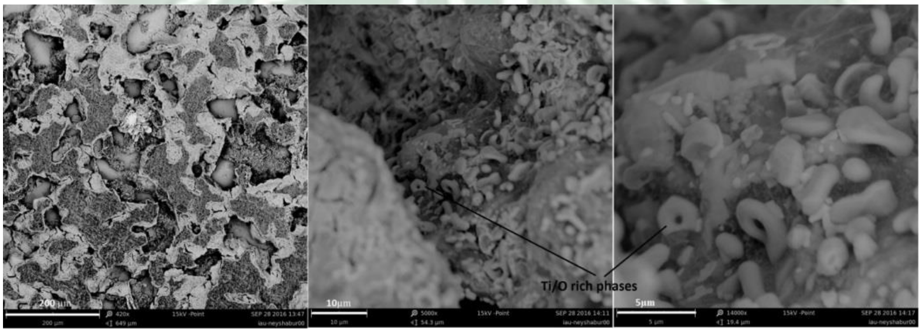

Figure 1 SEM micrograph of NiTi specimen's surface after electrochemical dealloying in different magnification.

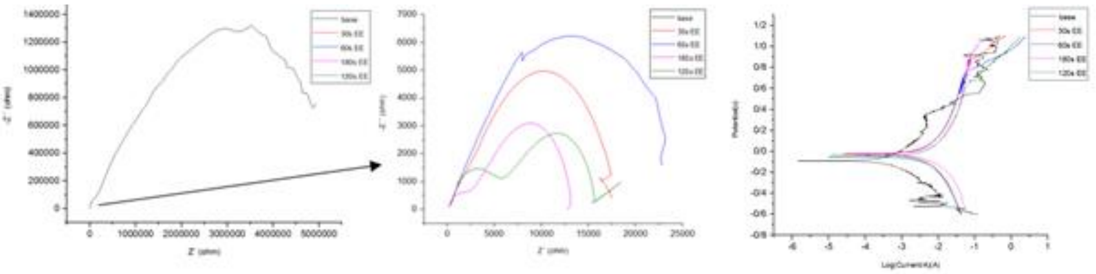

Figure 2 potentiodynamic polarization and EIS tests results of the base and dealloyed NiTi specimens.

Results show the porosity of the NiTi surface has been increased with electrochemical dealloying and 3D nano/micro structure on surface has been created as shown in figure 1. EDX analysis proves that the 3D structures are titanium/oxygen rich phases. Thus, Ni removal was effectively occurred from the NiTi specimen's surface during electrochemical dealloying. From electrochemical corrosion tests (figure 2), the corrosion potential is shifted to more positive values after dealloying. In other hand, the corrosion current density increases in contrast of base NiTi (not dealloyed) because of higher porosity of dealloyed NiTi specimens. However, increasing surface porosity leads to improve biocompatibility due to better adhesion of cells and enhance tissue ingrowth [3]. The semicircle diameter of the base NiTi is higher than the electrochemical dealloyed specimens which indicate higher corrosion resistance of the base NiTi that is in agreement with polarization results. Among dealloyed specimens, the specimen with 60s dealloying time shows higher corrosion resistance.

Consequently, the electrochemical dealloying process effectively removes Ni from the surface of NiTi specimens and 3D nano/micro titanium oxides structures are formed on the surface. This porous structure could be improved biocompatibility of the NiTi alloy.

Keywords: *Superelastic NiTi, Electrochemical Dealloying, Surface Modification, Biocompatibility.*

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An Electrochemical Nanosensor for Voltammetric Determination of Caffeine in Food Samples

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Abstract

Caffeine is classified by the Food and Drug Administration as "generally recognized as safe" (GRAS). Toxic doses, over 10 grams per day for an adult, are much higher than typical doses of fewer than 500 milligrams per day. So, determination of this compound is very important in food and drug samples [1]. In the present study an easy-to-make and sensitive sensor based on CdO/SWCNTs nanocomposite ionic liquid (IL) composite for voltammetric sensing of caffeine in real samples was developed. In the first step, CdO/SWCNTs synthesis using chemical precipitation method and characterized with different methods such as transmission electron microscopy (TEM) and X-ray diffraction (XRD). The propose sensor shows a better electrochemical response with lower over-potential and high sensitivity for caffeine compared with unmodified carbon paste electrode using cyclic voltammetry (CV). The electro-oxidation of caffeine occurred in a pH-dependent e^- and H^+ process, and the electrode reaction followed a diffusion-controlled pathway. Under the optimum conditions in cyclic votametric (CV), the voltammetric oxidation peak current of caffeine showed linear dynamic ranges with a detection limit of 0.02 μM for caffeine. The modified electrode was successfully used for the determination of the caffeine in food samples with satisfactory result.

***Keywords**: Caffeine analysis, Voltammetric sensor, food samples, Modified electrode*

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A DNA label free electrochemical nanostructure sensor for Fluorouracil analysis

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Abstract

5-Fluorouracil (5-FU) is a medication which is used in the treatment of cancer. It is a suicide inhibitor and works through irreversible inhibition of thymidylate synthase [1]. It belongs to the family of drugs called the antimetabolites. Determination of this drug is very important in biological and pharmaceutical samples. In this study, a graphene oxide/polypyrrole pencil graphite electrode was fabricated as a high sensitive electrochemical sensor for determination of 5-FU in real samples. The modified electrode was characterized by AFM and electrochemical impedance spectroscopy (EIS) methods. The signals of guanine and adenine oxidation were linear with respect to the 5-FU concentration in the range of 0.3−90 μmol L^{-1} with a detection limit of 0.09 μmol L^{-1}. The novel sensor was utilized for the determination of 5-FU in real samples.

***Keywords**: 5-Fluorouracil analysis, Voltammetric sensor, anticancer drug, Modified electrode*

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Voltammetric determination of 6-mercaptopurine as an anticancer drug using Pt based nano-structure voltammetric sensor

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Abstract

6-Mercaptopurine (6-MP), sold under the brand name Purinethol, is an immunosuppressive medication. It is used to treat acute lymphocytic leukemia, Crohn's disease, and ulcerative colitis [1]. A carbon paste electrode modified with Pt/CNTs and ionic liquid was used for determination of 6-MP in this work. Pt/CNTs was synthesized by polyol method and characterized with XRD and TEM methods. After optimization of electrochemical parameters at pH 8.0, the oxidation peak current for 6-MP was found to vary linearly with its concentration in the range of 0.05–550 µM with detection limit of 0.009 µM using square wave voltammetric method. Finally, the proposed sensor was used for determination of 6-MP in real samples such as tablet and urine.

Keywords: *6-Mercaptopurine analysis, Voltammetric sensor, Carbon paste electrode, Modified electrode*

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Palladium Alloys as Oxygen Reduction Reaction Electrocatalysts

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Abstract

In this research, we report a simple method for preparation of Palladium-based alloy electrocatalysts for cathodes in fuel cells. The morphology and structure of the electrocatalysts have been well characterized using X-ray diffraction (XRD) and scanning electron microscopy coupled to energy dispersive X-ray (SEM-EDX). It is found that the electrochemical active surface areas of the as-prepared electrocatalysts are higher than the Pd/C. Remarkably, the Pd-based alloys exhibit much higher activity and methanol tolerance for the oxygen reduction reaction in comparison with the Pd/C. The reported results reveal that such alloys with outstanding catalytic activity and durability can also be used in fuel cells as a more suitable cathode catalyst than Pd/C.

Keywords: *Palladium-based alloy, Electrocatalysts, Fuel cells, Oxygen reduction reaction*.

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Ex situ chemical synthesis of SnO_2 nanoparticles as anode materials for lithium-ion batteries

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Abstract

Lithium ion rechargeable batteries having high energy densities are widely used for portable electronic devices, and they are still the subject of intensive investigation because of the possibility on a wide range of future applications. Tin oxide (SnO_2) has been studied as a promising alternative to the commercially used graphite anode material because of its much higher theoretical specific capacity, which arises from different electrochemical reactions. Here, we report a method for synthesis SnO_2 as an anode material in Li-ion batteries. The performance of SnO_2 electrode as an anode in lithium secondary battery was evaluated using conventional electrochemical analysis such as cyclic voltammetry, charge discharge profile and electrochemical impedance spectroscopy (EIS). SnO_2 nanoparticles coating was prepared by a simple wet chemical method. The product exhibited an excellent lithium intercalation/deintercalation performance as anode materials for lithium-ion batteries. Our material displayed large specific capacity at high current density (Fig 1).

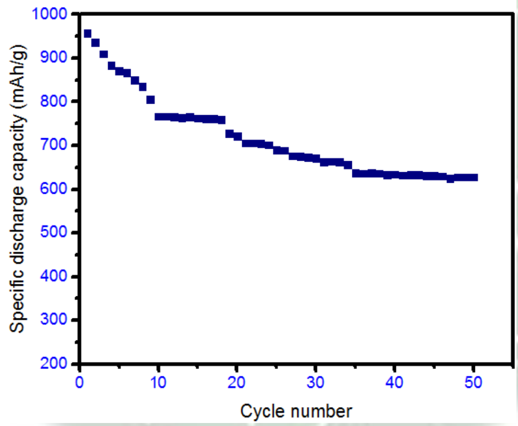

Fig1. Cyclic performance of SnO_2 nanoparticles electrode in the conventional electrolyte at 25◦C with the current density corresponding to 500 mAh/g.

Keywords: *Li-ion battery, SnO_2 nanoparticles, Electrochemical performance*

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Voltammetric determination of trace amount of norepinephrine using modified carbon paste electrode

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Abstract

The electrochemical determination of norepinephrine (NE) as a biomolecule has been investigated in the current work. NE is one of the derivatives of cathecholamines secreted in the adrenal medulla and plays important physiological roles in the central nervous. Hence, it is very necessary to develop sensitive, selective and practically reliable method for the direct determination of the NE dosage for monitoring physiological activities and diagnosing diseases [1-3]. The current work deals with fabrication of a high sensitive modified carbon paste electrode employing CdO nanoparticles and 1-butyl-3-methylimidazolium tetrafluoroborate (1B3MITFB) (CdO/NPs/1B3MITFB/MCPE) for determination of trace amount of NE using cyclic voltammetry (CV) and square wave voltammetry (SWV) techniques. After optimization of electrochemical analytical conditions using a CdO /NPs/1B3MITFB/MCPE at pH 7.0 phosphate buffer (0.1 M), the oxidation peak current was found to vary linearly with its concentration in the range of 20.0-300 µM for NE and satisfactory lower detection limit of 8.0 µM NE. The CdO/NPs/1B3MITFB/MCPE showed several advantages such as good reproducibility, low limit of detection (LOD) and simple preparation. The novel proposed sensor was employed for the analysis of NE in real samples. The synthesized CdO nanoparticles were characterized with different methods such as SEM, XRD and EDAX.

Keywords: *Norepinephrine analysis, CdO nanoparticle, 1-butyl-3-methylimidazolium tetrafluoroborate, Modified electrode*

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Determination of epinephrine in biological and pharmaceutical samples using modified carbon paste electrode employing CdO nanoparticle and ionic liquid

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Abstract

Epinephrine (EN) as one of the most important neurotransmitters in mammalian central nervous system controls the performance of the system by a series of biological reactions and nervous chemical processes. Many diseases are related to changes of the EN concentration in living systems [1-3]. Therefore, accurate determination of EN for monitoring the physiological activities and diagnosing diseases is highly desired. A fast, selective, high sensitive and simple electrochemical strategy was developed for trace analysis of EN by modified carbon paste electrode in the current work using cyclic voltammetry (CV) and square wave voltammetry (SWV) techniques. Carbon paste electrode (CPE) was modified with CdO nanoparticle and 1-butyl-3-methylimidazolium tetrafluoroborate (BMITFB) as a binder. Electro-oxidation behavior of EN on the modified electrode was investigated which indicated that the nanostructured modified electrode could efficiently promote electrocatalytic oxidation of EN. At pH 7.0 phosphate buffer (0.1 M), the catalytic oxidation signal exhibited a wide linear range from 10.0 to 300.0 µM towards the concentration of EN with a lower detection limit of 6.0 µM. The BMITFB/CdO/NPs/CPE was also used for quantitative determination of NE in biological and pharmaceutical samples. Scanning electron microscope (SEM) and X-ray powder diffraction (XRD) studies were applied to characterize the synthesized CdO nanoparticles.

***Keywords**: Modified electrode, Epinephrine analysis, CdO nanoparticle, 1-butyl-3-methylimidazolium tetrafluoroborate.*

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Effect of nitrogen on the corrosion properties of Fe-23Cr-2.4Mo stainless steel

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Abstract

In this study, the effect of nitrogen on the corrosion resistance of the passive films formed on Fe-23Cr-2.4Mo solution nitrided at 1200℃ in a nitrogen gas pressure of 0.25 MPa (2.5bar) for 12 h (HNASS) evaluated by recording open circuit potential (ocp),potentiodynamics polarization (PP), electrochemical impedance spectroscopy (EIS) in 0.5M H_2SO_4 solution. The results showed that nitrogen increased the general corrosion resistance compared with the Fe-23Cr-2.4Mo steel which was related to the formation of stable and protective passive film.

Keywords: *solution nitriding, open circuit potential, potentiodynamic polarization, electrochemical impedance spectra, general corrosion resistance*

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Designing of 3D LSG/$CoNi_2S_4$ nanosheets micro-electrodes for flexible high-energy integrated micro-supercapacitors

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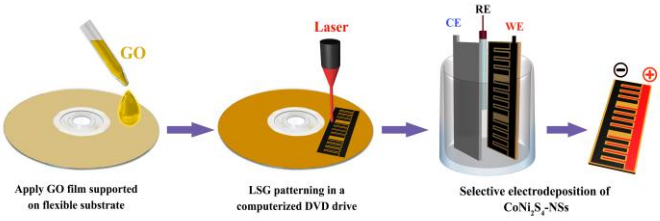
Abstract

Over the past years, self-powered micro-systems such as wireless sensor networks, wearable and biomedical implants, micro-robots, active tags and remote sensors have been developed dramatically [1-2]. Accordingly, extensive efforts have been devoted to design of in plane energy storage systems with high energy and power, small volume, light weight and low cost that can integrated on flexible chips [3-4]. Presently, although commercially thin-film micro-batteries are the major power sources for these devices but micro-supercapacitors (MSCs) are the most promising candidates because of their higher power density, much longer operating lifetime, excellent safety and better rate capability [5-6].

In order to introduce high performance MSCs, various kinds of carbon have been utilized. But, owning to EDLC mechanism, carbon based MSCs have a low energy density. In addition, conventional lithographic techniques are not cost-effective [7-8]. Thus, a facile and low cost preparation process resulting flexible high energy MSC devices is still challenging.

Herein, we report LSG/$CoNi_2S_4$//LSG interdigitated microelectrodes for the first time prepared by a facile, scalable and low cost process as an all-solid-state, flexible integrated hybrid asymmetric micro-supercapacitor. The LSG/$CoNi_2S_4$//LSG MSCs were prepared by two steps of LSG patterning and selective electrodeposition of $CoNi_2S_4$ nanosheets (Scheme 1). Firstly, a volume of 16 ml of 2.7 mg ml^{-1} GO aqueous dispersion was drop-cast on polyethylene terephthalate (PET) sheet glued to the surface of a LightScribe DVD disc. After then, the interdigitated micro-patterns were directly LightScribed onto the GO film by a consumer-grade LightScribe DVD burner. In the second step, $CoNi_2S_4$ nanosheets were selectively electrodeposited on one set of the LSG microelectrodes by cyclic voltammetry at a scan rate of 5 mV s^{-1} for 3-15 cycles within a voltage range of -1.2 to 0.2 V. Deposition bath contained 5 mM $CoCl_2\cdot6H_2O$, 7.5 mM $NiCl_2\cdot6H_2O$ and 0.75 M thiourea with the pH value of ~6.



Scheme 1 Schematic illustrating the fabrication processes of an asymmetric LSG/$CoNi_2S_4$//LSG micro-supercapacitor.

The composition and morphology of the samples was characterized using XRD, XPS, EDAX, SEM and TEM. All these techniques verified successfully synthesis of 3D LSG/$CoNi_2S_4$ nanosheets micro-electrodes. All-solid-state flexible MSCs were prepared by coating PVA-KOH gelled electrolyte onto them. The stack capacitance of the devices can be arrived to an ultra-high volumetric capacitance of 122.4 F cm^{-3} with 15 deposition cycles. The excellent cycling stability of the device was also confirmed by retaining 93.9% of the initial capacitance after 10,000 cycles. These MSCs can achieve energy densities of up to 49 Wh l^{-1} which is comparable to that of lead acid batteries. We believe that this work not only introduces a new flexible integrated asymmetric MSCs with ultra-high energy/power densities, but also constitutes a step forward towards novel, low-cost and flexible in-plane interdigitated microelectrodes that can be widely applied in various applications, such as Li-ion batteries, biosensors, gas sensors and other electronic devices.

Keywords: *Microsupercapacitor, LSG/$CoNi_2S_4$, Laser scribed graphene, Flexible.*

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First-principles study of phosphorene and graphene nanoflakes under the effect of external electric field as an anode material for Li-ion battery

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Abstract

Lithium ion batteries (LIBs) have been the subject of intense investigations due to their good cycling performance, high storage capacity and high energy density [1]. Despite all the studies, finding excellent anodes with good electrical conductivity and high reversible lithium storage are still under development [2]. Therefore, *in* this research *we investigated materials with improved properties for use in the anode electrode of* Li-ion *batteries, using* first-principles *calculations.* For this purpose, two-dimensional materials such as graphene and phosphorene because of their large surface-to-volume ratio and unique electronic properties are used. In this work the adsorption mechanism of Li metal atom and Li-ion in the absence, and presence, of a perpendicularly external electric field on the $P_{54}H_{18}$ phosphorene surface and $C_{54}H_{18}$ graphene surface (Fig 1) has been investigated using M05-2X/6-31G(d,p) density functional theory (DFT) and compare the results with those of $C_{54}H_{18}$ graphene surface [3]. The structural characteristics, charge transfer, electric surface potential (ESP) maps, equilibrium distances between atom/ion and the graphene or phosphorene surface and dipole moments of the atom/ion–graphene or phosphorene complexes were investigated (Table 1). In contrast to $C_{54}H_{18}$ graphene, interactions between Li metal atoms and Li-ions with $P_{54}H_{18}$ phosphorene surface are quite strong due to its highly reactive buckled hexagonal structure (Fig 2). As a consequence of structural properties adsorption height, most stable adsorption site and energy barrier against Li diffusion are also discussed here.

electric field(a.u.)	*Eint(Kjol/mol)*	*Dipole Moment (a. u.)*	*R(Å)*
0.000	-206.90	6.97	1.57
0.001	-213.25	9.06	1.59
0.002	-217.13	11.09	1.60
0.003	-220.76	13.13	1.62
0.004	-224.12	15.19	1.63
0.005	-227.24	17.26	1.66

Table1. Interaction energy, dipole moment and equilibrium distances between Li atom and the $P_{54}H_{18}$ surface related to electric field

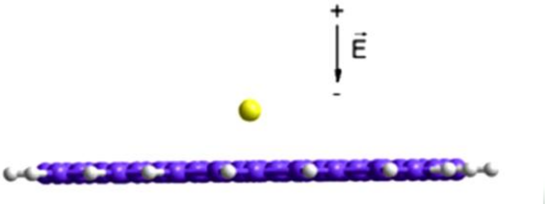

Figure 1. During the calculations the applied electric field was perpendicular to the grapheme surface

Here, it is shown that graphene has very limited Li storage capacity and low surface area than the phosphorene. As our models are in good agreement with previous predictions, this finding presents, a possible avenue for creating better anode material that can replace with graphene for higher capacity and better cycling performance of LiBs.

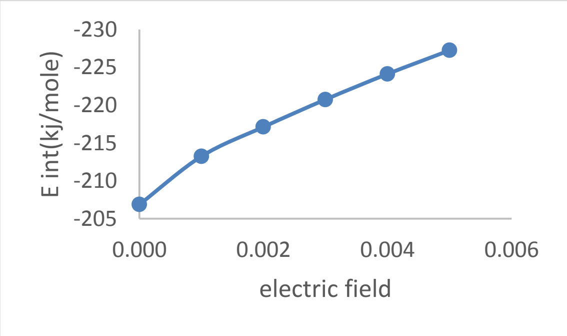

Figure2. Interaction energy between Li atom and the $P_{54}H_{18}$ surface related to electric field

Keywords: *Lithium ion batteries (LIBs), Density functional theory (DFT), Phosphorene, Graphene, External electric field*

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Protection Effect of $Mn_{0.5}Mg_{0.5}Fe_2O_4$/Chitosane/Formaldehyde/Thiourea Nanocomposite on the Corrosion of 304 Stainless Steel

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Abstract

Stainless steels are known for their good corrosion resistance in many corrosive environments, but hydrochloric acid solution causes corrosion of it [1-3]. Therefore various types of inhibitors are injected into corrosive media to decrease the corrosion rate to safe level [2-4]. In this study, application of $Mn_{0.5}Mg_{0.5}Fe_2O_4$/Chitosane/Formaldehyde/Thiourea nanocomposites for corrosion protection of 304 stainless steel for the first time was reported. The nanocomposites was characterised through Fourier transform infrared (FTIR) spectroscopy, UV-visible (UV-vis) spectroscopy and field emission scanning electron micrographs (FESEM). The corrosion behavior of 304 stainless steel in hydrochloric acid solution without and with various concentration of nanocomposites was studied by using gravimetric method and electrochemical methods including potentiodynamic polarization method and electrochemical impedance spectroscopy (EIS) method. The surface of steel samples were analyzed by scanning electron microscopy for further verification. The effect of temperature on the corrosion behavior of steel in the absence and presence of nanocomposites was studied in the range of 25-65 °C. The results indicate that protective effect of nanocomposites is very good in very low concentrations.

***Keywords**: Nanocomposites, Spinel, Chitosan, Corrosion protection, Electrochemical impedance spectroscopy (EIS), Potentiodynamic polarization.*

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Thermodynamic of Micellization and Free Energy Contribution for Aggregation of Cleavable Gemeni Surfactants

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Abstract

The physicochemical properties and thermodynamic of micellization for ester-containing cationic Gemini surfactants, dodecyl esterquat Gemini and dodecyl betainate Gemini were investigated using tensiometry and conductometry over the temperature range 298 K to 318 K. The changes in Gibbs free energy, enthalpy and entropy of the micellization have been determined at different temperatures. An enthalpy–entropy compensation effect [1] was observed and the plot of enthalpy–entropy compensation exhibit excellent linearity. In this paper to model the aggregation behavior of Gemini surfactants in aqueous solutions and to explore the origin of their very low CMCs and their unusual ability to generate large micelles when the spacer length is small, expressions for various contributions to the free energy of micellization were developed according to Nagarajan model [2]. The following expression was used for various contributions to the free energy of micellization:

$$\Delta\mu_g^0 = \left(\Delta\mu_g^0\right)_{tr} + \left(\Delta\mu_g^0\right)_{int} + \left(\Delta\mu_g^0\right)_{H} + \left(\Delta\mu_g^0\right)_{pack} \quad (1)$$

Where $\left(\Delta\mu_g^0\right)_{tr}$ refer transfer free energy, $\left(\Delta\mu_g^0\right)_{int}$ is interfacial free energy, $\left(\Delta\mu_g^0\right)_{H}$ and $\left(\Delta\mu_g^0\right)_{pack}$ are heading and packing free energy, respectively. The experimental free energy also obtained from surface tension and conductance measurements [3,4]:

$$\Delta_{mic}G^{\circ} /(kJ.mol^{-1}) = \mathrm{RT}\,(1.5-\alpha)\ln \mathrm{X_{CMC}} - (\mathrm{RT}/2)\ln 2 \quad (2)$$

There was a good agreement between theoretical free energy (equation 1) and the experimental free energy showing the Nagarajan model can good predict the thermodynamic of micellization for these Geminis.

Keywords: *Gemini surfactants, Thermodynamic of micellization, Enthalpy–entropy compensation, free energy*

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Voltammetric sensor based on a new synthesized ligand and Mn_3O_4/SnO_2 nanoparticles MCPE for determination of sumatriptan in biological fluids.

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Abstract

Sumatriptan succinate is a 5-HT1 receptor agonist which is used in the treatment of migraine. It shows low bioavailability (15%) due to high hepatic first pass metabolism (1). SUM reduces the vascular in flammation associated with migraines. However, an over dose is toxic and leads to several side effects viz. , paresthesia, warm/cold sensations, chest pain, fatigue and vertigo. Thus, its determination is of importance (2).

In this study, a new Schiff base ligand, N',2-bis(2-hydroxybenzylidene)hydrazine-1-carbothiohydrazide (figure 1) , has been synthesized by reaction of the hydrazinecarbothiohydrazide with 2-hydroxybenzaldehyde at ethanol under mixture stirred at room temperature for 30 Minute. The structure of the synthesized compound resulted from the IR and ^1H NMR. Afterwards, a carbon paste electrode modified with nanocatalyste (Mn_3O_4/SnO_2) and a new thiohydrazin derivative Schiff base was developed for the sumatriptan determination at nanomolar level concentration. The electrochemical behavior of this molecule was investigated employing cyclic voltammetry and anodic stripping voltammetric. The experiments were conducted with a certain electrode composition of 18.0% paraffin oil, 69.0% high purity graphite powder, 6% $NiFe_2O_4$ and 6% Shiff base as well as the usage of 0.2 M phosphate buffer as supporting electrolyte. Also the enhanced peak current response is a clear evidence of the catalytic of the modified carbon paste electrode towards oxidation of sumatriptan. The effect of pH and scan rate on the electrode process was investigated. The resulting electrode demonstrated linear response across a wide sumatriptan concentration range with a detection limit value of 10^{-8} M, on the basis of a signal to noise ratio of 3. The method was successfully applied to the determination of sumatriptan in pharmaceutical tablets and plasma.

***Keywords**: Carbon paste electrode, Schiff base, Nanoparticles, Sumatriptan, Biological fluids.*

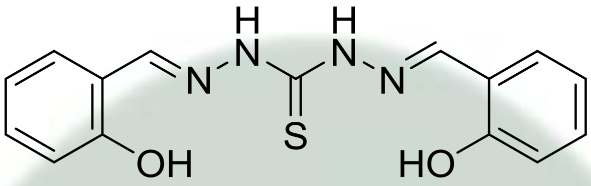

Figure 1. Chemical structure of N',2-bis(2-hydroxybenzylidene)hydrazine-1-carbothiohydrazide

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Preparation of electrochemical sensor base on carbon paste electrode modified by a new pentazene ligand for determination of mercury in aqueous samples

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Abstract

As one of the most toxic heavy metals, mercury pollution has attracted much attention in environmental and toxicological domains for decades. Inorganic mercury released mainly from industrial sources can be further converted into methylmercury by microorganisms and fish. Methylmercury, the most common organic mercury, is more toxic than inorganic mercury because it’s lipophilic and easily absorbed by aquatic organisms which finally bioaccumulate in the human body through the food chain leading to severe impact on human health due to its severe toxicity to the nervous and immune system[1].

Nowadays,different schemes have been reported for detection of water-soluble Hg^{2+} ion, e.g., colorimetricassay, electrochemical method, inductively coupled plasma mass spectroscopy (ICP-MS) and fluorescencespectroscopy. Among the methods, electrochemistry holds great potential as the next-generation detection strategy because of its high sensitivity, low cost, low power requirements and simple instrumentation[2]

In this study, a new ligand, 1,5-bis(4-methoxyphenyl)-3-methyl-1,4-pentazadiene (b-PMMP) (figure 1) has been synthesized by reaction of the 4-methoxyaniline (p-anisidine) with methanamine (methylamine). The mixture was stirred in an ice bath for 30 min. The structure of the synthesized compound resulted from the IR and ^{1}H NMR and ^{13}C NMR. Afterwards, a carbon paste electrode modified with a this new ligand was developed for the mercury determination at nanomolar level concentration. The electrochemical behavior of this molecule was investigated employing cyclic voltammetry and square wave voltammetric. The experiments were conducted with a certain electrode composition of 18.0% paraffin oil, 70.0% high purity graphite powder and 12.0% b-PMMP as well as the usage of pH=10 ammonia buffer as supporting electrolyte. Also the enhanced peak current response is a clear evidence of the modified carbon paste electrode towards oxidation of mercury. The effect of pH and scan rate on the electrode process was investigated. The resulting electrode demonstrated linear response across a wide mercury concentration range. The

method was successfully applied to the determination of water-soluble Hg2+ ion in environmental samples.

Keywords: *Carbon paste electrode, pentazadiene, Mercury, Electrochemical sensor.*

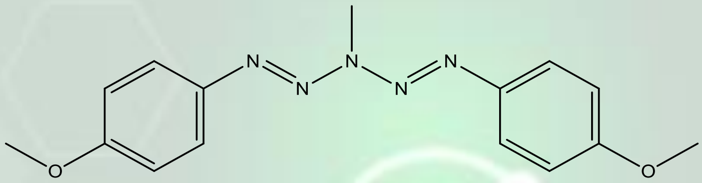

Figure 1. Chemical structure of 1,5-bis(4-methoxyphenyl)-3-methyl-1,4-pentazadiene (b-PMMP)

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Electrochemical pseudocapacitors: mechanism, materials, characterization and electrochemical performance

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Abstract

Electrochemical capacitors (ECs) have attracted great attention of scientist for their application in most technology such as electric vehicles (EVs), uninterruptible power supplies (UPS), DC power systems, and mobile devices. Filling the gap between capacitors and batteries, high power, high energy and long lifetime are some of benefits of using ECs. ECs are divided to two parts about charge storage mechanism; EDLC that store charge in electrical double layer and pseudo capacitor that energy storage is due to the faradic process. From the view of active material ECs are divided to four categories; carbon materials, metal oxides, conductive polymers (CPs) and hybrid materials. In recent years hybrid nanocomposite of conductive polymer/metal oxide and conductive polymer/carbon based materials have been given considerable attention due to its mechanical and chemical properties and fast electron transfer kinetics [1-5].

In the presented work, different electrosynthesized metal oxide, ionic liquid, ceramic material and graphene oxide/ conductive polymer as composite materials were electrodeposited on the surface of the working electrode and fundamental physielectrochemical aspects, electrochemical performance were evaluated in an aqueous acidic medium. Surface analysis and different electrochemical methods including galvanostatic charge–discharge (CD) experiments, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were carried out in order to investigate the applicability of the system as a hybrid supercapacitor.

Keywords: *electrosynthesis, impedance, nanocomposite, pseudocapacitors*

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Fabrication of MEA based on nitrogen doped graphene as highly efficient and durable support for oxygen reduction reaction in PEMFCs

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Abstract

In this work, we have used an efficient approach to prepare nitrogen-doped graphene supported Pt nanocomposites (Pt/N-rGO). The nitrogen-doped graphene nanocomposites (N-rGO) were derived from pyrolysis of graphene oxide /polyaniline composites in nitrogen atmosphere. X-ray powder diffraction, FTIR spectroscopy, Raman spectroscopy, X-ray photoelectron Spectroscopy and Transmission and Scanning electron microscopy (TEM&SEM) were used to characterize the morphology and microstructure of the prepared catalysts. The TEM and elemental mapping images indicate that metal nanoparticles are more uniformly dispersed on the surface of N-doped graphene than other supports, and Pt nanoparticles dispersed without any aggregation. The catalytic activity and durability of the catalysts was evaluated by various electrochemical techniques. Compared to undoped Pt/rGO and commercial Pt/C catalysts, an enhanced electrocatalytic activity was obtained in the case of the Pt/N-rGO with optimized composition and nanostructure. The maximum power density of MEA for Pt/N-rGO was 1.4 times more than that of MEA fabricated by commercial Pt/C 20%.

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

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High sensitive electrochemical lable free DNA biosensor for determination of Levodopa with Fe3O4 nanoparticle decorated reduced graphene oxide modified electrode

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Abstract

Levodopa (Lev) is an unusual amino acid that is used for the treatment of Parkinson's disease to provide symptomatic relief to most patients at the early stages of disease[1]. In the present work, an electrochemical biosensor was developed for Levodopa (LD) detection using label-free double strand DNA (ds-DNA) and graphene (Gr) decorated with Fe_3O_4 magnetic nanoparticles on a carbon paste electrode (CPE). Electrochemical studies revealed that modification of the electrode surface with ds- DNA and Gr- Fe_3O_4 nanocomposite significantly increases the oxidation peak currents but reduces the peak potentials of Levodopa. After the optimization of operational parameters, calibration curve was linear in the range of 5.0×10^{-8}- 1100×10^{-6} M with a detection limit of 1.7×10^{-8} M. The relative standard deviations for 20µM was 3.20% (n=5).The proposed biosensor was successfully applied to the analysis of Levodopa in human serum. A suitable selectivity was achieved for determination of Levodopa in real samples.

***Keywords**: Biosensor, carbon paste electrode, Levodopa, nanocomposite*

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A new electrochemical DNA biosensor for determination of menadione in human plasma

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Abstract

Menadione (vitamin K3, 2-methyl- 1,4- naphthoquinone) is a synthetic vitamin K analog which has been used chiefly as an antihemorrhagic agent [1]. In the present study, a fast, low cost and sensitive method for the electrochemical determination of menadione was proposed based on its intercalation into DNA double helix. The intercalation of menadione investigated using spectrofluorimetric technique. An electrochemical biosensor was fabricated using carbon paste electrode modified with Gr-Fe_3O_4 nanocomposite. A considerable increase was observed in the oxidation signal of menadione at carbon past electrode modified with Gr-Fe_3O_4 nanocomposite compared with unmodified electrode, After optimizing main experimental parameters such type of buffer, pH, accumulation time, etc. Its performance was evaluated from analytical point of view.A linear dependence of the anodic peak current of menadione on its concentration were observed in the range of 0.30–12 µM with detection limit of ٠,09 µM .

The relative standard deviations for 20 µM was 2.56% (n=5).

The proposed sensor was successfully applied to the analysis of menadione in the human plasma

Keywords*: biosensor, electrochemical modified methods, menadione*.

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Application of artificial neural network for the removal of azo dye by Multiwall carbon nano tubes coating on titanium

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Abstract

The present work discusses the removal of Acid red 33 (AR33) dye from aqueous solution by electrochemical advanced oxidation process using titanium coated with multiwall carbon nanotubes as anode. The said anode was prepared by the electrophoretic deposition (EPD) in an aqueous solution method and was characterized by field emission scanning electron microscopy (FE-SEM). The important process parameters, such as initial pH, current density and reaction time were investigated on color removal efficiency. The optimum color and COD removal efficiency of onto MWCNTs/Ti were determined as 90% and 15% respectively, at pH = 8, current density of 5.5 mA/cm^2 and reaction time of 60 min. Also, a three-layered feed forward back propagation artificial neural network (ANN) model was used for predicting removal(%) of AR33 dye based on experimental data. The coefficient of determination (R^2) of 0.9959 and the mean square error (MSE) MSE of 0.306×10^3 confirm accuracy of the neural network for modeling and can predict the decolorization efficiency with acceptable accuracy.

Keywords: *MWCNTs/Ti; Electrophoretic deposition; artificial neural network; Acid Red 33.*

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Artificial neural network modeling of photoeletrocatalytic removal of a azo dye using mwcnts-TiO_2 composite on titanium

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Abstract

In this work, performance of titanium electrode coated with multiwall carbon nanotubes – TiO_2 composite (MWCNTs-TiO_2/Ti) for the treatment of C.I. Acid Red 33 (AR33) in aqueous solutions was investigated. The MWCNTs-TiO_2/Ti electrode was prepared by the electrophoretic deposition (EPD) and was characterized by field emission scanning electron microscopy (FE-SEM) and Transmission electron microscopy (TEM) . The photoelectrocatalysis (PEC) performance of the prepared MWCNTs-TiO_2 composite electrode was studied in removal of Acid Red 33 (AR33)from water. The main influence factors on the PEC activity such as pH of solution and current density were studied. The result shows that, in optimum conditions, maximum color removal efficiency (98%) was obtained and the removal of chemical oxygen demand (COD) was reduced to 41.66%. Also, a three-layered feed forward back propagation artificial neural network model was developed to predict the PEC of AR33 using MWCNTs-TiO_2/Ti electrode. Obtained correlation coefficient (R^2= 0.98) and the mean square error (MSE) MSE of 0.186×10^3 show the good performance of ANN model in prediction of experimental data within adopted ranges.

Keywords: *MWCNTs-TiO_2/Ti, Electrophoretic deposition, artificial neural network, decolorization.*

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Enhanced electrochemical signal of BUP drug on a magnetic nano-mound structured surface

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Abstract

Herein, we report a highly sensitive voltammetric determination of buprenorphine using a citrate stabilized magnetic nanocrystal (CS-MNCs) modified carbon paste electrode (CP). The buprenorphine electro-oxidation peak current i_p at CS-MNs/CP electrode was 10 fold higher than that of unmodified CP electrode. CS-MNCs/CP electrode detects buprenorphine in the linear range of 0.02-68.0 µM with a detection limit (DL) of 4.3 nM. Fast response time, high sensitivity and ease of preparation method without using any specific electron transfer mediator or specific reagent are the advantages of the sensor. The modified electrode was applied to the determination of buprenorphine in human biological fluid at micromolar level without any pretreatment or separation step.

Keywords: *Buprenorphine; CS-MNCs/CP electrode; Voltammetry*

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Study of electrocatalytic oxidation of ethanol on Ni modified graphite electrode in NaOH solution

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Abstract

At present, the ever-increasing use of energy, and especially of fossil fuels, is a major source of air pollution. As a result of large energy consumption and global ecological awareness, direct alkaline ethanol fuel cell (DAEFC) has gained a lot of attention as an alternative to fossil fuel combustion since it satisfies critical criteria such as; fuel transportation, easiness of ethanol production, efficiency, safety, compatibility, and cost. A considerable number of studies, have been devoted to the electrocatalytic oxidation of ethanol, which is of paramount importance in the development of DAEFCs. In the present study, we investigated the activity of a modified Ni-based graphite electrode (G/Ni) and the effects on the electrocatalytic oxidation of ethanol in a NaOH solution (0.1mol/L). The catalysts were prepared by cycling the graphite electrode in solution containing Ni ion at cathodic potentials. The methods of cyclic voltammetry (CV) and chronoamperometry (CA) were employed. The result showed that, in the presence of ethanol, the modified Ni-based graphite electrode (G/Ni) exhibited a significantly higher response for ethanol oxidation while in the absence of ethanol, the graphite electrode presents no activity. More specifically, the growth of the anodic peak is considerable and the negligible cathodic peak in the presence of methanol is attributed to an irreversible oxidation process. It can be seen that the anodic peak current density increases with increasing methanol concentration. The peak current of the oxidation of nickel hydroxide increase is followed by a decrease in the corresponding cathodic current in presence of ethanol.

Keywords: *Fuel cells, Ethanol electro-oxidation, Modified electrode, Nickel*

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Effect of etching current density on photoluminescence properties of porous silicon

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Abstract

Due to the excellent properties such as efficient visible room-temperature photoluminescence (PL) and extremely large surface-to-volume ratio, porous silicon (PS) is material of interest in many applications such as photodetectors [1]. In this research, effect of etching current density (J) on optical properties of photo-electrochemically synthesized PS samples was characterized in order to achieve a porous morphology with maximum PL properties. PS samples were synthesized by photo-assisted electrochemical etching (PECE) of (100) oriented phosphorus doped crystalline silicon (c-Si) substrates with specific resistance of $0.05\ \Omega.cm$ and thickness of $680\ \mu m$. A thin film of silver (Ag) with the thickness of $\sim 150\ nm$ was deposited on the back side of c-Si substrates in order to facilitate anodization process. The metallization was taken place in a vacuum chamber of a sputtering system and an ultra-pure Ag plate was used as a target. This process decreased the surface resistivity to $0.001\ \Omega.cm$ after 15 min of annealing in tube furnace at a temperature of $430\ ℃$ under nitrogen gas flow [2]. The chemical solution used here was containing a mixture of hydrofluoric acid (HF 38-40%) and ethanol (C_2H_5OH 96%) in a volumetric ratio of 1:4. Current densities as critical experimental parameters were fixed at 10, 20, 40, 60 and 80 $mA.cm^{-2}$ for sample a, b, c and d respectively using DC source meter (Keitlly 2400, USA) throughout the etching time (20 min). A platinum mesh was used as a counter electrode (cathode) in PECE cell and it was located approximately $10\ mm$ directly above the surface of c-Si sample (anode). To create the required holes for occurrence of dissolution reaction on the surface layer of working electrode (anode) and PS formation, front side of the c-Si was irradiated by means of one 100 W tungsten lamp at a distance of $20\ cm$ above it during the etching process. Fig. 1 shows SEM micrograph of synthesized porous substrate. SEM view reveals that while the applied J increases from $20 mA.cm^{-2}$to $80 mA.cm^{-2}$, pore diameter of the PS samples increases and total volume of Si nanocrystallites on the surface decreases. Also, the decrease in pore density N_p(the number of

pores per unit area) was observed on PS surfaces by increasing J for sample c and d. The logical reason for the evolution in the morphological characteristics of the pores of these PS samples is influence of the electric field on carrier's movement and hence on dissolution [3]. The effect of J on the band gap structure (E_g) and emission properties of the PS samples was identify using PL spectra. In this experiment, in order to record S-band transition, excitation wavelength of PL was 405 nm. Fig. 2 shows the PL spectra of PS samples. A remarkable increase in intensities of the emitted photon from porous samples was observed with initial increase in J from $10mA.cm^{-2}$ to $20mA.cm^{-2}$. Then a slight decrease in PL intensity was shown by increasing J from 20 $mA.cm^{-2}$ to 80 $mA.cm^{-2}$. Maximum intensity was detected in sample b with J = 20 $mA.cm^{-2}$, at a wavelength of ~658.2 nm that can be due to the total amount of nanocrystallites on the surface of this sample compared to sample *a*. Applying higher current densities (more than 20 $mA.cm^{-2}$) will increase dissolution of silicon material on the surface (as shown in Fig. 1) and thus will reduce PL intensities in samples c and d compare to sample b. The larger macro-cavity pores reduce the amount of nanocrystallite and result in light trapping. Therefore, the specific surface area of PS will reduce by increasing macro-cavities which lead to decrease in PL peak in samples *c* and *d*.

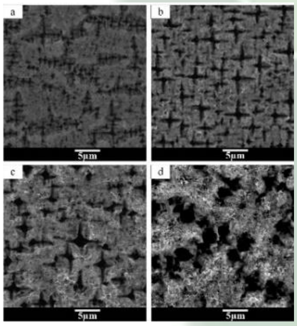

Fig. 1. SEM image of porous samples a, b, c and d

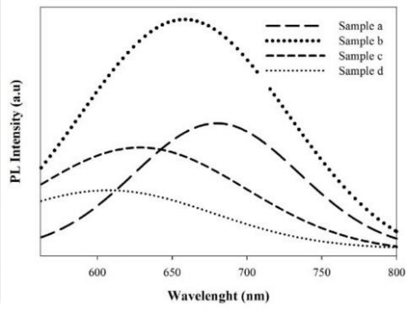

Fig. 2. Photoluminescence (PL) spectra of porous samples a, b, c and d.

Consequently, our PL analysis reveals that applied J has a significant effect on structural properties such as size of pores and crystalline properties of PS. Therefore, etching current density can be assumed as an outstanding parameter to optimized electronic structure of PS (e.g. band gap) and it has an important role in its light emitting properties. In the current report, it was shown that the porosity of PS is not the only parameter which affects the optical properties. The morphology of pores acts an important role to determine PS properties.

Keywords: *Porous silicon, Photo-electrochemical etching, Etching current density, Photoluminescence*

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Electrochemical polymerization of sunset yellow on carbon ceramic electrode and electrocatalytic activity for oxidation of tryptophan

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Abstract

The compounds which provide chromophore azo group (-N=N-) form a piece of conjugate system together with two or more aromatic ring in their structure and combination of these rings are called azo dye matrial [1]. Sunset yellow (E-110, sy) is one of the synthetic dyes that contain the azo group as chromophore in its molecular structure, have during several years widely use as food coloring agent in many countries[2-3]. In the present work, sunset yellow as a food dye, has been polymerized on ceramic carbon electrodes using cyclic voltammetry and the formation of polysunset yellow nano films has been confirmed. The characteristics and morphology of polysunset yellow synthesized on carbon cermic electrode were characterized by SEM and FT-IR, NMR and TGA. The electrochemical behavior of polysunset yellow modified carbon ceramic electrode showed a pair of symmetrical redox peaks at a formal redox potential, $E^{`0}$=-0.03V vs. Ag/AgCl. The carbon ceramic electrode modified with polysunset yellow showed eletrocatalytic activity towards oxidaization of tryptophan. Under optimal experimental conditions, the carbon ceramic electrode modified with polysunset yellow exhibited a EC´ mechanism for the selective electrooxidation of tryptophan in the presence of other amino acids (pH= 5, phosphate buffer solution).

Keywords: *Azo dyes, Sunset yellow, Nano polymeric films, Electrocatalytic activity, Tryptophan, Carbon ceramic electrode*

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Global sensitivity analysis and uncertainty quantification of Lead-Acid battery

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Abstract

Lead-acid batteries are one of the most important electrochemical energy storage devices which used in variety application due to their lower price, high rate discharge, recycling and deep cycling. But improvement of energy density of Lead-acid battery has become a research concern in nowadays. Improvement of this type of battery has significant dependency on determining of its effective parameters. But the most effective physical properties involved in battery performance and energy density may not be exactly known, possibly because of intrinsic variability which cannot be measured directly in practice. Thus, in the simulation process, some uncertainties are unavoidable. Quantification and understanding of these uncertainties are required to evaluate the differences between the actual system behavior and numerical predictions.

To this end, in this paper effect of these uncertainties on energy density of Lead-acid battery are quantified and propagated through its governing equations. Finally all the uncertainties roll up to evaluate convenient range of cell voltage. Also a global sensitivity analysis based on Sobol indices is carried out to determine the most effective parameters.

Frequently, the uncertain model parameters are denoted by random variables/processes which are known as probabilistic techniques. In this case, traditional methods such as Monte Carlo sampling (MCS) [1] and perturbation-based methods [2,3] is not suitable choice because MCS has low converging rate and perturbation-based methods have restriction on range of variation of the parameters of interest. In this paper, stochastic spectral methods [1,2] based on polynomial chaos (PC) expansions [1] are chosen because it can be implemented without any limitation. Moreover this method has higher rate of converging and accuracy [1]. In the present study, the coefficients of PC-expansion are calculated non-intrusively. Non-intrusive methods depend on individual realizations to recognize the stochastic model reaction to random inputs. Despite of intrusive methods, non-intrusive methods have less computational effort and easily can be implemented in complex physics such as lead-acid batteries.

Lead-acid battery is simulated using finite volume method. Results agree well respect to previous studies at different discharge rates. The numerical results show that the proposed UQ method can accurately compute the variability in the output quantity of interest such as cell voltage and energy density. The obtained numerical results can be used to design more efficient batteries.

Keywords: *Lead-acid battery, Simulation, Uncertainty quantification, Polynomial chaos.*

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A deconvolution method to model electrode processes in solid oxide cells

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Abstract

Electrochemical impedance spectroscopy (EIS) was utilized to characterize an anode-supported solid oxide cell. In order to define a suitable equivalent circuit model (ECM), the corresponding distribution of relaxation times (DRT) curves were calculated. DRT was implemented as a deconvolution method to pre-identify the electrode polarization processes at various temperatures and gas compositions. Based on the DRT plots, a general strategy for the identification of the reaction mechanisms was achieved. It was shown that gas diffusion process in cathode can be characterized only at low oxygen partial pressures.

Keywords: Solid Oxide Cell, Electrochemical Impedance Spectroscopy, DRT, LSCF

Introduction

Electrochemical impedance spectroscopy stands out among all other electrochemical techniques for the characterization of solid oxide cells (SOCs). It not only provides valuable information regarding ohmic resistances, charge transfer and mass transfer processes and kinetic of the reactions, but also can individually characterizes all processes in a single experiment. The impedance spectrum of a SOC is commonly analyzed by Complex Nonlinear Least Squares (CNLS) approximation to an equivalent circuit model. In this case, the equivalent circuit model needs to be pre-defined. Commonly, the ECM for SOC electrodes has primarily been evaluated by a fairly primitive approach consisting of a series of suppressed semi circles. Each suppressed semicircle is then assigned to a specific reaction or process. There are some limitations for this method as follows: i) some processes can be coupled such as Finite-Length-Warburg (FLW) impedance element (describing diffusion) with the gas conversion element and ii) not having a perfect knowledge about the real number of polarization processes contributing to the overall polarization loss of the cell. Normally, these limitations lead to uncertain adoption of models. Therefore, in this work an alternative approach for analyzing impedance spectra was employed. By calculating and analyzing the corresponding distribution function of relaxation times, the ECM can be better pre-identified.

Method

An anode-supported SOFC single cell was analyzed in this work. An anode functional layer (Ni/$Zr_{0.92}Y_{0.08}O_2$ (8YSZ)) and YSZ electrolyte were applied onto an anode substrate (Ni/8YSZ). $Ce_{0.8}Gd_{0.2}O_2$ (CGO) was screen-printed on the surface of electrolyte layer and fired to prevent chemical reaction between the electrolyte material and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF) cathode. The cathode electrode was subsequently screen-printed on top of the fired buffer layer.

The prepared cell was characterized under various gas compositions of H_2, H_2O and N_2 at the anode side and different mixture of air and N_2 at the cathode side. The overall gas flow rate was kept constant at 15 $l.h^{-1}$ for both electrodes. Impedance spectroscopy was carried out using a Solartron 1260 at frequencies between 30 mHz and 1 MHz. The acquired impedance data were analyzed by the Ravdav software.

Results and discussion

Figure 1 shows the influence of the variation of oxygen partial pressure (pO_2, *cat*) on the distribution of relaxation times. It is clearly visible that a new process (denoted as P_{1C}) evolves in the frequency range below 10 Hz at the oxygen contents of ≤ 0.05 atm. At the same time, the process P_{2C}, is shifted towards lower frequencies, thus overlapping with the two major peaks between 7 and 100 Hz related to the process P_{1A}.

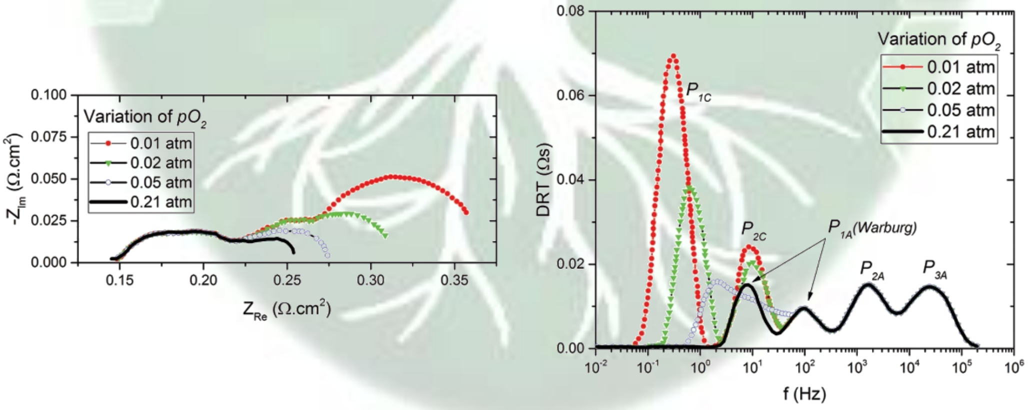

Figure 1: The EIS (left) and DRT (rigth) curves at four different pO_2 in cathode electrode.

Based on the DRT analysis shown above, the equivalent circuit model depicted in Figure 2 was proposed. The equivalent circuit consists of six serial impedance elements: the processes P_{1C}, P_{2A} and P_{3A} are modelled by an RQ-element, whereas P_{1A} and P_{2C} are modelled by a G-FLW-element and a Gerischer-element, respectively. The ohmic losses are accounted by an ohmic resistor R_1.

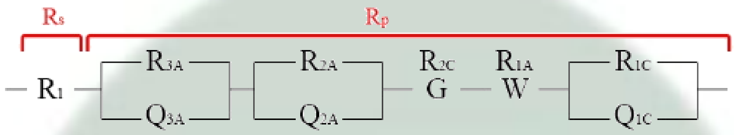

Figure 2: The equivalent circuit model for CNLS fitting

It was revealed that two processes of P_{1C} and P_{2C} are cathodic processes in which P_{1C} characterizes the gas diffusion losses within the pores of the cathode (and is, thus, negligible in air), whereas the faster process P_{2C} is inherently electrochemical.

Conclusion

The ECM was successfully pre-defined by DRT curves and well-fitted to the impedance spectra using the CNLS analysis. Different polarization processes were defined by using DRT plot.

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Sensetive detection of glutathione (GSH) by using dsDNA-templated copper nanoparticles (dsDNA-CuNPs) as electrochemical reporters: review

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Abstract

An electrochemical method for the detection of GSH is adoption of DNA-templated CuNPs as electrochemical reporters. GSH and Cu ions interact eachother strongly, so they will make great hindrances to DNA-templated formation of CuNPs on the electrode surfaces, and the electrochemical signals will decrease. Although this method exhibits desirable selectivity and producibility, shows superior sensitivity, but remains problematic, because of weak fluorescence and poor stability. In order to solve this problem, a novel concatemetris dsDNA-CuNPs strategy was proposed by introducing the rolling circle replication (RCR) techniques into CuNPs synthesis.
A short oligonucleotide primer could trigger RCR and be further converted to a long concatemeric dsDNA-CuNPs.These dsDNA-CuNPs can emit intense fluorescence in the range of 500-650nm under a 340nm excitation. Their sensitivity improved with ~10000 folds amplication, and fluorescence signal was detected to reserve ~60% at 25h after formation, revealing ~2 times enhanced stability.

Keywords: *Glutathione, dsDNA-templated , Cu nanoparticles, oligonucleotide*

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Electrochemical evaluation of various commercial expanders for lead-acid battery application

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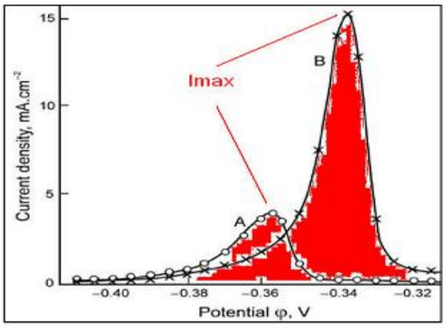
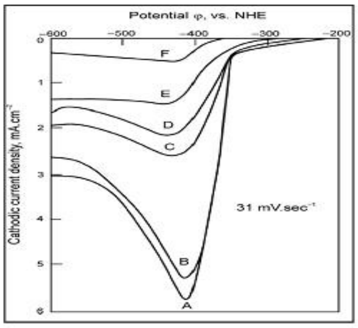
Abstract

As known, the performance of the negative plates of lead-acid batteries is strongly influenced by the presence of organic substances, usually referred to expanders. The expanders are generally added to the negative active material during manufacturing process. The effects of such additives mainly concern the performance at high rate of discharge and charge acceptance; additionally, they also exert other beneficial actions on the overall behavior of the negative plate. During discharge process ,passivation of the electrode starts due to the formation of a $PbSO_4$ layer. While using an expander, the passivation of surface is prevented by causing effect with its organic part that leads to increasing in the current passed through the negative plate during discharge process and the cranking ability of the battery. Thus, discharge process is more effectively occurred when a good expander is used. . During charge process The effects of expanders are simply explained by adsorption of expander onto the metallic surface and decreasing the surface area. an organic expander impedes the process of $PbSO_4$ reduction to Pb. This phenomenon brings about decreasing in charge acceptance ability. To evaluate different commercial expanders, the various electrochemical techniques may be used. As reported in the literature, the techniques based on cyclic voltammetry are of particular interested. the voltammetric curves provide reliable information about the amount of charge stored in the anodic part of the cycle, i.e., on the formation of sponge lead, while they do not give direct kinetic information about single processes, By plotting the amount of charge of the anodic peak as a function of the cycle number, a curve presenting a wide maximum. The difference between the maximum value of the amount of charge obtained in the presence of the expander and that obtained without the expander, has been related to the activity of the organic substance, while the difference between the number of cycles for which such maximum values are observed has been correlated to the stability of the expander.



Polarization curves for a stationary Pb electrode in 5M H2SO4 solution: A – no expander; B – with expander



Voltammogram for PbSO4 reduction to Pb in 1.25 rel. dens. H2SO4: A – no expander: B, C, D, E, F – different expanders

In this study, five types of commercial expander were considered: Penox PE110 ,New Penox formula, Texex SA&B and Jinkeli and then evaluated by 15-cycle potentiodynamic polarization test which was done in the range of -725 to -325 mV/SCE with scan rate of 120 mV/min. The working electrode was pure Pb. Also, the saturated calomel electrode and platinum wire served as reference and counter electrode respectively. To prepare the solution, 6 g of expander was directly added to 300 CC of 4.8 M H_2SO_4 solution, followed by mechanically stirring for 2 hr.

The results showed that all the expanders enhance the maximum current for the passivation Pb surface, leading to capacity improvement. Among them, the best performance belongs to Jinkeli Company. On the other hand, the expanders negatively affected the $PbSO_4$ to Pb reduction process, except for Jinkeli and New Penox formula. In addition based on the national standard tests on batteries, the battery made by Jinkeli and new Penox formula expander revealed a desirable capacity during cycling in low temperatures and a good charge acceptance.

Expander type	i_{max} anodic (mA/cm^2) (Discharge)		i_{max} catodic (mA/cm^2) (Charge)	
Cycle	**1st Cycle**	**15th Cycle**	**1st Cycle**	**15th Cycle**
Pb	**0.20**	**0.19**	**-1.03**	**-1**
PE110 Penox	**0.81**	**1.05**	**-0.58**	**-0.6**
Penox new formula	**0.80**	**1.41**	**-0.85**	**-0.92**
Texex-SA	**1.34**	**1.02**	**-0.46**	**-0.55**
Texex B	**1.39**	**1.02**	**-0.71**	**-0.79**
Jinkeli	**1.39**	**1.4**	**-0.85**	**-0.93**

Keywords: *Lead-acid battery , Expander , Cyclic voltammetery , Charge acceptance, cold cranking*

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Application of reactive DC magnetron sputtering system in fabrication of a nanostructure copper oxide thin film as a sensing transducer

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Abstract

Uniform sputtered nanostructure copper oxide (Nano-CuO) thin film on the conductive fluorinated-tin oxide (FTO) substrate was obtained by reactive direct current (DC) magnetron sputtering system at the optimized instrumental deposition conditions. The deposited Nano-CuO thin film was characterized by using X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), energy dispersive X-Ray spectroscopy (EDX), ultra-violet visible spectrophotometry and electrochemical methods. The crystalline phases, morphology, optical properties and resistivity of the Nano-CuO thin films are found to be significantly influenced by the changes in target-to-substrate distance, Ar to O_2 gas flow ratio, sputtering power and deposition time. The Nano-CuO thin film prepared at the optimum conditions has exhibited high porosity, uniformity and low resistivity; thus, it could be used as an excellent sensing transducer platform in biosensor fabrication.

Keywords: *Nanostructure CuO thin film, Reactive DC magnetron sputtering, Sensing transducer, Biosensor.*

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Fabrication of CuO nanoparticle/ionic liquid modified carbon paste electrode: Application for simultaneous determination of hydrazine and bisphenol A in water samples

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Abstract

In the present research, we report the application of synthesized copper oxide nanoparticles toghether with n-hexyl-3-methylimidazolium hexa-fluoro-phosphate in the constructuion of the modified carbon paste electrode (CuO/NP/IL/CPE) as high sensitive electrochemical sensor for simultaneous determination of hydrazine (HY) and bisphenol A (BPA). The electrochemical properties of CuO/NP/IL/CPE was carefully studied in aqueous media, using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), chronoamperometry and differential pulse voltammetry (DPV). The electron transfer coefficient (α), diffusion coefficient (D), and electron transfer resistant (Ret) of HY at the modified electrode were calculated. The experimental results show that, under optimized conditions, the modified electrode promoted electron transfer reaction for the oxidation of HY and BPA. The linear dynamic range were obtained in the ranges of 0.05–150 and 0.2–175 µmol L^{-1} with the detection limits (3sb/m) 0.03 and 0.1 µmol L^{-1} for HY and BPA, respectively. Finally, this new sensor was used for simultaneous determination of HY and BPA in some water samples such as river water and wastewater using the standard addition method.

Keywords: *Hydrazine, Bisphenol A, CuO nanoparticles, Ionic liquid, Water and wastewater*

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Simultaneous determination of epinephrine and folic acid using $Fe_3O_4@Sio_2$-GO nano composite modified graphite screen printed electrode

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Abstract

Nanocomposite materials have shown promising applications in the interdisciplinary research areas with significantly improved activity because of the synergistic contribution provided by the constituent components of the nanocomposite material[1]. Epinephrine (EP) belongs to the family of catecholamine neurotransmitters, which is widely distributed in the mammalian central nervous system for message transfer process[2]. It is also called as flight or fight hormone. High levels of EP are associated with stress and thyroid hormone deficiency [3]. Folic acid (FA) is a widely distributed water-soluble vitamin and can act as a coenzyme that controls the generation of ferroheme[4]. FA paucity mounts to gigantocytic anemia, neurosis, mental decentralization, leucopoenia, etc. FA determination is essential in pharmaceutical, clinical and food samples[5]. Electroanalytical methods have attracted more attention in recent years for environmented and biological compound determination due to their sensitivty, accuracy, low cost and simplicity [3]. The present study is aimed at synthesis of $Fe_3O_4@Sio_2$-GO nanocomposite and its application in the form of modified graphite screen printed electrode for trace, rapid and sensitive determination of EP and FA by using this modified eletrode EP and FA were determination in the range of 1-1000 μmol L^{-1} and 0.1-1000 μmol L^{-1} respectively.

Keywords:*Epinephrine. Folic acid . Nano graphene. Graphite screen-printed electrodes*

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Magnetic core–shell Fe3O4@Sio2-GO nano composite for sensitive and selective electrochemical sensing of levodopa and tryptophan using modified graphite screen printed electrode

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Abstract

Electroanalytical methods have attracted more attention in recent years for environmented and biological compound determination due to their sensitivty, accuracy, low cost and simplicity [1]. Levodopa (LD) (a precursor of DA) is an important neurotransmitter, which is used for the medication of neural disorders such as Parkinson’s disease[1]. People with Parkinson’s disease have depleted levels of dopamine and levodopa is used to increase dopamine in the brain, which reduces the symptoms of Parkinson’s disease[2]. Tryptophan (TRP) is an essential amino acid with various physiological roles[3]. TRP is commonly synthesized in plants and microorganisms from shikimic acid[4]. The improper metabolite of TRP leads to abnormal levels of melatonin and serotonin. Thus, the brain serotonin level depends on the TRP level in our body. The improper metabolite of TRP causes hallucination, delusions, depression, Alzheimer’s and Parkinson’s diseases [5]. The present work aims to employ electrochemical method for the individual and simultaneous determination of LD and TRP at a new synthesized $Fe_3O_4@Sio_2$-GO nanoparticles modified screen printed electrode. The modified electrode was used successfully as an electrochemical sensor for simultaneous determination of LD and TRP in real sample as a sensitive, selective, simple and rapid method. The linear dynamic range using this novel nano sensor for LD and TRP were 0.5-1000 µM and 1-1000 µM respectively.

Keywords: *Levodopa. Tryptophan. $Fe_3O_4@Sio_2$-GO nanocomposite. Graphite screen-printed electrodes*

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Electrosynthesized ZnO/p-Type Conductive Polymer Nanocomposite with Enhanced Catalytic Activity of Methanol Oxidation in Alkaline Media

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Abstract

The direct methanol fuel cell (DMFC), as an effective power source, has been attracting considerable attention for several decades, due to its high efficiency, very low polluting emissions, potential renewability as a fuel source, simple operation and ease of storage. The slow kinetics of the methanol oxidation reaction and poisoning of active sites with residual intermediates are two major problems with respect to the commercialization of DMFCs. The success of fuel cell technology depends strongly on electrocatalysts, which can lower electrochemical over-potentials and produce high voltage outputs. Therefore, the design of a catalyst with improved electrode kinetics for methanol oxidation and enhanced efficiency, stability and durability is highly desirable [1-3].

Herein, we describe a simple and facile strategy for synthesis of nanocomposite of poly ortho aminophenol (POAP) and ZnO nanoparticles namely (POAP/ZnO). Electropolymerization of nanocomposite was carried out by cyclic voltammetry (CV) method from an electrolyte containing ortho aminophenol and ZnO nanoparticles. Surface morphology of the composite film was studied by surface microscopy techniques and the presence of ZnO in the films was confirmed by EDS analysis. Furthermore, the fractal dimension of nanocomposite films in the presence of counter ions was investigated. To elucidate the effect of ZnO on the property of POAP films, the electrochemical performance of composite films was evaluated by carrying out CV measurements in 0.1 M HCl. Close comparisons of CV curves between POAP/ZnO electrode and pure POAP electrode show that a POAP/ZnO electrode not only displays a higher background current in the potential sweep but also there exist faradic currents, which are believed to arise from the contribution of the loaded ZnO. The results indicate that a strong interaction exist at the interface of POAP and nano-ZnO. In comparison with a Ni-POAP electrode, a Ni- POAP/ZnO electrode shows a better catalytic performance for the electrocatalytic oxidation of methanol in alkaline solution.

The larger methanol response at the Ni- POAP/ZnO electrode with respect to the POAP electrode is proposed to be due to the Ni- POAP/ZnO enhancing the electrochemical activity of the Ni^{2+}/Ni^{3+} redox reaction through fine dispersion of the particles into the conductive polymer matrix, resulting in a drastic increase in surface area. It is observed that in the presence of ZnO nanoparticles current density of electro-oxidation of methanol is almost constant in 400 cycles due to the stability of electrocatalyst in this cycle number and indicating that methanol reacted with the surface and no poisoning effect on the surface was observed.

Keywords: *Electrosynthesis, Methanol oxidation, POAP, ZnO.*

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Electrosynthesis of Porous Cu-Based Metal-Organic Framework and Its Nanocomposite with p-Type Conductive Polymer as a Novel Electrode Material for Highly Capacitive Pseudocapacitors

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Abstract

Metal–organic frameworks (MOFs) are a new member in the vast field of porous materials. MOFs are attracting considerable attention because of their unique structural properties, such as high surface areas, tunable pore sizes, and open metal sites, which enable them to have potential applications in gas storage, catalysis, sensors, drug release, and separation [1,2]. Several preparation methods for the formation of MOFs have been developed throughout the years such as hydro- and solvothermal, ionothermal, microwave assisted, sonochemical, electrochemical, and mechanochemical syntheses [3,4]. Among the common methods to prepare of MOFs, the mechanochemical method is a most promising technique due to its simple procedure, ease of handing, high yield efficiency, high purity of products and very short reaction time.

In this work, we have electrosynthesized Cu(btec)$_{0.5}$DMF (H_4btec = 1,2,4,5-benzenetetracarboxylate acid) on the surface of graphite electrodes by applying a constant voltage to the solution of H_4btec, metal ions and $NaNO_3$. The electrosynthesized Cu(btec)$_{0.5}$DMF was characterized by X-ray diffraction and scanning electron microscopy. Furthermore, POAP/ Cu(btec)$_{0.5}$DMF nanocomposite film has been synthesised by using a simple and general strategy namely in situ electropolymerization on the surface of the working electrode. Different electrochemical methods including galvanostatic charge–discharge experiments, cyclic voltammetry and electrochemical impedance spectroscopy are carried out in order to investigate the performance of the system. The electrochemical behavior shows that the POAP/Cu(btec)$_{0.5}$DMF composites possess excellent electrochemical stability with 91% of its initial capacitance retained after 1000 charge/discharge cycles. The enhancement of electrochemical performance of the POAP/Cu(btec)$_{0.5}$DMF composite originate from the high specific surface area of Cu(btec)$_{0.5}$DMF.

Therefore, Cu(btec)$_{0.5}$DMF has an obvious improvement effect, which makes the composites have more active sites for faradic reaction and larger specific capacitance than pure POAP.

Keywords: *Electrosynthesis, Metal-organic framework, POAP, Pseudocapacitors.*

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Electrochemical determination of oxazepam drug using molecularly imprinted polymer modified carbon paste electrode

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Abstract

Determination of benzodiazepines in biological fluid is object of great interest for many scientists. Oxazepam is a short-to-intermediate benzodiazepine, which is used for the treatment of anxiety, insomnia and control of symptoms of alcohol withdrawal. In this research an electrochemical sensor based on carbon paste electrode (CPE) modified with molecularly imprinted polymer (MIP) for selective determination of Oxazepam was developed. The MIP particles were synthesized by precipitation polymerization method and characterized by scanning electron microscopy (SEM) and used for modification of CPE. The non-imprinted polymer (NIP) was synthesized using the same process as MIP but without template (Oxazepam). Oxazepam binding results indicated that the sensor modified by MIP had much higher adsorption ability than the NIP based sensor. Some parameters affected on the experimental results such as composition of electrode, extraction and analysis conditions were optimized using experimental design method. Under optimized conditions, Oxazepam peak current showed a linear relationship with its concentration in two linear range of 1.0×10^{-5} - 5.0×10^{-6} M (R^2=0.993) and 5.0×10^{-7} -3.5×10^{-8} M (R^2=0.994). The relative standard deviation for five measurements of Oxazepam solution by proposed method was obtained 3.35% and the limit of detection (LOD) was 1.45×10^{-8} M. The developed sensor was successfully used for determination of Oxazepam in tablet and human serum real samples.

Keywords: *Molecularly imprinted polymer, Microparticles, Electrochemical sensor, Oxazepam, Carbon paste electrodes.*

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Covalent functionalization of carbon nanotubes with safranin O for electrocatalytic determination of nitric oxide

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Abstract

In this research, we have demonstrated that *safranin O* (SAF) can be coupled to acid-treated multiwalled carbon nanotubes (MWNTs) in the presence of 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide (EDC) and N-hydroxysuccinimide (NHS) and assembled as SAF-MWNT composites. These functionalized MWNTs can be used for modification of glassy carbon electrode and applied for electrocatalytic determination of nitric oxide.

In a typical experiment, MWNTs were sonicated in ultrasonic bath for 2 h and refluxed in conc. nitric acid for 5 h. The black MWNTs suspension was filtered and then washed with doubly distilled water until neutral pH was reached. The treated MWNTs were dried at 80 °C and stored for further use. After that, SAF was covalently attached to the broken tips containing carboxylic acid groups of the MWNTs using water-soluble coupling agents EDC and NHS by forming amide linkages between the amine residue of SAF and carboxylic acid groups on the MWNTs. This was done by adding the carboxylated MWNTs (200 mg) into a freshly prepared 15 mL DMF solution of EDC (200 mg). After that, 500 mg of NHS was added to the solution. After 2 h, these MWNTs were filtered, washed and dried. After that, MWNTs was added to 200 mg SAF in KHP buffer solution. The reaction was allowed to complete at room temperature for 10 h and then the MWNTs were washed thoroughly with water and filtered. A glassy carbon electrode was modified with these functionalized MWNTs to cast 5 µL of a 1 mg/mL SAF-MWNT/nafion solution.

The results of voltammetric studies indicate that the carbon nanotube and safranin o system can enhance electrocatalytic activity toward the reduction of nitric oxide. Under the optimized conditions, in 0.1 M KHP buffer solution pH 1, the reduction current increased linearly in the range of 0.08 - 2.10 mM. The detection limit was 0.05 mM and RSD for 2 mM nitric oxide was 1.7 %.

***Keywords*: *Safranin O, Carbon nanotubes, Functionalization, Electrocatalysis*.**

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Determination of cobalt (II) with 1-(2-Pyridylazo)-2-naphthol modified carbon nano tube paste electrode in electrowinning solution of Sarcheshmeh-copper complex by stripping voltammetry

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Abstract

A method for the determination of cobalt(II) by stripping voltammetry using a carbon paste electrode constructed by incorporating 1-(2-pyridylazo)-2-naphthol(PAN) into a conventional carbon paste mixture composed of nano tube, graphite powder and Nujol oil has been developed. Several influencing factors for the determination of cobalt(II) were studied in detail and the optimum analytical conditions were found to be as follows: pH 2.5; composition of electrode, 20% and time of preconcentration 3 min. The calibration curve for cobalt(II) obtained by stripping voltammetry was linear range of 10-50 ppb. The effects of coexisting ions were also investigated to test the applicability of the proposed method to the determination of cobalt(II) in electrowinning solution of Sarcheshmeh-copper complex sampels.

Keywords: *Cobalt, Electrowinning, Sarcheshmeh-copper complex, Stripping voltammetry*

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Electrochemical sensor based on Carbon Ceramic Electrode modified by molecularly imprinted polymer nanoparticles for determination of Alprazolam drug

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Abstract

The determination of benzodiazepines in biological fluids has been a field of interest for many researchers. Alprazolam (ALP){8-chloro-1-methyl-6-phenyl-4H-s-triazol-o(4,3-a)(1,4) benzodiazepine } belongs to the class of benzodiazepine with anxiolytic, muscle relaxant, anticonvulsant properties which is generally used as a hypnotic and as a tranquilizer.

In this research, a selective and sensitive voltammetric sensor based on carbon ceramic electrode modified by molecularly imprinted polymer (MIP) nanoparticles for determination of alprazolam drug is developed.

The MIP nanoparticles were synthesized by suspension polymerization method and characterized by scanning electron microscopy (SEM). The non-imprinted polymer (NIP) nanoparticles were synthesized in a similar manner but in absence of alprazolam molecules. Then, the MIP nanoparticles were used as the recognition elements in construction of the sensor.

The determination of alprazolam after its extraction onto the electrode surface was carried out by square wave voltammetry (SWV) method. The results show that the nano-MIP modified carbon ceramic electrode (MIP-CCE) had much higher adsorption ability to alprazolam than the non-imprinted polymer carbon ceramic electrode (NIP-CCE).

The effect of some parameters on the sensor response, such as electrode composition, extraction and analysis conditions and electrochemical measurements conditions were studied. For optimization of parameters, Design Expert 7.0.0 software was used. Under optimized extraction and analysis conditions, Peak current showed a linear relationship with Alprazolam concentration, in the range of 7.0×10^{-9} to 5.0×10^{-7} M (R^2=0.998) with a detection

limit of 5.01×10^{-9} M. The repeatability of the developed sensor in terms of relative standard deviation was 3.83%. The developed sensor was successfully applied for determination of alprazolam in pharmaceutical formulation and human serum samples.

Keywords: *Electrochemical sensor, Molecularly imprinted polymer, Nanoparticles, Carbon ceramic electrode, Alprazolam.*

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Phosphine-Functionalized Graphene Oxide, A High Performance Electrocatalyst for Oxygen Reduction Reaction

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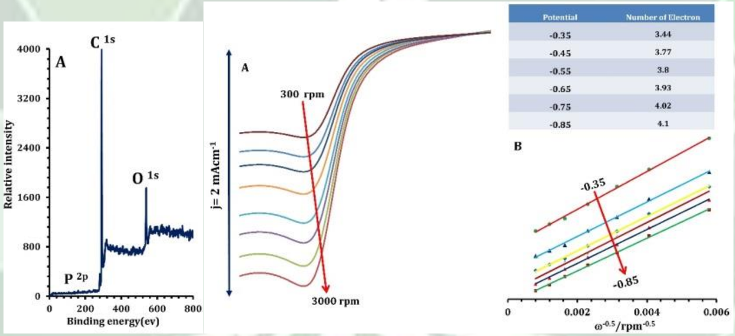
Abstract

Recent interests in generating a sustainable energy economy have given much interest to the concept of the hydrogen economy[1]. Fuel cells have drawn substantial interest as energy production devices, due to their potentials in low pollution output and high theoretical energy densities. Proton exchange membrane fuel cells (PEMFCs) are, arguably, the most commercialized fuel cells, but one of the key practical challenge for PEMFCs is the slow cathodic kinetics of oxygen reduction reaction (ORR) at the cathode that reduces the performance of fuel cells. Another major challenge is the high cost of Platinum based catalysts. Also platinum can suffer from strong adsorption of carbon monoxide (CO) at the platinum surface and blocking the active sites, so dictating the use of highly purified hydrogen sources. Among the various alternatives for Pt-based catalyst, carbon-based materials are of great interest as non-precious metal catalysts for the ORR due to their relatively high activity and superior stability[2].

Here, a novel approach for the preparation of phosphine-functionalized graphene oxide (GO-PPh_2) is developed. Using a simple method, diphenylphosphine group was linked to the hydroxyl group of OH-functionalized graphene. The GO-PPh_2 catalyst was characterized using some different microscopic and spectroscopic techniques including XPS, XRD, TGA, SEM and FT-IR analysis. The electrocatalytic activities of GO-PPh_2, rGO, and Pt/C toward the ORR were studied using linear sweep voltammetry (LSV) in N_2 and O_2 saturated 0.1 mol L^{-1} KOH solution, from +0.20 V to –0.60 V vs. Ag/AgCl and at a scan rate of 10 mV s^{-1} for GO-PPh_2, rGO, and Pt/C catalysts displayed featureless curves in N_2-saturated solution. On the other hand, the LSV curves present a well-defined ORR peak in O_2-saturated solution for proposed electrocatalysts, which demonstrate the good electrocatalytic activity of GO-PPh_2 in comparison with unmodified glassy carbon electrode and rGO modified glassy carbon electrode catalyst toward the ORR. For

investigation the number of electron at different potential (from –0.3 to –0.8 V), the slopes remain nearly constant, which confirms that at the different electrode potentials, numbers of the electron transfer for reduction of oxygen are analogous. Based on the K–L equation, the calculated n was 3.83 for GO-PPh_2 (closing to $4e^-$ pathway) and 2.27 for rGO. These results confirm that the ORR activity of GO-PPh_2 follows the 4-electron transfer pathway. The electrocatalytic activity of GO-PPh_2 in ORR vs. the electrooxidation of methanol was studied. After addition of methanol into the O_2-saturated solution for Pt-rGO, a large current from the oxidation of methanol was observed. On the other hand, with GO-PPh_2 electrode at the same conditions, no significant difference between the peak currents can be observed, with and without methanol. From these results, it is suggested that GO-PPh_2 is free from methanol poisoning.

So the modified electrode exhibit a high selectivity for ORR in a nearly 4e transferred per O_2 molecule, with a remarkable tolerance to crossover effects compared to platinum nanoparticle decorate on reduce graphene oxide (Pt/rGO) and they have good durability over the several hours. Therefore GO-PPh_2 is convenient electrocatalyst for its further applications in fuel cells.



Potential	Number of Electron
-0.35	3.44
-0.45	3.77
-0.55	3.8
-0.65	3.93
-0.75	4.02
-0.85	4.1

Figure. (Left) Survey XPS data for GO-PPh_2; (Right) (A) The GO-PPh_2 LSV curves of ORR of modified GCE obtained at different rotating rates; (B) K-L plots of current reciprocal ($-i^{-1}$) versus $\omega^{-1/2}$ at different potential on GO-PPh_2 modified GCE.

***Keywords**: Graphene Oxide, Phosphine-Functionalized, Oxygen Reduction Reaction, Electrocatalyst.*

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Fabrication of WO_3/MWCNT/graphite nanocomposite as a novel electrode in vanadium redox flow battery

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Abstract

The need for grid-connected energy storage systems will grow worldwide in the next future due to the expansion of intermittent renewable energy sources and the inherent request for services of power quality and energy management. Electrochemical storage systems will be a solution of choice in many applications because of their localization flexibility, efficiency, scalability and other appealing features. Among them redox flow batteries (RFBs) exhibit very high potential for several reasons, including power/energy independent sizing, high efficiency, room temperature operation, and extremely long charge/discharge cycle life. RFB technologies make use of different metal ion couples as reacting species. The best-researched and already commercially exploited types are vanadium redox flow batteries (VRFBs) [1]. One of the typical electrode materials for VRFB is graphite felt. The advantages of this material are its suitable porosity, high surface area, wide operation potential range, and low cost. However, graphite felt still show poor kinetic reversibility. Considerable studies on the modification of the electrode materials have been carried out to enhance their electrochemical performance; those methods include ion exchange, heat or acid treatment, electrochemical oxidation, metal deposition, etc [2].

The present work describes the preparation and electrochemical characterization of WO_3/MWCNT/graphite electrode as compared with a graphite electrode for VRFB application. Multi-walled carbon nanotubes (MWCNTs) has been introduced as a new electrode material for VRFBs because of its large reactive surface area, high stability in acidic solutions and relatively low cost [3]. It has been known that electrode based WO_3 possess excellent electro-catalytic activity and reversibility because of its facile preparation, stable in sulfuric acid and low cost compared to other metal oxides like IrO_2 or RuO_2, which used to be employed as VRFB electrode materials [2]. The WO_3/MWCNT/graphite electrodes were prepared by electrochemical

reduction of functionalized multi-walled carbon nanotubes (fMWCNTs) and $W_2O_{11}^{-2}$ onto graphite electrode. The electrochemical characterization of prepared electrode was carried out using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and chronopotentiometry (CHP) procedures. Results show that WO_3/MWCNT/graphite exhibits excellent electro-catalytic activity and kinetic reversibility toward the vanadium redox couples.

As can be seen from Fig. 1, there are significant differences in the peak potentials (E_{pa} and E_{pc}) and peak currents (I_{pa} and I_{pc}) values, which reflect substantial differences in the electrochemical performance, by adding the WO_3/MWCNT, the charge transfer resistances for both the positive and the negative reactions are significantly reduced. These good electrochemical results, together with the long term stability of the prepared electrode, represent a significant step forward in the development of highly effective electrode materials for VRFBs. Also characterization of the graphite, MWCNT/graphite, WO_3/graphite and WO_3/MWCNT/graphite was carried out by FT-IR spectra in Fig. 2. The broad absorption peaks in the range 500–1000 cm^{-1} are characteristic of the different O-W-O stretching vibrations in the WO_3 crystal lattice.

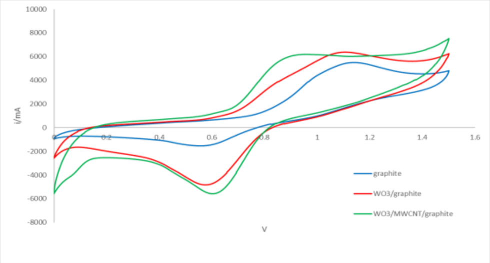

Fig. 1. Cyclic voltammogram of the graphite electrode compared to the WO_3/graphite electrode and the WO_3/MWCNT/graphite electrode in 0.14 M $(VO)^{2+}$ + 2 M H_2SO_4 at a scan rate of 20 mV s^{-1}.

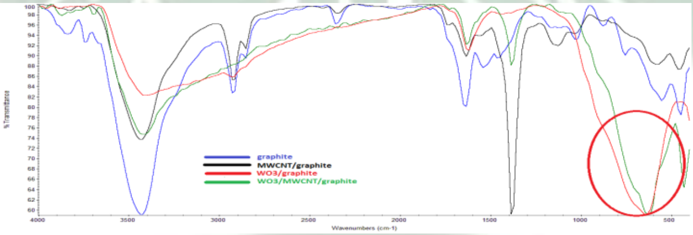

Fig. 2. FTIR spectra of graphite, MWCNT/graphite, WO_3/graphite and WO_3/MWCNT/graphite

Keywords: *Fabrication, Nanocomposite, Novel Electrode, Vanadium Redox Flow Battery*

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Preparation of Carbon-Ceramic Electrode Modified with Multiwalled Carbon Nanotubes (MWCNTs) and its Application in Simultaneous Determination of Mefenamic Acid and Acetaminophen in Pharmaceutical Preparations and Biological Samples

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Abstract

Drug analysis is essential in various stages of drug design and development, such as formulation, quality control stability studies, pharmacokinetics and pharmacodynamics, pre clinical and clinical trials. Mefenamic acid (MEF, 2-[(2,3-dimethylphenyl) amino] benzoicacid) is a non-steroidal anti-inflammatory drug with anti-inflammatory, analgesic and antipyretic properties. It is extensively used in the treatment of many diseases like rheumatoidarthritis, osteoarthrits, nonarticular rheumatism and sport injuries. Acetaminophen(paracetamol) (N-acetyl-p-aminophenol) is a popular, antipyretic and non-steroidal anti-inflammatory drug.

Combinations of MEF and ACT are frequently prescribed for analgesic and anti-inflammatory use in rheumatoid arthritis. Accordingly determination of the levels of these present in pharmaceuticals is of considerable importance, to prevent overdoses leading to toxic effects. Electrochemical analysis offers a number of important advantages over traditional chemical analyses for providing information on drug analysis and its metabolic fate in vivo, redox processes and pharmacological activity. So, the carbon-ceramic electrode was modified by multiwalled carbon nanotubes (MWCNTs) by drop casting of suspension of carbon nanotubes in dimethylformamide (DMF). The surface morphology and interfacial properties of the modified electrode was characterized by scanning electron microscopy (SEM) and electrochemical impedance spectroscopy techniques, respectively. This modified electrode was applied for electrochemical behavior study and simultaneous determination of acetaminophen and mefenamic acid. Cyclic voltammetry experiments showed two well defined, resolved and sensitive peaks for acetaminophen and mefenamic acid compared with bare electrode. So, the

experimental parameters which affect the analytical performance of modified electrode towards acetaminophen and Mefenamic acid were optimized. After that the calibration graphs were constructed for analytes by simultaneous increasing of them concentration in the range of 0.08-3 μM and 0.1-3.5 μM with the detection limit of 0.073 μM and 0.09 μM by differential pulse voltammetry for acetaminophen and Mefenamic acid, respectively. Lastly, the modified electrode was used for simultaneous determination of acetaminophen and mefenamic acid in some pharmaceutical and urine samples with satisfactory discovery percents.

Keywords**:** *Multiwalled carbon nanotubes, Acetaminophen, Mefenamic acid, Simultaneous electrochemical determination, Carbon-ceramic electrode.*

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Well-regulated synthesis of conductive polymer by bipolar electrochemistry: an effective substrate for enzyme immobilization toward oxygen reduction reaction

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Abstract

Optimizing the electrical connection between enzymes and electrodes surface is critical in the development of biosensors, enzymatic biofuel cells, and other bioelectrocatalytic applications. There are some limitation to achieve those aims, therefore introducing of suitable support for enzyme immobilization was used to overcome this limitation [1]. A variety of materials including metals, alloys, inorganic substances polymers and composites are used to modify the surface of electrodes for enzyme attachment. Conducting polymers (CPs) based on the macromolecular systems have been used for many application areas such as electrochromic devices, energy storage, and biotechnology in material science. In view of their attractive properties, CPs are promising candidates for biomolecule immobilization in biosensing and biofuel cell systems [2]. Electrochemically synthesis of polymer films is a suitable way for adjusting the surface of electrodes to produce functionalized CPs with enhanced controlling the film thickness and morphology even at a micro /nanoscale substrate [3].

Bipolar electrochemistry (BPE) has been recently explored for the modification of various conductive substrates. The BPE features particular advantages compared to conventional electrochemistry especially in a simple setup, which involve one direct current (DC) power supply, low cost, ease of setup, no direct electrical connection is required and many electrodes can be controlled simultaneously with a single DC power supply [4]. Here we report the electropolymerization of 3-thiophenecarboxcylic acid on the suitable support such as Au by bipolar electrochemistry method, which provide polymer functional groups on surface of the support. The synthesized polymer film on the Au support shows preferable substrate for

immobilization of bilirubin oxidase enzyme. The resulting polymer films were characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), and electrochemical impedance spectroscopy. The prepared bioelectrodes as novel system were characterized by voltammetric techniques such as cyclic voltammetry in order to investigate its electrocatalytic activity for oxygen reduction reaction (ORR) and calculate kinetics parameters. The onset potential and the magnitude of current density for oxygen reduction on the modified electrode were 0.55 V (vs. Ag/AgCl) and 967 μA cm^{-2}, respectively. Furthermore, the electrocatalytic performance of the proposed system toward ORR was better than the immobilized bilirubin oxidase enzyme on synthesized poly -3-thiophenecarboxcylic by conventional three-electrode system.

***Keywords*:** *enzyme immobilization, modified electrode, bipolar electrochemistry, electropolymerization.*

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Investigation of Electrochemical Performance of NiO Nano Rods/Plates Prepared by Cathodic Electrochemical Deposition—Heat-treatment (CED-HT) Method

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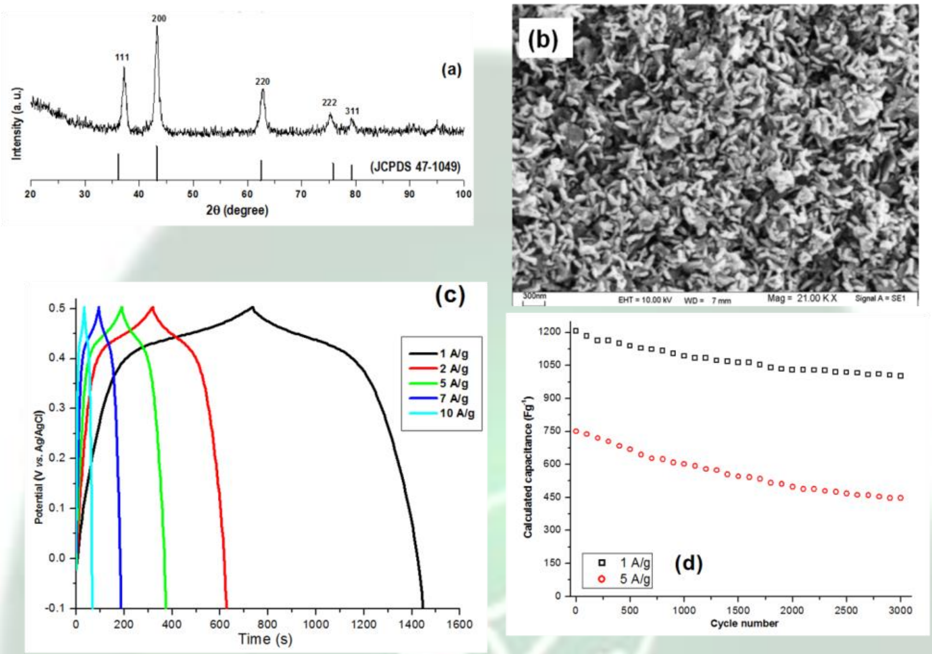
Abstract

In pseudocapacitors, the structure of electrode materials plays an important role in determining the electrolyte accessibility and electrode stability, and thus the device performance. To this end, extensive research efforts have been devoted to the control of structures of NiO electrode materials. Uniform NiO structures in a variety of forms, such as nanocapsules and nanoparticles have been found that exhibit superior supercapacitive performance [1,2]. Up now, nanostructured NiO has been produced by electrochemical deposition (ED) methods including anodic and cathodic routes. In this research, cathodic electrochemical deposition-heat treatment (CED-HT) was used as an effective method for synthesis of nanostructured NiO. In this way, nickel hydroxide precursor was first deposited through CED step. Then, the final oxide was obtained by applying the HT procedure. The structural and morphological evaluations by XRD and SEM revealed that the prepared oxide has crystalline NiO structure (Fig. 1a) with mixed rod/plate texture at nanoscale (Fig. 1b). The supercapacitive performance of the prepared NiO nanoplates/rods was studied by techniques of cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) within the potential window of -0.1 to 0.5V in 1 M KOH electrolyte. The measurements (Figs. 1c and d) revealed that the prepared sample have high reversibility (ΔE_p =15 mV), high specific capacitance (1265 F g^{-1} at 1 A g^{-1}) and proper long-term cycling stability of 92.4% capacity retention after 3000 cycling at the current density of 1 A g^{-1}.



Keywords*: NiO, Nano-plates/rods, electrochemical synthesis, Heat-treatment, Electrochemical performance

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Preparation, Characterization and Study of Charge Storage Ability of Nanostructured Co_3O_4

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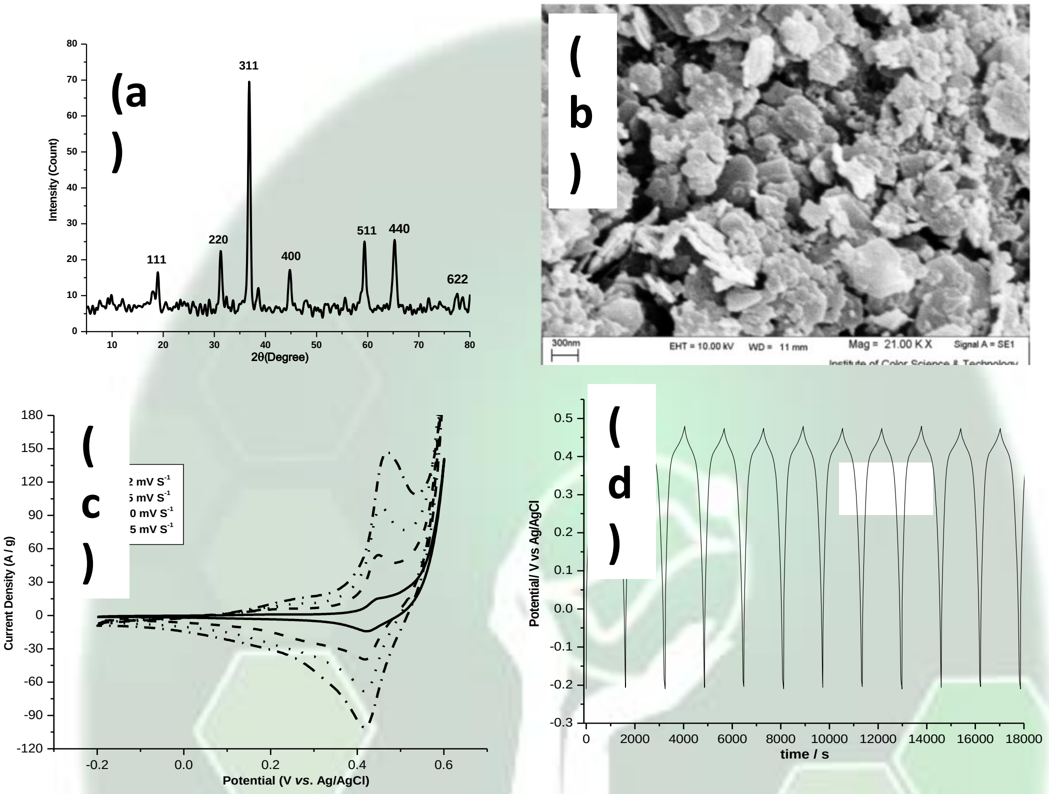
Abstract

Research has revealed that sheet- or plate-like structures can very well improve the supercapacitive behavior of Co_3O_4 as the electrode material [1,2]. These nanostructures possess large material–electrolyte interface areas, increased electrolyte penetration into the electroactive materials, large inter-sheet spacings for the rapid ions transport, large surface areas for better electrochemical reactions, and high utilization of the electrode materials. In this research, cathodic electrodeposition followed by heat-treatment, was applied as a powerful technique for the preparation of nanostructured Co_3O_4 with particular characteristics. In this two-step route, cobalt hydroxide ($Co(OH)_2$) is first electrodeposited via pulse base (OH^-) electrogeneration from a nitrate bath and the product of this step was heat-treated under a proper atmosphere and temperature to yield cobalt oxide. The structural and morphological evaluations by XRD and SEM revealed that the prepared oxide has crystalline Co_3O_4 structure (Fig. 1a) with plate morphology (Fig. 1b). The supercapacitive performance of the Co_3O_4 was also studied by cyclic voltammetry (CV) and charge-discharge cycling as shown in Figs. 1c and d. The results showed that the prepared Co_3O_4 nanoplates are capable to deliver specific capacitance as high as 565 F g^{-1} at the scan rate of 2 mV s^{-1}) and excellent long-term cycling stability of 89.1% capacity retention after 3000 cycling.



Keywords: *Co_3O_4, Nano-plates, Pulse Electrosynthesis, Heat-treatment, Supercapacitive performance*

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Application of NiO/CNTs nanocomposite ionic liquid paste electrode as a voltammetric sensor for determination of ascorbic acid in fruit juices samples

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Abstract

Ascorbic acid (AA), as a water soluble vitamin, is an effective reducing agent and a powerful antioxidant in food, preventing color changes and alterations of aroma and flavor as well as extending the storage time of the products. So, determination of AA is very important in food samples [1]. In this study, a simple and rapid analytical method developed for ascorbic acid (AA) determination in fruit juices by using square wave voltammetry (SWV) method using NiO/CNTs nanocomposite ionic liquid modified carbon paste electrode as a sensor. Important parameters such as NiO/CNTs nanocomposite ratio, ionic liquid ratio and pH, have been optimized in this work. The cyclic voltammogram showed an irreversible oxidation peak at 0.4 V (vs. $Ag/AgCl_{sat}$), which corresponded to the oxidation of AA. Compared to common carbon paste electrode, the electrochemical response was greatly improved. Under the optimized conditions, the oxidation peak current of AA showed linear dynamic range 0.09–800.0 μ mol l^{-1} with a detection limit of 0.05 μmol L^{-1}, using the SWV method. The proposed sensor was successfully applied to the determination of AA in fruit juices without previous preparation and was compared with a published electrochemical method

Keywords**:** *Fruit juices analysis, Ascorbic acid, Voltammetry, Ionic liquid NiO/CNTs nanocomposite*

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Starch-assisted Electrochemical Synthesis of Uniform Cobalt Hydroxide Nanoplates as High Performance Electrode Material for Supercapacitors

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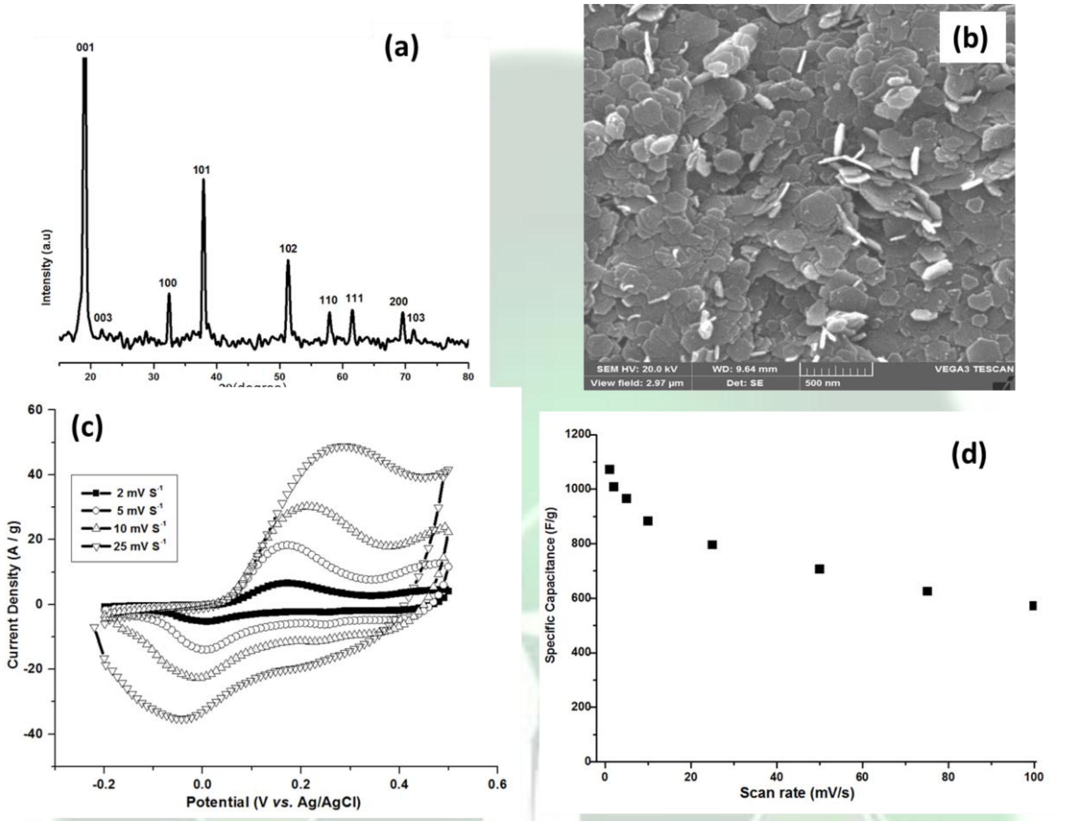
Abstract

Two-dimensional nanoplates or nanosheets possess interesting properties because of their high anisotropy and ultra-thickness [1]. Nanoplates are considered as ideal systems for the investigation of dimensionally confined transport phenomena and as the ideal bases upon which to build functional devices [2]. Therefore, it would be interesting to develop new methods for the synthesis of nanoplates of a variety of compounds. $Co(OH)_2$ materials have been attractive in view of their layered structure with large interlayer spacing, their well-defined electrochemical redox activity, and the possibility of enhanced performance through different preparative methods. An emerging application of $Co(OH)_2$ is an electrode material for electrochemical supercapacitors [3]. In this research, cathodic electrodeposition of cobalt hydroxide was performed in the presence of starch. The prepared sample was characterized through XRD, IR, DSC-TGA, SEM and cyclic voltammetry. The analyses results revealed that the deposited hydroxide has pure crystalline β cobalt hydroxide composition with uniform hexagonal plate morphology at nanoscale (Figs. 1a and b). The supercapacitive performance of the prepared nanoplates was also investigated by cyclic voltammetry (CV) as shown in Figs. 1c and d. The results showed that the prepared β-$Co(OH)_2$ nanoplates exhibit excellent charge storage ability (SC= 1015 F g^{-1} at the scan rate of 5 mV s^{-1}).



Keywords: β-*Co(OH)$_2$, Nanoplates, Electrodeposition, Supercapacitive performance*

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A simple and efficient nano-structured gold film sensor for gallic acid electrochemical determination

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Abstract

A straightforward, rapid and “green” approach was proposed for the fabrication of gold nonporous film. A gold electrode was firstly oxidized under a high potential of 5 V, and ascorbic acid, as a nontoxic reducing agent, was then chosen to reduce the gold oxide. This process gives a fractal gold nonporous film on the top of the gold electrode in a way of completely “green” chemistry. The nanostructure modified electrode greatly facilitates the electrochemical oxidation of Gallic acid (GA). As the gold nonporous film was formed in situ on the gold electrode, additional immobilization procedures are not necessary. A sensitive sensor can be easily developed for the detection of GA. In the present study, the oxidation peak current of the GA in a 0.10 M phosphate buffer solution was optimized for its determination by the differential pulse voltammetry method. The variables which optimized include scan rate, step potential, and pH. Then, under the optimized conditions the dynamic range for GA 41 µM to 150 µM and the detection limit was found to be 1.2 nM. Cyclic voltammetry and other electrochemical methods such as chronocoulometry, was used to investigate the electrochemical behavior of Gallic acid on the gold nano-structured modified electrode. Using these methods, the diffusion coefficient (D = 1.03 × 10^{-4} cm2 s−1) and the kinetic parameters such as the electron transfer coefficient (α = 0.55) and exchanging current density ($j0$ = 4.28 µA cm−2) for GA were determined. The number of proton and electron transfer for the oxidation of GA was investigated to be two protons and two electrons.

Keywords: *Gold nano-structured film, Gallic acid (GA), electro catalysis, Cyclic voltammetry*

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Comparison of degradation of an environmental pollutants by nanophotocatalysts pure ZnO and ZnO doped Mg metal in aqueous solutions by UV light

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Abstract

ZnO doped Mg and pure ZnO nanoparticles were successfully synthesized by sedimentary method . The products were characterized by XRD and TEM.. XRD patterns showed that the doped nanoparticles had the same crystals structures as the pure ZnO nanoparticles .ZnO doped Mg nanoparticles had larger lattice volume than the pure nanoparticles.

The photocatalytic degradation of indole 3- butyric acid in aqueous solutions was investigated by both pure and ZnO doped Mg under UV light irradiation in this study. In this study the effect of different parameters such as indole 3- butyric acid concentration, photocatalyst amount, PH ,Oxidant concentration ,degradation of I-3BA and optimum condition was obtained.

Key words: *ZnO doped Mg, nanoparticles ,photocatalyst , photocatalytic degradation , indole 3-butyric acid*

Electrochemical Synthesis of PEI/PVP Coated Superparamagnetic Iron Oxide Nanoparticles for Biomedical Applications

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Abstract

In the recent decade, there has been a considerable development of magnetite nanoparticles (MNPs) for biomedical applications like magnetic carriers for drug delivery and targeting supported by external magnetic fields, magnetic resonance imaging (MRI) contrast agents for clinical diagnosis, cancer therapy compounds for hyperthermia, etc. [1-3]. Superparamagnetic Fe_3O_4 nanoparticles double coated with poly(vinylpyrrolidone)/polyethylene imine polymers were successfully fabricated through cathodic electrochemical deposition. In this method, in situ polymer coating of the surface of Fe_3O_4 nanoparticles was achieved through electrodeposition process. The evaluation by XRD analysis confirmed that the electrodeposited nanoparticles are composed of pure phase of iron oxide i.e. magnetite (Fe_3O_4). The structure and composition of the prepared nanoparticles were characterized by SEM, TEM, DLS, XRD, FTIR, and TG analyses. The DLS analysis revealed that the bare and prepared polymer coated Fe_3O_4 nanoparticles have size of 20 nm and 72 nm, respectively. The polymer coated nanoparticles with having 15 nm in size, suitable magnetization value (Ms=25 emu/g), and negligible coercivity (Ce=0.62 emu/g) and remanence (Mr=1.5 Oe) are proper candidate for biomedical applications. This electrochemical strategy is proposed as facile and efficient route for preparation of polymer coated Fe_3O_4 nanoparticles.

Keywords: *Magnetite, Electrochemical deposition, Polymer coating, Biomedical Applications*

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Electrosynthesis of PEG/PEI Coated Fe_3O_4 Nanoparticles for Biomedical Applications

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Abstract

Recently, increased investigations with several types of iron oxides have been carried out in the field of magnetic nanoparticles (NPs) mostly includes magnetite (Fe_3O_4, superparamagnetic when the size is less than 15 nm), hematite (α-Fe_2O_3), maghemite (γ-Fe_2O_3) [1]. Among them, magnetite is the very promising and popular candidates [2]. However, it is a technological challenge to control size, shape, stability, and dispersibility of NPs in desired solvents. Magnetite NPs have a large surface-to volume ratio and therefore possess high surface energies. Consequently, they tend to aggregate so as to minimize the surface energies. Moreover, they have high chemical activity, and are easily oxidized in air, generally resulting in loss of magnetism and dispersibility. Therefore, providing effective coating strategies and developing novel synthetic methods to prepare stable monodisperse iron oxide NPs is very important. Herein, we report preparation of naked and polymer coated Fe_3O_4 nanoparticles by an effective electrochemical method. In this way, in a two-electrode system and using base electrogeneration on the cathode surface, pure magnetite phase of iron oxide and also double coated with polyethylene glycol/polyethyleneimine polymers were successfully electrodeposited on the cathode surface. The structure and composition of the prepared nanoparticles were identified by SEM, TEM, DLS, XRD, FTIR, and TG analyses. The PEG/PEI coat on the surface of Fe_3O_4 nanoparticles was confirmed by IR and TG data. The superparamagnetic properties of the prepared nanoparticles were characterized through VSM data.

Keywords: *Fe_3O_4, Electrochemical synthesis, Polymer coating, Biomedical applications*

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Enhancement of the corrosion protection performance, cathodic disbanding resistance and adhesion properties of epoxy coating through treatment of steel substrate by Nano structured vanadium-based conversion coating In the presence of Ni ions

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Abstract

Corrosion resistance of the mild steel must be improved before any outdoor applications by various techniques such as cathodic/anodic protection, coatings, surface treatments, inhibitors and application of anti-corrosion pigments. It is known that chemical conversion coatings are one of the most cost-effective methods of surface modification. They facilitate bond formation between the substrate and the organic coating together with improving corrosion resistance. Hence, in this study nanostructured vanadium conversion coatings were deposited on the surface of mild steel(st 37) on the basis of vanadium (VCC) and vanadium-Nickel (VNiCC) based conversion coating solutions. An epoxy/polyamine coating was then applied on the VCC and VNiCC substrates. The surface characterization was performed by field emission scanning electron microscope (FE-SEM) and atomic force microscopy (AFM) measuring device. The adhesion strengths of the epoxy coatings applied on the surface treated samples were measured before and after 30 days of immersion in 3.5 wt.% NaCl solution by a pull-off test. In addition, The effect of VCC and VNiCC treatment on the epoxy coating performance was studied by electrochemical impedance spectroscopy (EIS) and cathodic disbonding (CD) tests. FE-SEM and AFM study show that the VNiCC is denser, More continuous and more surface roughness than VCC. The dry and recovery (adhesion strength after 30 days immersion in the 3.5 wt% NaCl solution) adhesion strengths of

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2- Professor, Polymer Eng. and Color Tech., Amirkabir University of Technology, Tehran the coatings applied on the VNiCC samples were greater than VCC sample. In addition, the adhesion loss of the coating applied on the VNiCC substrate was lower than other samples. Also, the results obtained from EIS and cathodic disbonding test clearly revealed that the VNiCC could enhance the corrosion protective performance and reduced cathodic disbonding of the epoxy coating than other samples.

Keywords**:** *Nano structured vanadium-based conversion coating, Nickel, Corrosion resistance, Epoxy coating, cathodic disbanding, FE-SEM/AFM*

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Facile synthesis of nickel nanoparticles supported on porous silicon flour for non-enzymatic glucose sensing

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Abstract

In this study, a non-enzymatic amperometric sensor is fabricated for glucose detection based on nickel nanoparticles supported on porous silicon flour. A facile procedure was introduced for the in-situ electroless assembling of nickel nanoparticles on porous silicon (PS) flour without using any reducing agent.The formation of the Ni@PS nanocomposite was confirmed by scanning electron microscopy (SEM), X-ray diffraction spectroscopy (XRD), energy dispersive spectroscopy (EDS) and FT-IR spectroscopy as well as cyclic voltammetry (CV). The synthesized nanocomposite was employed as an electrode material for non-enzymatic glucose (Gl) sensing using carbon paste electrode (CPE). The prepared amperometric sensor exhibited excellent applicability of the proposed sensor for determination of Gl in human blood serum with good accuracy and reproducibility.

Keywords: *Nickel nanoparticles, Porous silicon, Glucose, Non-enzymatic sensor.*

Introduction

In recent years, considerable research studies have been devoted to the nanostructured materials due to their extensive applications in different fields of science and technology. Therefore, economical and efficient synthesis of these materials is attractive. Among various nanomaterials, Ni nanoparticles have a great potential for application in many fields such as glucose sensing. In the current study, we have used porous silicon to develop a simple method to synthesize Ni nanoparticles. In this way, Ni nanoparticles were loaded on PS (Ni@PS) by a simple in-situ redox reaction.

Results and discussion

The synthesis of PS was done according to our previous work. Briefly, 1.0 g of commercially available Si-powder was dispersed in 100 mL of an etching solution, which consisted of HF 48% (8 mL), HNO_3 70% (2 mL) and H_2O (90 mL). After mild stirring for about 10 min, it was observed that the initial gray color of the silicon powder altered to brown, which confirms that PS has been formed. To synthesis Ni@PS nanocomposite, 0.25 g of PS was dispersed in a solution containing 0.05 mol L^{-1} nickel sulfate and 0.1 mol L^{-1} of ammonium fluoride and stirred for one hour.The modified carbon paste electrode was fabricated by hand mixing of 300 mg paraffin oil, 600 mg graphite powder and 100 mg Ni@PS nanocomposite in an agate mortar and packing into a plastic syringe. The concentration of OH^- and applied potential for amperometric sensor were optimized. The results showed that the 0.1 mmol L^{-1} NaOH and 0.55 V were appropriate. The prepared amperometric sensor exhibited a wide linear range of 2.0 – 5000 µmol L^{-1} with a low limit of detection (0.2 µmol L^{-1}) as well as high stability and fast response time (< 3 s). Also, no significant interference was observed from potentially interference species such as dopamine, ascorbic acid, uric acid and Cl^- ions. The excellent applicability of the proposed sensor for determination of Gl in human blood serum with good accuracy and reproducibility made Ni@PS nanocomposite promising for the development of effective electrochemical non-enzymatic Gl sensor.

Conclusion

In this paper, a facile approach was introduced to synthesis nickel nanoparticles on a porous silicon support. The resulting nanostructure was characterized with different techniques such as SEM, XRD, EDS, FT–IR and CV. The obtained nanoparticles showed good stability as well as high electrocatalytic activity toward Gl oxidation.

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Electrochemical sensor based on porous silicon/silver nanocomposite for the determination of hydrogen peroxide

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Abstract

Sensitive and selective determination of H_2O_2 is of great significance in biological, clinical and environmental and many other fields. Among several analytical techniques that have been employed for the determination of H_2O_2, electrochemical methods have received significant importance due to their low detections limit, high selectivity and sensitivity [1]. Because electrochemical reduction of H_2O_2 with the conventional electrodes is not effective for analytical application, surface modification of the electrode is necessary and important [2]. Recent studies have shown that surface modification with metal nanoparticles exhibit good synergetic effect on H_2O_2 reduction.

Because of the unique properties of porous silicon (PSi) such as high specific surface area, high tendency for oxidation/reduction reaction and capability for surface functionalization, it was chosen suitable substrate for decoration of metal nanoparticles. PSi is a porous medium, which can be easily produced by chemical etching of silicon in HF solution [3]. PSi has many applications in the field of chemical sensors and biosensors [4].

In this work, a porous silicon/silver nanocomposite was prepared and used as a modifier in carbon paste electrode, as an electrochemical sensor for the determination of hydrogen peroxide (H_2O_2). By using a simple and fast galvanic replacement reaction between Si atoms in the porous silicon and silver cation in aqueous HF solution, silver nanoparticles were decorated on the porous silicon without using any reducing agent. This novel nanocomposite was characterized by means of X-ray diffraction, scanning electron microscopy, Fourier transform infrared spectroscopy and cyclic voltammetry. The modified car-bon paste electrode was used to study the reduction of H_2O_2 in 0.1 mol L^{-1}phosphate buffer solution (pH 7.0). Moreover, chronoamperometery was used for determination of H_2O_2at the applied potential of -0.45 V (vs.

Ag/AgCl). The sensor has a linear response range of 1.65 μmol L^{-1} -0.5 mmol $L^{-1}$with a detection limit of 0.45 μmol L^{-1} H_2O_2. The electrochemical sensor showed fast and selective responses to H_2O_2 concentration. The applicability of the sensor was checked using real samples with satisfactory results.

Keywords: *Hydrogen peroxide detection, Porous silicon/silver nanocomposite, synergetic effect, electrochemical sensor, Amperometry*

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Green Synthesis of Gold Nanoparticles for Fabrication of an Electrochemical Sensor Sensitive to Nitrophenial based on Graphene Nanoplatelets/Gold Nanoparticles

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Abstract

Synthesis of chemical compounds using environmentally friendly materials is the goal of green chemistry. In recent years use of planets as stable and available sources to prepare metal nanoparticles has more attention for researchers. Synthesized nanoparticles using the aim of green reagents can be used in the bio application such as fabrication of electrochemical sensors [1]. In this regard, gold nanoparticles (AuNPs) due to unique properties such as high conductivity, high surface area and electro catalytic properties recently used in the fabrication of optic and electrochemical sensors [2]. Analysis of nitrophenols in natural water resources is an important indicator to quality control of water. 4-Nitrophenol (4-NP) is one of the hazardous chemicals in contaminate list of environmental protection agenay (EPA) duo to its stability and poisonous. Respiration or eating of 4-NP in the short period causes hard headache and drowsy, nausea and dark blue skin. In addition 4-NP was reported as cancerous tratogen and tagen so its application should be under control [3]. So, monitoring of 4-NP in water resources using a sensitive and selective electrochemical sensor is highly interested. In this work, a novel method is presented for green synthesis of AuNPs using extracted *E.* tereticornis leaves as the reducing agent in the presence of $HAuCl_4$ in ambient temperature. The synthesized AuNPs was mixed with graphene nanoplatelets (GNPs) under sonication to form a homogeneous nanocomposite (AuNPs/GNPs). Characterization of the nanocomposite using UV-Visible spectroscopy, Fourier transform infrared spectroscopy (FTIR), and field emission scanning electron microscopy coupled with energy dispersive spectroscopy (FESEM-EDS) showed a homogeneous distribution of AuNPs nanoparticles on GNPs sheets. Due to synergetic effect of good electrocatalytic properties as well as conductive nature of AuNPs microspheres and large surface area with high

conductivity of GNPs, the synthesized nanocomposite was drop casted on the surface of glassy carbon electrode and used as an electrochemical sensor (AuNPs/GNPs/GCE) for determination of 4-NP using differential pulse anodic stripping voltammetry. Under optimal conditions of phosphate buffer (0.01 M, pH 4.0), scan rate of 0.05 V/s, drop casting volume of 10 □L and nanocomposite ratio (AuNPs/GNPs) of 5 (V/V), differential pulse voltammetry of 4-NP showed an oxidation peak at around 0.025 V due to exchange of 2 electrons and protons. The fabricated sensor has good potential for determination of 4-NP in lake water, reverse osmosis drink water and natural mineral water with satisfactory results.

***Keywords*:** Gold nanoparticles, Graphene nanoplatelets, 4-Nitrophenol, Electrochemical sensors, Water.

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Investigation of the oxygen reduction reaction on palladium nanoparticles decorated chlorine doped RGO in alkaline media

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Abstract

The oxygen reduction reaction (ORR) on Pd nanoparticles decorated chlorine doped reduced graphene oxide (Pd/Cl-RGO) electrocatalyst have been investigated in alkaline media. Pd is a promising alternative to the expensive platinum. The surface morphology of prepared materials (RGO, Cl-RGO and Pd/Cl-RGO) is studied by transmission electron microscopy (TEM). The characterization of synthesis catalysts was performed by FT-IR, XRD and Raman techniques. The electrocatalyst performances are investigated by cyclic voltammetry, linear sweep voltammetry, and electrochemical impedance spectroscopy in 0.1 M KOH solution. The Pd/Cl-RGO exhibited excellent eletrocatalytic activity towards the ORR in alkaline media. The ORR proceeds via 4-electron pathway using rotating disk electrode (RDE) technique.

Keywords: *Electro-catalyst, Oxygen reduction reaction, Graphene, Palladium nanoparticles*

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Graphene–polydopmine–Pt nanoparticles hybrid nanomaterial for electrocatalytic glucose oxidation

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Abstract

A novel electrocatalytic nanomaterial was prepared by anchoring Pt nanoparticles on polydopamine reduced graphene and its electrocatalytic activity for glucose oxidation is evaluated at different conditions. Pt@rGo modified glass carbon electrode are characterized with different techniques like (FE-SEM) high resolution transmission electron micrograph (TEM) and The electrocatalytic oxidation of glucose at Pt@-rGO electrode is significantly improved especially with Pt@-rGO is believed to play a crucial role as a catalytic mediator to facilitate the charge transfer during the oxidation of glucose.

Keywords: *Electrocatalysis, Glucose*

Introduction

Enzymatic biofuel cells (EFCs) are bioelectrochemical devices capable of converting chemical energy into electrical energy using enzymes as catalysts [1,2]. Usage of an enzyme as biocatalyst instead of conventional noble metal catalysts can render the catalytic reaction more specific towards fuel or oxidant [3,4]. The aim of this work is to use solegel technique to fabricate nanostructured material of Pt@rGO with outstanding technological applications such as electrocatalysis for glucose oxidation. The fabricated Pt@ rGO nanoparticles will be morphologically and electrochemically characterized. The effects of the annealing temperature on the morphology and elec trocatalytic properties of Pt@ rGO are also examined.

Results and Discussion

The CVs of different modified electrodes in 0.1 MPB with or without 15 mM glucose are presented in Fig. 1 In the presence of 15 mM glucose, two obvious peaks (I, II) corresponding to the oxidation of glucose and resulting intermediates are observed for Pt@ rGO and Pt/C (b´) during the positive potential scan, while the C/GCE has no obvious oxidation peak (a´). During the negative potential scan, the oxidation of glucose is suppressed in the higher potential range because of the presence of surface platinum oxide. After the reduction of Pt oxide (III), more surface-active sites are available for the oxidation of glucose, resulting in large and broad oxidation peak (IV)

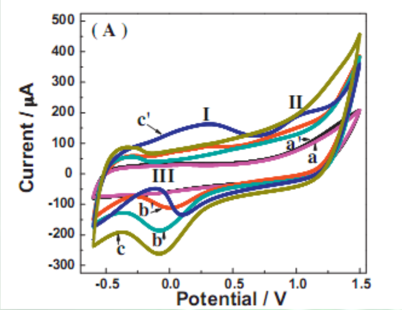

Fig1.The CVs of the C/GCE (a, a´), Pt/C/GCE (b, b´), Pt@ -rGO/C/GCE (c, c´) in 0.1M PB (pH 7.0) with (a´, b´, c´) and without (a, b, c) 15mM glucose, scanning rate: 20mVs^{-1}.

Conclusions

The Pt@ rGO nanoparticles were successfully synthesized using a sol gel process and used to fabricate a novel electrochemical sensor. The results indicate that the Pt@ rGO electrode shows good eleccatalytic activity towards hydrogen peroxide, glucose and formaldehyde with high sensitivity, good stability and excellent reproducibility. The excellent electrocatalytic performance of the Pt@ rGO makes it a promising application for the oxidation of, glucose.

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Electrochemical sensor based on surface modification of graphene nanosheets with gold nanoparticles for determination of 5-fluorouracile anticancer drug

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Abstract

In this paper, we selected electrochemical strategy to determination of 5-fluorouracile by graphene-Au NPs nanocomposites-modified glassy carbon electrode (GN/Au NPs/GCE). 5-Fluorouracil (5-FU) is an anti-neoplastic agent, it has been used for the treatment of solid tumors of the breast and rectum [1]. It is also used in treatment of colorectal cancer, and pancreatic cancer. High over voltage of drugs, especially cancer drugs, at a bare electrode suggested necessary modification of electrodes with conductive materials such as polymers, electroactive mediator and nanocomposites [2, 3]. Graphene together with its' various derivatives, such as graphene oxide, graphene nanoribbon, chemically reduced graphene oxide [4, 5] has shown fascinating advantages in electrochemistry such as electrochemical devices and capacitors due to its remarkable electrochemical properties. Especially, a chemically reduced graphene nanosheet (cr-Gs) is popular and robust in bioelectrochemistry communities because of its easy functionalization, rich surface chemistry, and biocompatibility [6-8]. Many efforts have been devoted to improve the capability of cr-Gs through association of cr-Gs with metallic nanoparticles. Gold nanoparticles are always considered as an advanced candidate due to their amazing surface properties and quantum-mechanical rules with diameters less than 10 nm [9, 10]. For example, graphene-Au NPs (GN/Au NPs) nanocomposites have been used as substrates of surface enhanced Raman scattering (SERS), hydrogen peroxide sensor and monolayer graphene fabrication [11-13]. On the basis of the outstanding properties of GN/Au NPs nanocomposites in electronics and chemistry, it is highly desired to be used as the sensing platform in electrochemical biosensors for sensitive detections. Herein, the electrochemical behavior of 5-FU was investigated employing cyclic voltammetry (CV), chronoamperometry (CA) and electrochemical impedance spectroscopy (EIS). After optimization of experimental conditions, the electro-oxidation peak currents for 5-FU at pH 9.0 phosphate buffer solution was found to vary linearly with its concentrations in the range of 0.1–50.0 µM using differential pulse voltammetry (DPV) method. The detection limit is 0.04 µM. Furthermore, GN/Au NPs/GCE was successfully applied for the analysis of 5-FU in blood serum samples with recovery 100.5% and 99.23% respectively. The modified electrode showed good stability and repeatability.

Keywords: *5-Fluorouracil, Graphene nanosheet, Gold nanoparticles, Modified glassy carbon electrode.*

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Synthesis a new Ni-MOF and study effect of contemporary TMU-10 and new Ni-MOF synthesis and survey a new bi MOF-rGO composite as material for positive electrode in supercapacitors

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Abstract

Nowadays due to the rapid progress of electronic science and the increasing expansion of mobile electronic devices, also due to increasing energy consumption and etc, electrical energy storage systems have been highly regarded. Among electrical energy storage systems, electrochemical energy storage systems such as fuel cells, batteries (Li-ion) and supercapacitors (SCs) are considerable candidates. One of the smart choices for SCs active materials are metal organic frameworks. Emerging this class of nano porous materials with high surface area, large electrolyte-accessibility and also transition metal in their structures (transition metal/oxides due to Faradaic redox reactions have a higher capacitance and energy compare to carbonaceous materials) open a new window to fabricate and present high performance SCs. Based on the above considerations in this communication, we propose a new method with interesting results to enhance MOF-SCs. We tried to synthesis two MOFs at same time, and we have gained interesting result. Existing secondary metal interestingly effect on another MOF morphology and finally we found a synergic effect. Our first step was synthesized a new nickel MOF that has good stability in water with same linker toward TMU-10, in the second step we synthesized both MOFs at same time and after characterization by SEM, TEM, EDX, XPS, XRD, elemental mapping and IR, we found changes in TMU-10 morphology also we have seen interesting synergic effect on electrochemical performance. In next step we tried to enhance the material electrochemical properties and synthesized our new MOF composite in presence of rGO and achieved a more applicable composite. In final step we used synthesized composite as active material to prepare cathode electrode and design a supercapacitor (SC) high performance (table

1). The designed 2electrode supercapacitor showed good retention in 6000 charge-discharge cycles (92% retention) and interesting performance e.g turn on a watch for about 2h by only 14mg active material. In this study we try to expand and survey some details that no one didn't attended them till now, like as effect of MOF activation on its electrochemical performance, or effect of contemporary MOFs synthesis on their morphologies.

Keywords: *MOFs, Supercapacitors, Electrochemical capacitors, Metal organic frameworks*.

	Used active materials	**Capacitance (F/g)**	**Energy (Wh/g)**	**Power (W/g)**	**Num of Electrode**
1	TMU-10	215	32.52	0.19	3E
2	TMU-10_ RGO (50%) composite	430	65.1	0.28	3E
3	Ni-MOF	280	48.9	0.25	3E
4	TMU-10_ Ni-MOF_rGO (50%)	860	130.67	0.6	3E
5	Device 2 electrode	215	310.67	1.8	2E

Table 1. Enhancement results

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High-performance supercapacitor based on Cl-doped reduced graphene oxide

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Abstract

Heteroatom doping has been proven as an effective way to tailor the properties of graphene and render its potential use for energy storage devices. In this work, we report a facile method to synthesis of reduced graphene oxide (RGO) from graphite electrodes using ionic liquid-assisted electrochemical exfoliation and the competent doping of RGO by Chlorine (Cl-RGO) in solution phase. Its capacitive performance was calculated by cyclic voltammetry and charge–discharge cycling in 6M KOH solution. The characterization of synthesized catalysts has been investigation by FT-IR, Raman, XRD and XPS techniques. We have evaluated the effectiveness of doping and performed by electrochemical measurements (involving cyclic voltammetry, galvanostatic charge/discharge and electrochemical impedance spectroscopy). It was found that the chlorine groups making the as-prepared Cl-RGO exhibited remarkably enhanced electrochemical performance when used as electrode materials in supercapacitors. The supercapacitor based on the Cl-RGO exhibited a high specific capacitance of 180.5 F g^{-1} at current density of 1 A g^{-1} and remains a relatively high capacitance even at a high current density more than RGO.

Keywords: *Reduced graphene oxide, Supercapacitor, Charge/Discharge, Chlorine doping*

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Synthesis of Palladium nanoparticles decorated N-doped reduced graphene oxide and their application for ethanol oxidation in alkaline media

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Abstract

We report a facile one pot electrochemical Pd/N-doped RGO (Pd/N-RGO) catalyst for the ethanol oxidation in alkaline media. Graphene is synthesized from graphite electrodes using ionic liquid-assisted electrochemical exfoliation. Pd electrocatalyst then was reduced by ethylene glycol as a stabilizing agent to prepare highly dispersed Pd nanoparticles on carbon graphene oxide to be used as ethanol oxidation in direct ethanol fuel cell (DEFC) catalysts. X-ray diffractometer and scanning electron microscopy techniques are used to investigate the crystallite size and the surface morphologies respectively. The electrochemical characteristics of the Pd/N-RGO catalyst is investigated by cyclic voltammetry (CV) in nitrogen saturated ethanol aqueous solutions and KOH aqueous solution. Detailed electrochemical studies (involving chronoamperometry, cyclic voltammetry and linear sweep voltammetry) prove that the electro-catalytic oxidation of ethanol at the Pd/N-RGO is more stable, occurring at lower potential, giving lower Tafel slopes compared to Pd/RGO catalyst, which can reveal the particular properties of the exfoliated N-graphene and Pd supports.

Keywords: *Electrochemical exfoliation, Graphene oxide, Palladium nanoparticles, Ethanol oxidation*

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A bismuth (II) selective modified carbon paste electrode with multi-walled carbon nanotubes for potentiometric analysis in real samples

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Abstract

A novel modified carbon paste electrode with Amino-Functionalized multi-walled carbon nanotubes (F-MWCNT) based on -schiff base (2-thienyl pyridine) was prepared for potentiometric determination trace amounts of bismuth (III) in real solution. This sensor showed excellent sensivity, highly selectivity to Bi (III) compared with other cations and very low detection limit. The uniqe physicochemical properties of carbon nanotubes (CNT_s) improved sensing and performance of bismuth sensor [1]. Central composite chemometrics design (CCD) and response surface methodology (RSM) was applied to evaluate the effects of significant and independent parameters, multivariate optimization and to gain better results [2]. Four factors containing ionophore, F-MWCNT, graphite powder and pH were investigate in twenty eight completely randomized trials CCD. So, the optimized bismuth sensor with the best amounts of ingredients in the optimal condition exhibits a nernestian slope of 19.325 mv/decade in the linear dynamic range of 1×10^{-10} to 1×10^{-3} with detection limit of 1.057×10^{-10} The optimized electrode shows a fast response time less than 10s and applicable for 8 consecutive weeks without any change in PH range 3.8 - 10.0. The molecular geometric optimization and vibrational frequencies of synthesized ionophore and complex (ionophore-Bi (III)) in the ground state have been calculated by using B_3LYP with 6-31G (d , p) basic set in solution phase [3].

Keywords: *Carbon Paste, Potentiometric, Carbon Nanotubes (CNT_s), Schiff Base, Sensor*

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The Effect of Various Contents of PTFE on the electrochemical performance of the Acetylen Black-Polytetrafluoroethylene Composite Cathode in Lithium-Thionyl Chloride Batteries

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Abstract

Lithium-thionyl chloride cell (Li-$SOCl_2$) has a metallic lithium anode and a liquid cathode comprising a porous carbon current collector filled with thionyl chloride. It delivers a voltage of 3.6V and is cylindrical in shape, in 1/2AA to D size, with spiral electrodes for power applications and bobbin construction for prolonged discharge. Among of all primary batteries, lithium thionyl chloride batteries have the highest voltage and energy, longest storage period, and the least self-discharge rate. Those batteries are suitable for such long-term applications as power for electric devices and electric power, water and gas meters, and especially as a backup power source for memory ICs. The cathode is made of highly porous Teflon-bonded carbon black whose electronic conductivity is needed for the charge transfer to take place. Thionyl chloride cathodic reduction is catalyzed by the cathode surface when a load is connected. The pores of the carbon cathode retain both the reactants and the products of this process.

It is well known that in case of discharge, reaction products of LiCl, SO_2 and S are created caused by chemical reaction [1]. Lithium chloride and Sulfur in a solid phase deposited to porous carbon cathode. Therefore, cathode should provide enough pore space until completion of discharge and efficient structural design is required because speed of reaction products deposition is different according to discharge current. PTFE increases the mechanical strength of porous carbon cathode but also decreases the electrical conductivity of positive electrode and it occupies the pores of acetylene black, that it can cause a drastic failure in the performance of the battery [2].

The chief objective of this work is to evaluate the effect of various contents of polytetrafluoroethylene on electrochemical performance of positive electrode in lithium thionyl chloride battery. Polarization curves indicate that the performance of a Li/$SOCl_2$ battery is

sensitive to the Acetylen-Black: PTFE (AB/P) ratio in the cathode. All electrochemical characteristics were measured by SCRIBNER 850E test station. The electrochemical measurements were carried out in a designed test cell which made by PTFE and 316 stainless steel. An optimal value of 40 wt. % PTFE in Acetylen-Black was found to be the best to balance the structural strength of cathode and the battery electrochemical performance based on polarization curve and discharge profile.

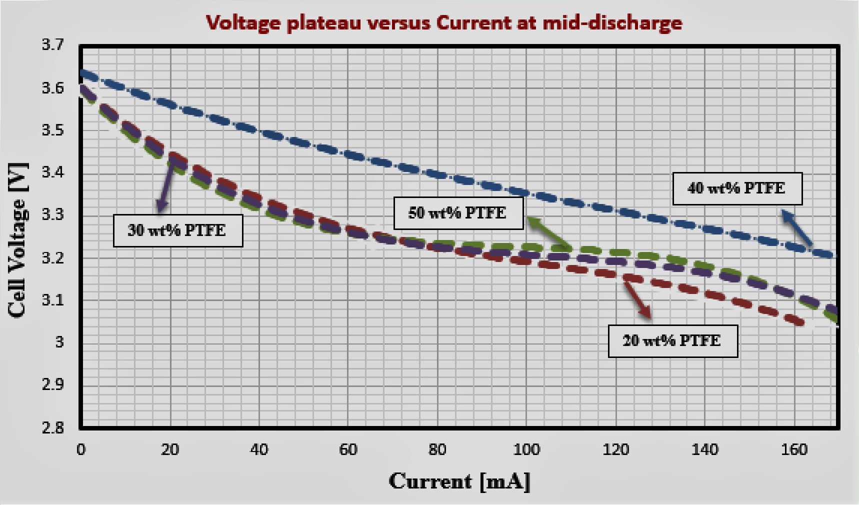

Figure 8. Voltage plateau versus Current at mid-discharge for various kinds of cathode composites

Keywords: *Li-SOCl$_2$ battery, PTFE, Porous carbon cathode, Polarization curve, Discharge Profile*

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Reduction of Voltage Delay and Improving the Shelf Life of $Li/SOCl_2$ Battery System by Using Poly-Vinyl Chloride (PVC) as an Electrolyte Additive

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Abstract

The 3.6 V thionyl chloride – lithium system ($SOCl_2$ – Li) is a high-energy system, which is considered as a promising power source because of its high energy density, high operation voltage, long storage life and wide operation temperature range. The $Li/SOCl_2$ cell belongs to a family of liquid oxidant cell systems in which the reductant component (lithium) and the oxidant component ($SOCl_2$) are initially placed in direct contact with each other. The mechanism for the discharge at the anode is the oxidation of lithium to form lithium ions with the release of an electron. The lithium ion moves across the cell to the porous carbon cathode (PCE) where it reacts with $SOCl_2$ to form lithium chloride (LiCl). The electron moves through the external circuit to the cathode where it reacts with $SOCl_2$, which is reduced. It is well known that a LiCl passivating film is formed on the anode surface when it comes in to contact with the $SOCl_2$ electrolytic solution. This film reduces any chemical interaction between the lithium and the $SOCl_2$ and it serves to protect the lithium from discharging on its own when the load is removed from the cell [1]. In addition, it causes a drastic voltage depression under current load, especially when cells are discharged after storage periods [2]. The film of LiCl, which is essentially a high resistance layer between the electrodes, is primarily responsible for the long shelf life (>10 years) of lithium thionyl chloride cells.Poly-Vinyl chloride as a kind of vinyl polymers with chlorine substituent groups has been evaluated as voltage-delay reducing additives. PVC powder was added to a 1.8 M $LiAlCl_4$/ $SOC1_2$ electrolyte at a concentration of 0.2 gL^{-1} and was stirred. All electrochemical characteristics were measured by SCRIBNER 850E test station. The electrochemical measurements were carried out in a designed test cell which made by PTFE and 316 stainless steel. Observations indicate that by adding PVC to electrolyte, which it caused a polymer film formed on the lithium anode, the growth rate of LiCl passivating film is decreased.

Figure 9 Impedance variation for cells with different electrolytes: (a) increase in internal resistance as a function of discharge time (b) nyquist diagram of ohmic resistance after complete discharge for PVC added Cell in comparison with PVC non-added Cell

PVC, which is added to the electrolyte, is considered to stick to the lithium anode surface and formed a film on it, due to an affinity between the lithium and the chlorine group. This film controls growth rate of the LiCl-passivating film and changes the film morphology. A cell with reduced voltage delay shows more promising discharge characteristics in comparison with a cell without polymer additives.

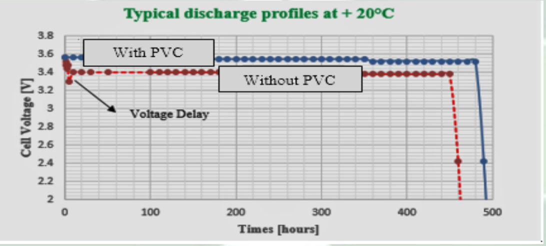

Figure 10 Discharge characteristics for Li/$SOCl_2$ batteries; PVC added in comparison with PVC non- added battery

Keywords: *Lithium thionyl chloride battery, Passivating film, Polyvinylchloride, Discharge characteristics, Impedance analysis*

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Cobalt ferrite nanoparticles decorated on exfoliated graphene oxide, application for amperometric determination of NADH and H_2O_2

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Abstract

Here, cobalt ferrite nanocomposite decorated on exfoliated graphene oxide ($CoFe_2O_4$/EGO) was synthesized. The nanocomposite was characterized by different methods such as X–ray diffraction spectroscopy, scanning electron microscopy, energy dispersive X–ray diffraction microanalysis, FT-IR, Raman spectroscopy and electrochemical methods. The $CoFe_2O_4$/EGO nanocomposite was used to modify glassy carbon electrode (GCE). The voltammetric investigations showed that $CoFe_2O_4$/EGO nanocomposite has synergetic effect towards the electro-reduction of H_2O_2 and electro-oxidation of nicotinamide adenine dinucleotide (NADH). Rotating disk chronoamperometry was used for their quantitative analysis. The calibration curves were observed in the range of 0.50 to 100.0 µmol /LNADH and 0.9 to 900.0 µmol/ L H_2O_2 with detections limit of 0.38 and 0.54 µmol /L, respectively. The repeatability and reproducibility of the electrochemical sensor for NADH and H_2O_2 analysis were studied too. The selectivity of the electrochemical sensor was investigated. The new electrochemical sensor was successfully was applied for the determination of NADH and H_2O_2 in real samples with satisfactory results.

Synthesis and electrochemical supercapacitive performance of copper cobalt spinel hollow spheres

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Abstract

Supercapacitor is a rapidly growing industry that is revolutionizing the energy storage technology today. Their high power density and excellent low temperature performance have made them the technology of choice for back-up power, cold starting, flash cameras and regenerative braking. They also play an important role in the progress of hybrid and electric vehicles, consumer electronics, military and space applications [1]. Supercapacitors are expected to have more industrial applications if their energy density could be improved. This has triggered tremendous research efforts in order to develop new electrode materials that are capable of providing a huge amount of energy in a short period of time [2]. Metal oxides have a higher capacitance/energy than carbonaceous materials due to Faradaic redox reactions [3]. Among them, binary metal oxides such as spinels are more efficient than single metal oxides owning to their richer redox reactions [4]. Herein, for the first time, we report mesoporous copper cobaltite ($CuCo_2O_4$) hollow spheres prepared by a facile method as a high-performance supercapacitor electrode material.

Mesoporous $CuCo_2O_4$ hollow spheres was prepared as follow: 0.5 mmol of $Co(NO_3)_2·6H_2O$, 0.25 mmol of $Cu(NO_3)_2·6H_2O$, and 16 mL of glycerol were dissolved into 80 mL of isopropanol. The solution was then transferred to a Teflon-lined stainless steel autoclave and kept at 180 °C for 6 h. After cooling, the brown precipitate (CuCo-glycerate) was centrifuged, washed with several times with ethanol and dried in an oven at 80 °C. In order to obtain the $CuCo_2O_4$ hollow spheres, the as-synthesized CuCo-glycerate was annealed at 350 °C for 2 h. XRD, XPS, SEM and TEM images confirm the preparation of $CuCo_2O_4$ hollow spheres. Also, BET and BJH isotherms confirm mesoporous structure of sample. The electrodes were prepared by the painting of mixing active material, acetylene black, and polyvinylidene fluoride (PVDF) (with a mass ratio of 85:10:5) on the Ni foams. The half-cell electrochemical performance of the electrodes were

investigated in a 6 M KOH solution. The Mesoporous $CuCo_2O_4$ hollow spheres electrodes exhibit excellent electrochemical performance, including an ultra-high specific capacitance of 1212 F g^{-1} at 2 A g^{-1} and 605 F g^{-1} at ultra-high current density of 60 A g^{-1} (50% retention) and excellent cycle life (only 7 % capacitance loss after 5000 cycles at current density of 5 A g^{-1}).This outstanding electrochemical performance of these electrodes can be attributed to their hollow sphere morphology with unique properties, such as mesoporous structure, high surface area and nano-scale shell thickness. Mesoporous structures minimize the diffusion distance from the external electrolyte to the interior surfaces by acting as ion-buffering reservoirs which enhances the accessibility of electrolyte not only at its surface but also throughout the entire material [5]. High specific surface area improves the utilization of the active material by providing more active sites with larger interfacial area between the electrode material and the electrolyte ions [6]. Nanosized shell thickness lead to faster kinetics and higher conductivity by providing short transport pathways for electrons [5]. We envision these electrodes to be useful in a broad range of applications such as supercapacitors, lithium ion batteries, fuel cells, gas sensors, biosensors, catalysis, and other electronic devices.

Keywords: *Supercapacitor, Hollow spheres, $CuCo_2O_4$, Spinel.*

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Synthesis of lithium nickel cobalt manganese oxide Nano powder by ultrasonic spray pyrolysis as cathode active material of lithium ion battery

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Abstract

Nowadays, lithium ion batteries (LIBs) have special situation in portable electronics market and widespread researches have carried out in a various fields of LIBs such as cost reduction, preventing environmental damages, and improving performance. The main components of a LIB are anode, cathode, electrolyte and separator, among which the cathode material is a limiting factor in terms of both cost and performance [1]. The first cathode material for commercial LIB was lithium cobalt oxide (LCO) which has problems like cobalt resource constraints, high cost, toxicity, and low safety, and these problems has limited use of LCO in high power batteries of electric and hybrid electric vehicles [2]. Therefore researchers are looking for alternatives, for which their $LiNi_xCo_yMn_{1-x-y}O_2$ (NCM) compositions are one of the candidates owing to have higher capacity, lower cost and better thermal stability than LCO [3]. This work focused on synthesis of lithium nickel cobalt manganese oxide using ultrasonic spray pyrolysis. This method produces high purity material, easily control properties of product, and have low cost compared to other conventional synthesis methods including solid state, sol-gel and co-precipitation [4]. The effect of concentration of precursor solution on morphology and particle size, effect of synthesis temperature and calcination temperature on morphology, structure, and capacity were investigated. Crystal structure of $LiNi_{0.4}Co_{0.2}Mn_{0.4}O_2$ powder was studied by X-ray diffraction (XRD), and all patterns indicated ordered layered structure. Scanning electron microscopic (SEM) images showed micron-sized spherical particles composed of nanoparticles. Initial charge capacity of $LiNi_{0.4}Co_{0.2}Mn_{0.4}O_2$ as cathode material in voltage range of 2.5-4.4V reached to124 mAh/g, for the sample synthesized in 600ºC and calcinated in 850ºC. The coulombic efficiency and capacity retention after 10 charge-discharge cycles were 90% and 80% respectively.

Keywords**:** *Lithium ion battery, Cathode active material, Lithium nickel cobalt manganese oxide, Ultrasonic spray pyrolysis*

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A New Droplet-based Polymeric Banana Electrochemical Biosensor for One Microliter Paracetamol Analysis

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Abstract

Modern researches and also the laboratories increasingly need the methods to measure the small volumes as microliter of analytical samples to identify various analytes with the high accuracy. An electrochemical biosensor based on a modified carbon paste electrode with hydrogel as an absorbent polymeric matrix and banana as a source of polyphenol oxidase was constructed and it was used for determination of paracetamol. The ability of the hydrogel to absorb and retain the liquids, allows us to insert only 1 µL of standard paracetamol solution into the surface of the electrode, in fact we measure the concentration of paracetamol which is at the surface of the electrode, not in solution. The electrochemical oxidation of paracetamol was studied by cyclic voltammetry and square wave voltammetry. The effective parameters on the voltammetric response of the constructed biosensor were optimized. The results obtained by cyclic voltammetry revealed that the banana-hydrogel carbon paste electrode shows a higher current response compared to a banana carbon paste electrode and hydrogel carbon paste electrode. The proposed electrode shows excellent capability to measure only one µL of sample solution, which is very important and considerable property for limited samples in volume. The modified electrode also exhibits an excellent sensitivity (1.6 picomole), a good linear range (10-250 picomole), good reproducibility and stability in both basic and acidic environments even in the presence of the enzyme and a long life time (20 days) for measurement of paracetamol in solutions.

Keywords: *Banana biosensor, Carbon paste, Polyphenol oxidase, Hydrogel, Paracetamol, Low volume consumption sensor*

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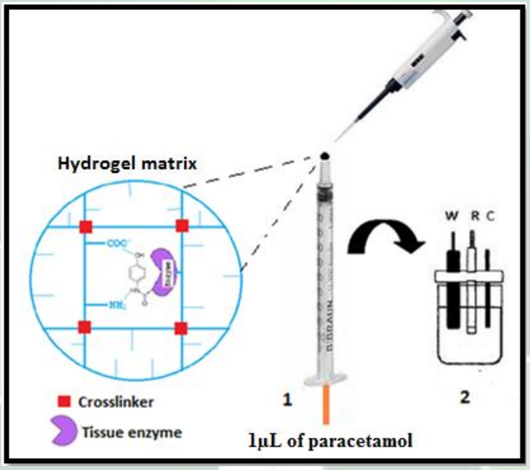

An electrochemical sensor based on carboxylated multiwalled carbon nanotubes with [bmmim]PF6 ionic liquid for simultaneous determination of hazardous dyes in wastewaters

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Abstract

There are many negative effects on the environment and human health as a result of industrial textile chemical wastes. It is important to proffer right removal or use management methods to safeguard life. Water is the main medium for the removal of impurities in the application of dyes and finishing agents during their major operations in the textile industry. Therefore, the main concern is constant discharge of untreated dye effluents from the processing units to the surrounding water streams, making it highly polluted with toxics and recalcitrant substances.

This research, is tried to develop a simple and sensitive electrochemical sensor for the determination of acid blue 29 (AB 29) and mordant yellow 10 (MY 10), as textile dyes pollutants in industrial waste waters. Therefore, the first electrochemical sensor was developed for their simultaneous determination by modifying a glassy carbon electrode (GCE) with a composite arranged from 1-Butyl-2,3-dimethylimidazolium hexafluorophosphate ([bmmim]PF6) 98% as an ionic liquid (IL) and carboxylated multiwalled carbon nanotubes (CMWCNTs). Direct electrochemical oxidation of AB 29 and MY 10 at the modified electrode was investigated, showing that their peak currents were significantly enhanced due to the presence of the ionic liquid-carboxylated multiwalled carbon nanotubes glassy carbon electrode (IL/CMWCNTs-GCE). The effects of different parameters such as pH, accumulation time, accumulation potential, and scan rate on the sensitivity were investigated. Individual and simultaneous determinations were performed by Differential pulse voltammetry (DPV) technique at optimum conditions.

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Investigating the Role of PH and Soil Resistivity in the Corrosion of Carbon Steel

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Abstract

Carbon steels have so many uses in power and gas transmission. These steel materials have been mainly placed in the soil. Such factors as PH and soil resistivity caused the corrosion of main expensive facilities. The purpose of present research is to investigate the role of PH and soil resistivity of different soils on the rate of steel corrosion. Here four pieces of the same steel with the same size were kept in different climates for 3 months and their changes were monitored weekly. Finally, the effects of these two factors have been studied, then compared. At following, it is attempted that by applying computational methods and modelling, the behavior of these alloys against these factors have been simulated , also predicted. Then, the theoretical and experimental data were compared in order to attain generalized results for various types of steel.

***Keywords**: Carbon Steel, Corrosion, PH, Soil Resistivity*

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Evaluation of $ZnMnFe_2O_4$ as supercapacitor

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Abstract

Supercapacitors as a storage electrical energy system due to their high power density and charge/discharge cycle number and suitable specific energy, have very intention in new research and industrial application. Ferrite compounds have good oxidation state and with nanoparticle synthesis of that, have good active surface area, so could be a valuable choice for use as electrodic active material in supercapacitor that have electrical double layer and pseudocapacitor property.

In this work, firstly synthesize $ZnMnFe_2O_4$ by solution chemical codepositon method and produced nanosize powder characterized by SEM, XRD, FTIR and VSM for demonstration of morphology, crystal lattice, structure and magnetic properties. SEM image reveals semispherical particle shape with size range less than 100 nm, and XRD analyze exhibits spinel lattice structure with rearrangement of Zn and Mn cation in Octahedral and Tetrahedral site of Fe_3O_4 spinel structure.

Electrochemical evaluation of capacitive properties of ferrite compound is done by cyclic voltammetry, chronopotentiometery and electrochemical impedance spectroscopy method. At the first, the ferrite powder mixed with 15 weight percent acetylene black as conductive agent and 5 weight percent PVDF solute in NMP as binder and then a drop of composite coated on glassy carbon electrode that used as working electrode in three electrodic test. Primarily, best electrolyte was selected between a series of alkali and chloride salt solution and potassium hydroxide and chloride was boarder domain in CV diagrams. Suitable concentration of these solutions was obtained too. Cyclic voltammograms appears EDLC and pseudocapacitance property for $ZnMnFe_2O_4$ and by laviron equation of peak current versus scan rate, surface active area was calculated.

By three and two electrodic chronopotentiometery test, specific capacity and columbic efficiency of ferrite compound was obtained. In two electrodic test, prepared composite was coated in two pieces of graphite with 1*1 cm dimension that separated with a cotton paper as insulator.

EIS test reveals specific capacity and electrochemical charge transfer between ferrite and proton and appears pseudocapacutive as well as ELDC property of $ZnMnFe_2O_4$ compound.

Keywords: *Electrochemical double layer capacitance (ELDC), Pseudocapacitance, Ferrite compound,* $ZnMnFe_2O_4$

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Behaviour of Nanostructure Polyoxometalates Containing Co, Ni, and Cu as a Powerful and Stable Catalysts for Hydrogen Evolution Reaction in Acidic and Alkaline Solutions

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Abstract

A new form of $[PW_{11}MO_{39}]^{5-}$@Ru-reduced graphene oxide (rGO) (M: Co, Ni, and Cu) was prepared by deposition of $[PW_{11}MO_{39}]^{5-}$ on the surface of Ru-rGO. The different behaviours of the polyoxometalates (POM) in acidic and alkaline media were studied for hydrogen evolution reaction (HER). Transmission electron microscopy, scanning electron microscopy, energy dispersive X-ray spectroscopy, X-ray diffraction pattern and infrared spectroscopy were used for characterization of the nanocomposites. The electrocatalytic properties of the nanocomposites toward HER were studied by voltammetry and electrochemical impedance spectroscopy. The kinetic parameters were computed from the Tafel plots, and the possible mechanisms of the HER were considered. The results showed that the HER on $[PW_{11}MO_{39}]^{5-}$@Ru-rGO electrodes obeyed Volmer-Heyrovsky mechanism. It was taken that the enhancements in the rate of the HER on the modified electrodes may be associated with the presence of the nanoparticles of POM on the electrode surface and enhancement of the surface area. These results demonstrated that the nanocomposites could be effective HER catalysts in acidic and alkaline media with considering green chemistry. These have good catalytic capacities, durability, favorable kinetics, and low price.

Keywords: *Polyoxometalates; Ru-reduced graphene oxide nanocomposites; reduced graphene oxide; Electrocatalyst; Hydrogen evolution reaction.*

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Ni-Co-Se nanoparticles modified reduced graphene oxide nanoflakes, an advance electrocatalyst for highly efficient hydrogen evolution reaction

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Abstract

The present manuscript reports a simple one-step wet chemical approach to synthesis reduced graphene oxide nanoflakes (RGONF) from graphite by a thermal reduction at low temperature. The optical, Fourier Transform Infrared, X-ray diffraction, Raman, X-ray photoelectron spectroscopy, electrochemical impedance spectroscopy and transmission electron microscopy are used to demonstrate the synthesis RGONF. This method is simple and avoids the usage of harmful chemical reductants. Then, Ni-Co-Se nanoparticles were solvothermal deposited on RGONF in aqueous media (RGONF/Ni-Co-Se) with an average size of 80 nm. Then, a glassy carbon electrode (GCE) was modified with RGONF/Ni-Co-Se and is used as an electrocatalyst for hydrogen evolution reaction (HER) in 0.50 mol L^{-1} sulfuric acid. The results showed an excellent catalytic activity of RGONF/Ni-Co-Se with an overpotential of 5 mV (vs. RHE) to achieve high current densities of 600 $mA.cm^{-2}$ (at -780.0 mV). As well, the applied overpotential and slope for HER is better than expensive Pt/C (20%) catalyst, which used in fuel cells[1]. Also, the Tafel slope was about 30±3 mV $decade^{-1}$ and suggested the Tafel mechanism for HER.

***Keywords*: Reduced graphene oxide nanoflakes; Thermal reduction; Ni-Co-Se nanoparticles; Solvothermal deposition; Hydrogen evolution reaction.**

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Experimental and quantum studies on [BMIM] BF4 ionic liquid as corrosion inhibitor for mild steel in H_2SO_4 solution

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Abstract

Ionic liquids have attracted considerable attention in recent years. They are described as having many potential applications. In particular, they have been identified as powerful solvents for green synthesis, and electrically conducting fluids. Salts that are liquid at near-ambient temperature are important for electric battery applications, and have been considered as sealants due to their very low vapor pressure [1, 2]. In this work the inhibition behavior of [BMIM]BF_4 (1-butyl-3-methyl imidazolium tetrafluoroborate) on mild steel corrosion in 0.5 M H_2SO_4 as corrosive solution was evaluated by the weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques in the absence and presence of different concentrations of [BMIM]BF_4. Surface analysis using energy dispersive X-ray (EDX) and scanning electron microscope (SEM) allowed us to clarify the mechanistic aspects and evaluate the relative inhibition efficiency. Density functional theory (DFT) calculations were performed to gain some insight into the interactions of [BMIM]BF_4 with the St-37 mild steels surface. Results obtained from experimental and quantum studies are in good agreements. This work has shown that the [BMIM]BF_4 has an desirable inhibition effect on St-37 mild steel corrosion in corrosive solution.

Keywords: *Ionic liquid, Inhibition, Corrosion, Density functional theory (DFT)*

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DFT study and determination of metronidazole based on ionic liquid mediated carbon nanotube modified carbon paste electrode

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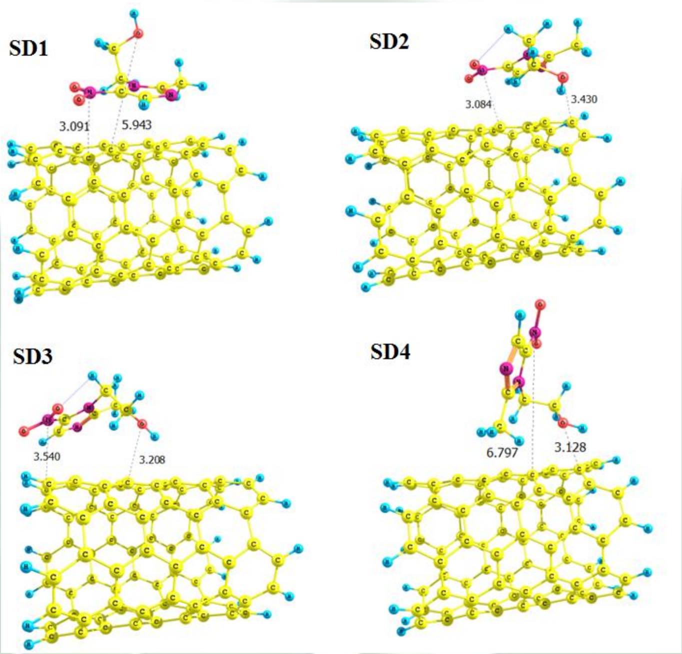
Abstract

In this work, we prepared a new high sensitive sensor for metronidazole (MNZ) by Single-walled carbon nanotube (SWCNT) and ionic liquid (IL). The use of SWCNT-IL nano composite in the paste increased the response of the electrode, significantly. The performance of the proposed carbon paste electrode was investigated by differential pulse voltammetry (DPV). The sensor prepared based on methods that have been previously reported [1-3]. Various factors such as electrode composition, types of supporting electrolyte, pH, stirring rate, scan rate were studied and optimized. The best performance of the electrode was obtained with composition of 76 % graphite powder, 20% ionic liquid and 4% SWCNT. In the optimum experimental conditions (pH=7 Britton-Robinson (B-R) buffer, stirring rate = 400 rpm, scan rate= 50 mV/s) , the current response of the electrochemical sensor studied for metronidazole solution and linearity was obtained in the range from 5.00×10^{-5} to 5.00×10^{-3} mgL^{-1}, with the detection limit of 1.238×10^{-5} mgL^{-1}. The interference study was performed for some drugs and cations that do not show any significant interference. This method was successfully applied to the analysis of MNZ in the milk and egg samples with acceptable recoveries of 90.33–108.0% with RSD ≈ 4.41 %.
Also, the non-covalent interactions of the metronidazole with the SWCNT in four different manners were investigated by using the density functional theory (DFT) Methods[4] with the M062X and B3LYP functional. Geometries of the investigated species were fully optimized at 6-31+G (d, p) basis sets and Polarizable-Continuum Model (PCM)[5] for investigation of solute-solvent interactions in aqueous solution. The order of the DFT-calculated binding energy of the optimized geometries is SD2 >SD1>SD3>SD4. The most stable form (SD2) of them involves the interaction of the Metronidazole with the SWCNT *via* the nitrogen atom of the nitro group.(Fig. 1) that confirms catalytic reduction nitro group in experimental study[6, 7].



Keywords: *Carbon paste electrode, Metronidazole, Differential pulse voltammetry, Single-walled carbon nanotube, Density functional theory, Ionic liquid.*

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Wood surface preparation by silane Nano film formation using sol-gel method to improve the adhesion of alkyd and polyurethane coatings

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Abstract

In this research, the effect of Silane nanofilm formation using sol-gel method on improving the adhesion of Alkyd and Polyurethane coatings to wood surface in urban furniture was investigated. For this purpose, the surface of spruce wood (Picea abies L.) was modified with Tetraethoxy¬silane (T) and glycidoxy¬propyl¬trimethoxy¬silane (G) sol-gel materials. Then, solvent-borne alkyd (AS), solvent-borne polyurethane (PS) and waterborne polyurethane (PW) coatings were applied. Microscopic observation by fluorescence, confocal laser scanning microscopy (CLSM) and SEM showed that the silica component of nanosol covered the whole wood surface homogeneously, while alkyd and polyurethane coatings were deposited preferentially in the surface depressions. The combined analysis of ATR-FTIR, XRD and XPS demonstrated that the surface was covered with silicon oxides (SiO2) attached to hydrocarbon chains. The results of accelerated weathering test showed that the surface modification by sol-gel improved the weathering resistance of top coatings and reduced their roughness. The silane-based materials improved the adhesion and abrasion resistance properties, and Tetraethoxy¬silane had a better performance in comparison with glycidoxy-propyl¬trimethoxy¬silane. Among coatings, the highest tensile strength was observed for waterborne polyurethane. Solvent-borne alkyd showed the lowest tensile strength. Overall, the sol-gel derived hybrid inorganic–organic thin film was found to enhance the adhesion strength of coatings to wood surface and improve the weathering resistance of wood.

Keywords: *Coating; Sol-gel, Alkyd, Polyurethane, Nano silane*

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An investigation on the inhibitory effect of Allopurinol on mild steel st 37 corrosion in hydrochloric acid solution

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Abstract

Steel corrosion is a costly problem and is one of the most important issues in materials science. The corrosion of mild steel is the most common form of corrosion, especially in acid solution. Inhibitors are commonly used to reduce the corrosion attack on metallic materials. Most of the commercial inhibitors are toxic in nature and therefore it is necessary to replace them by environmentally benign inhibitors. The use of pharmaceutical compounds offers interesting possibilities for corrosion inhibition due to the presence of hetero atoms like nitrogen, sulphur and oxygen in their structure, and they are of particular interest because of their safe use, high solubility in water and high molecular size [1].

In the present work, the inhibition effect of allopurinol drug on the mild steel in 1 M hydrochloric acid solution is studied using the potentiodynamic polarization, the electrochemical impedance spectroscopy (EIS), the infrared spectroscopy (FT-IR) and the scanning electron microscopy (SEM) methods [2]. The experiments have been performed for various inhibitor concentrations using these methods and the optimum concentration of the inhibitor has been determined. Furthermore, the influence of the temperature on the corrosion inhibition of the allopurinol at the optimum concentration has been investigated. Results show that the addition of the allopurinol to the hydrochloric acid solution reduces the corrosion of the mild steel. It has also been shown that the corrosion inhibition efficiency increases by increasing the concentration of allopurinol to a certain value and increasing temperature. Potentiodynamic polarization measurements show that allopurinol acts as mixed-type inhibitor. Electrochemical impedance measurements show that increasing the inhibitor concentration to a certain value increases the charge transfer resistance and decreases the capacity of the double layer (C_{dl}). The results obtained using the potentiodynamic polarization and electrochemical impedance techniques are in good agreement.

Furthermore, the adsorption of the allopurinol inhibitor on the alloy surface obeys the Langmuir adsorption isotherm model. The absorption process is a combination of the physical and the chemical adsorption and it is spontaneous. In the hydrochloric acid solution, the adsorption process is endothermic with an increase in the entropy. The results obtained from infrared spectra confirmed the formation of a protective layer on the alloy surface after immersion in hydrochloric acid solution containing allopurinol. SEM investigations also validate the adsorption of inhibitor.

Keywords: *Natural corrosion inhibitor, Allopurinol, Potentiodynamic polarization, Electrochemical impedance spectroscopy, Adsorption isotherms, Mild steel.*

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Effect of metal oxides nano structured on Pt catalyst in fuel cell

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Abstract

Proton exchange membrane fuel cells (PEMFCs) have been considered as a promising power technology for applications in portable and stationary. The prohibitive cost of platinum for catalyzing the cathodic oxygen reduction reaction (ORR) has hampered the widespread use of polymer electrolyte fuel cells (PEFCs). In this study, Pt catalyst was precipitated on Vulcan XC-72R containing 5 wt.% NiO,Feo and using NaBH4 as a reducing agent. XRD and SEM characterizations were carried out to determine the morphology of the catalysts. XRD patterns of sample showed peaks characteristic of Pt/C and metal oxide nanoparticles. Cyclic voltammetry was recorded to evaluate ORR performance.

***Keywords**: electrocatalyst، Nanocomposites، proton-exchange membrane، Fuel Cells،Oxygen Reduction Reaction ،Platinum*

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Electrosynthesized reduced graphene oxide-supported platinum nanoparticles on carbon-ceramic electrode for electrooxidation of ethanol

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Abstract

The challenges of climate change and energy access have raised the tremendous efforts to introduce renewable and green energy sources for the replacement of fossil fuels [1-3]. Ethanol appears to be the promising alternative candidates as sustainable and renewable energy sources for the future perspectives. The electrochemical oxidation of ethanol (EOR) has attracted great attention for the development of low-temperature fuel cells where, offers a high energy density (8 kWh/kg) without the hazardous effects. Moreover, large amounts of ethanol biofuel can be produced during the fermentation of biomass such as numerous available agricultural products [2,4,5]. Achieve high efficiency of EOR need to introducing the capable electrocatalyst materials to enhance the kinetic reaction rate. It is well known that Pt is the most active electrocatalyst for energy production and conversion. Pt is commonly supported on the activated carbon or carbon black in order to enhance its activity and stability. In the recent years great efforts have been made to develop noncarbon materials for catalyst supports [6] such as grapheme (Gr). Gr has exhibited excellent electrical conductivity and extremely high specific surface area (2600m2/g), and therefore, Gr should be explored as a support material to improve electrocatalytic activity of catalyst particles for ethanol oxidations. Gr is widely used as catalysts support for ethanol oxidation [7,8]. In this study, we have systematically investigated the effects of reduced graphene oxide (rGO) as a catalyst support on the electrocatalytic activity of Pt for ethanol oxidation used in acidic media. The electrocatalyst was deposited on the carbon-ceramic electrode (CCE). Then, the electrooxidation of ethanol on rGO-supported Pt and Pt nanoparticles was characterized by cyclic voltammetry in an electrolyte of 0.3 M CH_3CH_2OH and 0.1 M H_2SO_4.

Fig.1. shows the cyclic voltammograms (CVs) of ethanol electrooxidation.

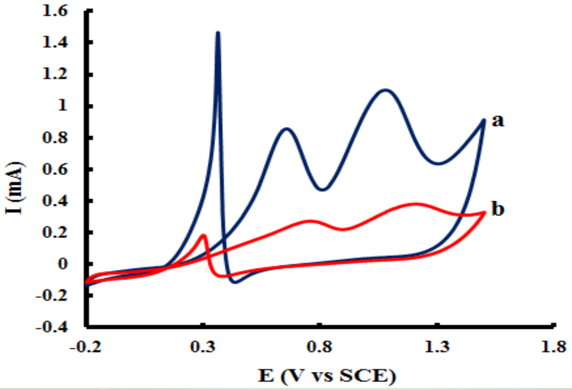

Fig.1. CVs of 0.3 M ethanol on the Pt/rGO/CCE (curve a) and on the Pt/CCE (curve b) in 0.1 M H_2SO_4 at a scan rate of 50 mV.s^{-1}.

As seen in Fig.1. Pt/rGO/CCE was provided higher currents than Pt/CCE therefore the Pt/rGO/CCE has high electrocatalytic activity for ethanol electrooxidation. The effect of some experimental factors was studied and optimum conditions were suggested. Then, the long-term stability of modified electrode has also been studied.

Keywords: *Electrosynthesize, Graphene, Platinum, Nanoparticles, Ethanol.*

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

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Abstract

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

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

Introduction

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

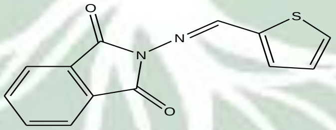

Fig. 1. 2-[(thiophene-2-yl-methylene)-amino]-isoindole-1,3-dione.

Experimental

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

Results and discussion

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

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

Table 1. Membrane compositions optimization

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

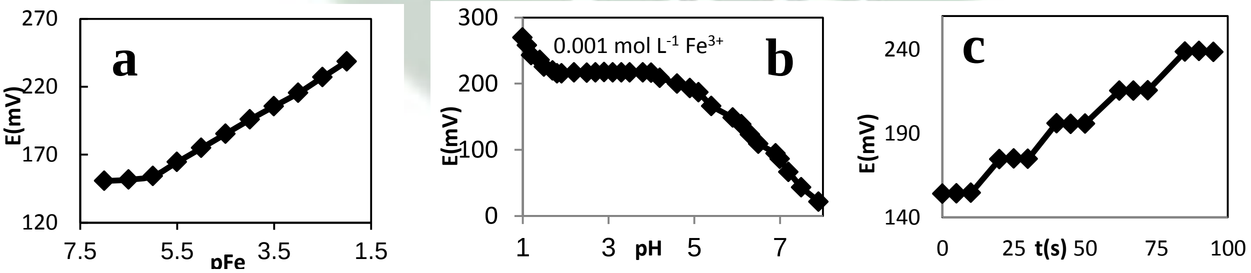

Fig. 2. a) Calibration curves; b) the effect of pH on the potential response; c) Dynamic response time

Conclusion

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

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

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Abstract

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

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

Introduction

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

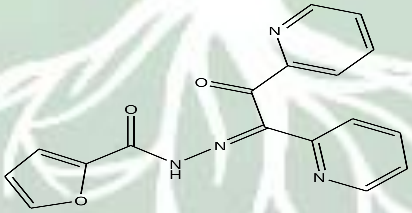

Fig. 1. N'-(2-oxo-1, 2-di (pyridine-2-yl) ethylidene) furan-2-carbohydrazide.

Experimental

The sufficient amount of membrane ingredients were blended and dissolved in 3-4 mL of THF. The resulting mixture was evaporated slowly to obtain an oily concentrated blend. Then, the

Pyrex tube (3–5 mm i.d.) was dipped into the membrane solution for about 5 s and kept at room temperature for at least 12 h. Finally, it was filled and conditioned in 1.0 ×10^{-3} M $GdCl_3$ solution.

Results and discussion

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

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

Table 1. Membrane compositions optimization

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

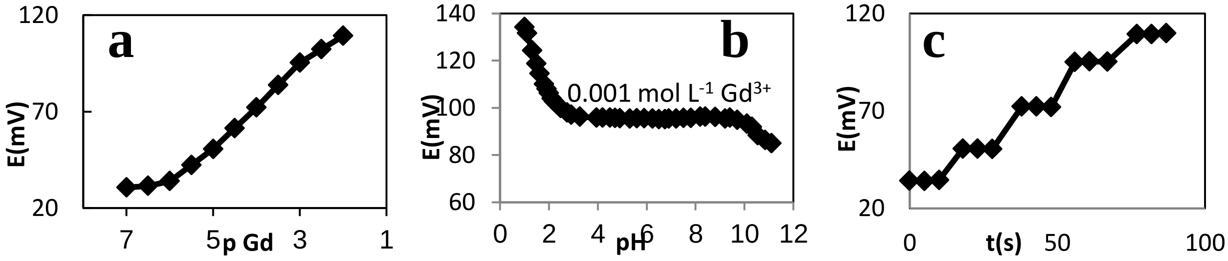

Fig. 2. a) Calibration curves; b) the effect of pH on the potential response; c) Dynamic response time

Conclusion

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

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A novel modified carbon paste electrode for the determination of chromium (III) in water sample

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Abstract

Two kinds of modified carbon paste electrodes for chromium (III) ion based on zeolite as ionophore were prepared. 3-methyl-pyrazol-5-one (MP) was used as modifier in sensor 1. Sensor 1 exhibits a Nernstian response for Cr(III) ions over a wide concentration range from 1×10^{-6} to 1×10^{-2} mol·L^{-1} with a slope of 19.8 ± 0.1 mV·decade^{-1}.Sensor 2 was modified by using chlorinated nanotubes. This sensor shows a Nernstian response for Cr(III) ions over a concentration range from 1×10^{-7} to 1×10^{-2} mol·L^{-1} with a slope of 19.74 ± 0.1 mV·decade^{-1}. Some parameters were optimized for two sensors such as pH of solution, composition of membrane and response time of electrode. And results were compared. They were successfully applied to direct determination of chromium (III) in water samples and as an indicator electrode in potentiometric titration of Cr(III) with EDTA.

Keywords:*Ion selective electrode, Functional multi-walled carbon nanotubes, Potentiometry, Zeolite***,** *3-methyl-pyrazol-5-one*

Introduction

Carbon paste electrodes (CPEs) are the most popular types of carbon electrodes which are widely used in electrochemical studies. The aim of this work was comparison two modified electrodes based zeolite structure for selective response in determination Cr(III) in sample water.

Methods

Desired amount of zeolite, graphite powder, paraffin oil and modifier were thoroughly mixed and then transferred into a glass tube, of i.d. 5mm and a height of 3 cm .After the mixture homogenized. The paste was packed carefully in to the tube. This can prevent an increased in the electrical resistance of the electrode .Then electrical contact was made by inserting a copper wire in to the opposite end. The working surface of the electrode was polished using soft abrasive paper.

Results and discussion

Results of two sensors show that potential response of sensor 2 is more than sensor 1. According to MWCNT in the composition of the carbon paste causes to increase in conductivity of the sensor and the dynamic working range of the sensor improves. As a result, the potential response of the sensor improves to Nernstian values. A composition of 10% ionophore, 10% functional MWCNT, 20% paraffin oil and 60% graphite powder was chosen as the optimum composition of sensor 1 showing a Nernstian slope of 19.8±0.1 mV decade^{-1}. The optimum composition of sensor 2 is similar to sensor 1, but its Nernstian slope is 19.74±0.1 mV decade^{-1}.

Conclusions

Sensor 2 has wider measuring range, lower detection limit and wider pH range than sensor 1. But sensor 1 has shorter response time and more performance for determination of chromium (III) than sensor 2.

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Fabrication of Integrated Dehydrogenase-Based Electrochemical Biosensors in order to detection of amino acids in biological samples

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Abstract

One method to detect the Phenylketonuria (PKU) disease, is the using an enzyme electrochemical biosensors that they have to be more selectivity than other biosensors. In this biosensors, different substrates are used for immobilization of enzymes and electrocatalytical structures[1]. This study describes a facile approach to the preparation of integrated dehydrogenase-based electrochemical biosensors through noncovalent attachment of an oxidized form of β-nicotinamide adenine dinucleotide (NAD^+) onto graphene and graphene-based materials such as graphene oxide and graphene quantum dots with the interaction between the adenine subunit in NAD^+ molecules and graphene nano-structures. With phenylalanine dehydrogenase (PDH) as a model dehydrogenase-based recognition unit, electrochemical studies reveal that phenylalanine is readily oxidized at the PDH/NAD^+/GO-modified electrode without addition of NAD^+ in the phosphate buffer. graphene-based materials employed here not only serve as the electronic transducer and the support to confine NAD^+ cofactor onto the electrode surface, but also act as the electrocatalyst for NADH oxidation in the dehydrogenase-based electrochemical biosensors[2, 3]. Also, In this research, for the first time, the carbon ceramic electrodes will be used that they are modified with carbon structures as a substrate with high active surface to stabilize the enzyme of phenylalanine dehydrogenase and preparation of electrochemical biosensors phenylalanine amino acid with high stability and selectivity. At the PDH/NAD^+/GO-based phenylalanine biosensor, the current is linear with the concentration of phenylalanine being within a concentration range from 200 to 500 μM. This study offers a facile and versatile approach to the development of integrated dehydrogenase-based electrochemical devices, such as electrochemical biosensors and biofuel cells.

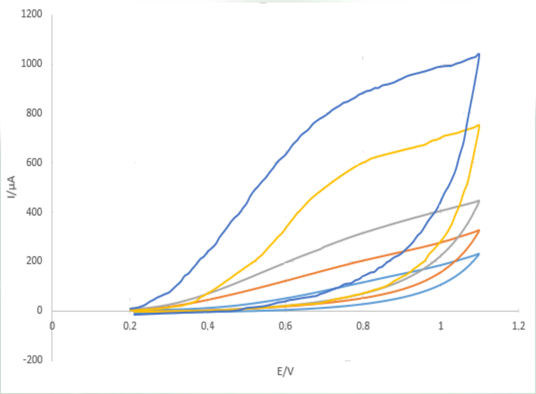

Fig 1. Cyclic voltammograms of the enzyme electrode at scan rate of 50 mV/s, without L-phe, 0.5, 1, 2, 2.5 mM,

Keywords: *Electrochemical biosensor;Graphene nano-structures; Phenylalanine; Carbon-ceramic*

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MnO_2/graphene Nanocomposite Electrode Using for Supercapacitors

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Abstract

In the new century, energy storage has emerged to be one of the major topics, of various power source devices, supercapacitors, also known as electrochemical capacitors (ECs), have raised much attention in the field of applied electrochemical energy conservation/storage systems. Supercapacitors are electricity storage devices between conventional capacitors and rechargeable batteries. They have a wide application in electric vehicles, portable electronic devices, memory back-up devices, large industrial equipment [1]. By contrast with traditional capacitors, supercapacitors offer advantages of faster dynamics of charge–discharge, higher power and energy density, longer cyclic life, and lower maintenance. In order to increase the energy density of supercapacitors, electrode materials with higher active surface area and conductivity are required. Carbon nanomaterials, in particular as electrode materials for supercapacitors, have attracted the attention of the scientific community in electrochemical double layer capacitors (EDLCs). As a typical carbon material, graphene, with sp2-hybridized carbon atoms packaged into a honeycomb lattice structure, is identified as having great chemical and thermal stability, high mechanical flexibility, superior electrical conductivity, and large surface area. However, the maximum capacitance is limited by the active electrode surface area and can't meet the requirements for a capacitor [1]. Compared with one dimensional carbon materials, the unique planar structure of graphene makes it easier and more flexible to integrate with metal oxides. Various noble and transition metal oxides such as MnO_2, RuO_2, NiO, and SnO_2 were used as electrode materials for pseudocapacitors. Among these oxides, MnO_2, due to its high theoretical specific capacitance (1370 Fg^{-1}), low cost, abundance, and environmentally friendly nature, has drawn tremendous attention as an active electrode material [1-3]. But the major challenge is to increase the performance of the metal oxide that makes adding materials to it in order to achieve

this goal. Therefore, we have investigated graphene nanosheets with its special feature. Graphene oxide nanosheets were synthesized by using a Hummers method from graphite in our experiment. The graphene thin film will be deposited on the conductive substrate by the suspension of graphene. Then, MnO_2 nanostructures were electrodeposited from a mixture of two different types of solutions (0.1 M Na_2SO_4 and 0.1 $Mn(CH_3COO)_2$) onto the graphene film. We have deposited nanostructured MnO_2 materials on graphene through an electrochemical deposition process. The mass loading of MnO_2 can be well controlled by adjusting the deposition current and deposition time. The morphologies of the graphene–MnO_2 nanocomposites were examined by scanning electron microscopy (SEM). FT-IR spectra of products in KBr pellets were recorded. Power X-ray diffraction (XRD) patterns of samples were detected using a Philip XRD X'PERT PRO diffractometer with Cu Ka X-ray radiation. To test the electrochemical properties of the samples, a classical three-electrode cell was used electrochemical workstation. The electrochemical behaviors of the supercapacitor systems were estimated by cyclic voltammograms (CV) and galvanostatic charge–discharge and electrochemical impedance spectroscopy (EIS). The synergistic effect between the high conductivity of graphene and pseudo capacitance of MnO_2 generates large capacitance of composites. The GO/MnO_2 composite exhibits a considerable specific capacitance current density in 1 M Na_2SO_4 aqueous solution and good long-term cycle stability.

Keywords: *Supercapacitor, Electrode, MnO_2, Graphene*

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Chemical Modification of Ag Nanoparticles Coated Cotton Textile with Valdecoxib Derivate and Study of its Electrochemical Behavior

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Abstract

Electrically conductive textiles have been of increasing research interest due to potential application in clothing as well as in the medical and military fields, as sensors, actuators, electromagnetic shields etc. In this study, conductive cotton textile was prepared by in situ synthesis of Ag nanoparticles using inkjet printing on surface textile. For preparation of flexible electrode, conductive textiles was coated with hydrophobic agent contain potassium trimethoxy methyl silane, then with waterproof glue (PVA) was attached on plastic film. Different printing procedures for achievement of highest conductivity were examined, that its results are presented in Table 1.

Table 1- The surface resistance of printing procedures with inkjet printer on fabric

printing procedures	Width (mm)	surface resistance (Ω) of two point with distance 2 cm
AS	5	8700
ASA	5	1300
AASSAA	5	150
AAAASS	5	8

* A= Once printing Ascorbic Acid solution (2.0 M) and S= Once printing $AgNO_3$ solution (1.0 M).

Electrochemical experiments were performed with a μ-Autolab potentiostat (Eco Chemie Utrecht) with GPES 4.9 software. The cell was equipped with a flexible electrode as a working electrode, a platinum electrode as an auxiliary electrode and a Ag/AgCl /3 M KCl as a reference electrode. The prepared flexible electrodes was immersed in 0.1 M phosphate buffer solution (pH 7.0) and cyclic voltammetry (CV) experiments was conducted in − 0.4 to 1.1 V at a sweep rate of 20 mV/S. The resulted CVs were compared to confirm the performance of the every printing procedures (Fig. 1). Redox characteristic peaks is not observed in of the graphs of a, b and c, however, in graph (d), an oxidation peak and a reduction peak is observed at 0.58 V and - 0.073

V, which are related to the redox of silver. Thus AAAASS procedure as proper design to prepare a flexible electrode is chosen. The Valdecoxib derivative modified Flexible Electrode (VFE) was prepared by the self-assembling technique, just by placing 20.0 μL of a 1.0 mM Valdecoxib derivative solution directly onto the FE surface and drying it at room temperature.

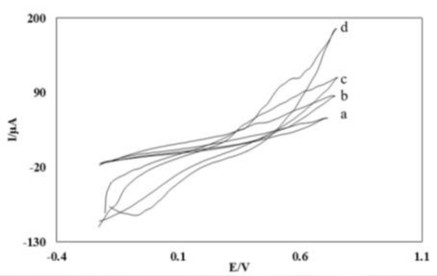

Fig. 1. Cyclic voltammogram of Ag nanoparticles coated textile with procedure (a) AS; (b) ASA; (c) AASSAA; (d) AAAASS in 0.1 M phosphate buffer solution (pH 7.0).

The CVs of VFE in a 0.1 M phosphate buffer (pH = 7.0) at various scan rates (10-70 mV/S) are shown in Fig. 2. As shown in Fig. 2, the ratio of cathodic-to-anodic peak currents obtained at various scan rates is almost constant. Furthermore, the cathodic and anodic currents increase linearly with the scan rate in the whole worked scan rate potentials as predicted theoretically for a surface-immobilized redox couple. The linear dependence indicates that the nature of the redox process is diffusionless and controlled.

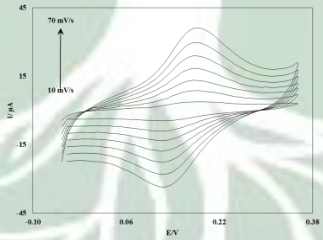

Fig. 2. Cyclic voltammetric responses of VFE in 0.1 M phosphate buffer (pH = 7.0) at different scan rates.

***Keywords**: Flexible sensor, Valdecoxib, ink jet print, silver nanoparticle, conductive textile.*

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Optimization of a cerium(IV) carbon paste electrode based on 2-hydroxy-1, 4-naphthoquinon / MWCNTs by using experimental design

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Abstract

Box–Behnken designs were used as experimental design method to optimize the influence of ingredients of membrane on the electrode performance. A nanocomposite was designed by using 2-hydroxy-1, 4-naphthoquinon as ion carrier with multi-wall carbon nanotubes (MWCNTs), in order to determination of Ce(IV). Box–Behnken response surface was led to find a model for optimizing the response. The best performance was obtained with 5 % wt of lawsone, 10 % wt of MWCNTs, 20 % wt of paraffin oil and 65 % wt of graphite powder. The optimized membrane electrode shows a Nernstian response (15.08±0.2 mV decate^{-1}) toward Ce(IV) ions in linear range from 1.0×10^{-7} to 1.0×10^{-2} mol L^{-1} with a detection limit of 5.0×10^{-8} mol L^{-1}. The proposed sensor was employed in pH range of 4 to 8 with a fast response time (10 s).

Keywords: *Box-Behnken design, Cerium(IV) Carbon paste electrode, Multi-wall carbon nanotubes, Potentiometry; Lawsone*

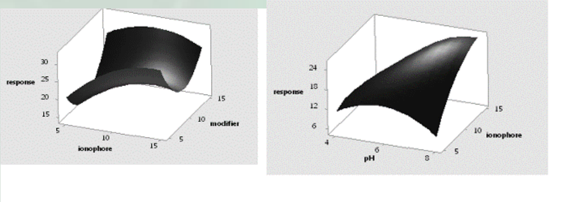
Introduction

Carbon paste electrode is one kind of ion selective electrode that has some advantage over other membrane electrodes. An experimental design is a plan for assigning experimental units to treatment level and the statistical analysis associated with the plan. In this research, we used statistical design of experiment for optimization of a Ce(IV) selective carbon paste electrode which is based on 2-hydroxy-1, 4-naphthoquinon. The ultimate goal of this research was to study the interaction of factors and modeling the slope of calibration curve as analytical response. So the effect of main factors such as ionophore (lawsone), modifier (multiwall carbon nanotubes), and pH were investigated and optimized.

Methods

Desired amount of 2-hydroxy-1,4-naphthoquinon, graphite powder, paraffin oil and MWCNT were thoroughly mixed and then transferred into a glass tube, of i.d. 5 mm and a height of 3 cm. After the mixture was uniform as well as possible, to avoid the formation of air gaps, the paste was packed carefully in to the tube. This can prevent an increased in the electrical resistance of the electrode .Then electrical contact was made by inserting a copper wire in to the opposite end. The working surface of the electrode was polished by using soft abrasive paper.

Results and discussion



Conclusions: The fabricated sensor with optimized structure has many advantages such as wide linear range, low detection limit, fast response time, good selectivity with respect to different metal ions in pH range from 4 to 8. As well as, it was used for determination Ce(IV) sample water

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Synthesis and Investigation of Nano $LiMn_2O_4$-rGO as a Positive Electrode in Energy Storage Systems

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Abstract

Supercapacitors (SCs) deliver high power density but low energy density [1]. One way for increasing the energy density of a SC is improving the efficiency of charge storage that is affected by the electrode materials [2]. Mn-based oxides such as $LiMn_2O_4$ (LMO), have economic and environmental advantages and excellent electrochemical performance as attractive positive electrode materials in aqueous-electrolyte supercapacitors [3,4]. The performance of SCs can be improved via shortening the ionic diffusion length and providing large surface areas for electrode reactions and the easiness of electron transfer. In this regard, the nanosize materials and composites of high conductive compounds such as reduced Graphene Oxide (rGO) [1,5,6] play the main role. In this work, we have synthesized nano LMO oxides and LMO-rGO composites by a simple, low temperature and fast hydrothermal method. Thus, these materials have been investigated as positive electrode materials by CV, chrono-potentiommetry, and EIS. After optimization of the ratio of the composite components, that is LMO: GO ratio of 40:60% as positive electrode material, the composite was characterized with different techniques including XRD, Raman, EDX, SEM and TEM as well as BET and TGA analyses. The LMO-rGO electrode shows a wide potential window of 1.1 V in Li_2SO_4 aqueous electrolyte. The specific capacitance of the composite electrode at 1 A/g is 215 F/g, which shows superiority over an LMO electrode, 130 F/g. The 65% increase in capacitance of the material shows a synergistic effect of rGO on electrochemical performance of the LMO electrode.

Keywords: *$LiMn_2O_4$, Graphene, Supercapacitor, Hydrothermal synthesis, Energy Storage.*

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Synthesis of Ni-Co nanocomposite based on nitrogen doped graphene for supercapacitor

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Abstract

Nickel-cobalt binary oxide/reduced graphene oxide (NiCo/N-RGO) composite with high capacitance is synthesized via mild method for electrochemical capacitors. As an appropriate matrix, RGO is beneficial to form homogeneous structure and improve the electron transport ability. Graphene is synthesized from graphite electrodes using ionic liquid-assisted electrochemical exfoliation.

Herein, we report the synthesis and electrochemical properties of heteroatoms -doped reduced graphene oxide (NRGO) supported Co, Ni and NiCo nanocomposites. We demonstrate the efficient doping of reduced graphene oxide (RGO) by hetroatoms and its capacitive performance was calculated by cyclic voltammetry and charge–discharge cycling in 6M KOH solution.

***Keywords**: Nanocomposite, Nickel, Cobalt, Super capacitor, Graphene, Hetroatoms*

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Development of electrochemical aptasensor for point of care detection of cardiac Troponin I biomarker

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Abstract

In recent years, myocardial infarction (MI) has posed a threat to human health, leading to higher rates of mortality and morbidity. According to the latest "world health organization" data, published in May 2014, heart disease deaths in Iran reached 29% of total deaths [1]. Among different biomarkers, cardiac Troponin I (cTnI) shows the highest specifity with the lowest amount in healthy people. Following myocardial damage Troponin complex is broken up, releasing into the blood stream. After 4-8 hours, cTnI increases from 0.1 ng/ml to a detectable range as high as 100 ng/ml and remains elevated for 4-10 days after the onset of MI. Therefore, the awareness of the concentration of this biomarker, considered as "gold standard", gives the healthcare team to make vital decision in order to prescribe the right medicine in right time [2]. Meanwhile, a method capable of evaluation the amount of this biomarker with very fast response and acceptable analytical criteria plays a significant role. In this regards, electrochemical biosensors such as aptasensors are important in early diagnosis of MI where time-consuming and expensive laboratory tests are replaced with a range of point of care, low cost and friendly used devices [3]. Aptamers with the specific target binding are a powerful alternative for antibodies which have opened new horizons to achieve such desirable sensors [4].

The present study tries to introduce a label free single-step detection of cTnI in human blood serum. The thiolated aptamer has been immobilized on surface of screen printed gold electrode. The impedance spectroscopy and differential pulse voltammetry have been applied to monitor the attachment of cTnI with aptamer and record the analytical signal. The aptasensor works on signal-off mode which decreases the electrochemical signal of redox probe due to the capture of cTnI by an aptamer (Figure 1). The sensor shows the favorable correlation between the concentration of cTnI and analytical signal which has been led to the promising detection limit. It

is anticipated that the high selective aptasensor for cTnI and enormous potential of mass-production could be readily applicable for the accurate early diagnosis of MI.

Keywords: *Myocardial infarction, Cardiac troponin I, Label-free detection, Signal-off mode, Aptasensor*

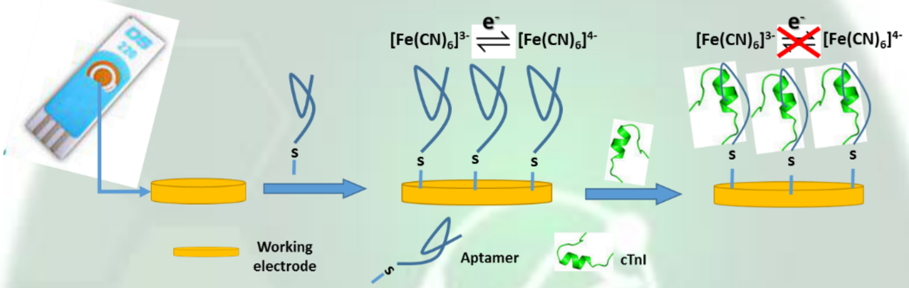

Figure 1: Signal off mode of aptasensor

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Anodic stripping voltammetric determination of copper (II) ions using a graphene quantum dot Modified pencil graphite Electrode

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Abstract

Copper is essential to all living organisms as a trace nutritional mineral because it involves in the synthesis of hemoglobin, a variety of enzymes, and the metabolism of the body [1-3]. However, copper deficiency or elevated levels of copper can bring about opposite health effects. Due to physiological importance of copper and widely usage of it in industrial and agricultural sectors, determination of copper in various matrices is very important and numerous analytical techniques have been used for the accurate and sensitive determination of trace quantities of copper [4-10]. Among these, electrochemical techniques have attracted extra attention because of many advantages such as simplicity, cost effectiveness, small instrumentation and etc. Graphene quantum dots (GQDs), a new kind of carbon nanomaterials, with great surface area and quick electron transfer ability are one of the best electrode modifiers which can increase the rate of electrochemical reactions and attracted more attention as electrode modifier [11]. Recently, Wang et. al developed graphene quantum dots as a fluorescent sensing platform for highly efficient detection of copper (II) ions [12]. In this work, we described a simple and sensitive electrochemical approach for the determination of low concentration of Cu^{2+} ions using GQD modified pencil graphite electrode by square wave adsorptive stripping voltammetric method. The sensing mechanism could be attributed to the formation of complex between Cu^{2+} ions and oxygen containing groups in GQDs which result in increased SWV signal compared to bare electrode. Optimization of various experimental parameters such as pre-concentration time, pre-concentration potential, pH, and buffer type which influenced the performance of the sensor, were investigated. Under optimized condition, GQD modified electrode was used for the analysis of Cu^{2+} in the concentration range from 0.05 to 4 nM, and a lower detection limit of 0.012 nM with

good stability, repeatability, and selectivity. Finally, the practical applicability of GQD-PGE was confirmed via measuring trace amount of Cu (II) in water samples. The GQD-PGE surface could be regenerated by exerting more positive potential than the stripping potential of the Cu (II) ion and then used for another deposition. This is the first usage of untreated graphene type nano particles, GQD, for the simple, cheap, sensitive and selective determination of copper ions with excellent performance and low detection limit.

Keywords: *Graphene quantum dot, Electrochemical detection, Cu (II) ions, Adsorptive stripping voltammetry*

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Amperometric determination of H_2O_2 based on Prussian blue @ palladium nanoparticles/graphene oxide nanocomposite modified electrode

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Abstract

Hydrogen peroxide (H_2O_2), a hazardous chemical, is known to be developing severe health issues, widely used in various fields, involved in several biological events and intracellular pathways and is the by-product of oxidase enzyme-based catalyzed reactions. Therefore, it is very important to develop rapid, simple, sensitive, inexpensive, reliable, and accurate H_2O_2 detection sensors. Up to date, various analytical methods have been used for the accurate and sensitive determination of H_2O_2 [1-5]. Among these methods, electrochemical techniques have received extensive interest compared with the existing traditional methods. Nonenzymatic H_2O_2 sensors based on nanoscale materials have attracted much attention due to their unique characteristics, such as high sensitivity, large specific surface area, low detection limit, wide respond range and chemical stability [6]. To date, plenty of nanomaterials have been used to achieve a better sensitivity and selectivity in the enzyme-free H_2O_2 sensors [5, 7, 8]. Transition metal hexacyanoferrates (Mhcf) have achieved significant interest due to their important properties such as magnetism, electrochromism displays, electrocatalysts, and applications in sensor design and batteries. Prussian blue (PB) has been described as ‘‘artificial peroxidase’’ for H_2O_2 electrocatalysis. However, rapid desorption of PB film from electrode surface is the main problem that resulted in losing its catalytic activity. In order to overcome this problem, researches focused on developing methods for the synthesis of nanostructured PB objects and their deposition onto various conductive materials, such as carbon nanotube, graphene, bulk metal substrates and other substrates [9, 10]. The performance of the composite materials relies on the properties of the individual components, and on the effective structural combination of the components [11]. Here, we fabricated a new triple-component non-enzymatic sensor by sequential deposition of Pd and PB nanoparticles on GO modified PGE for the determination of

H_2O_2. To create close contact between PB and GO we have electrodeposited Pd on GO modified PGE and used this electrode for the chemically deposition of PB because noble metals are actively promote the growth of PB. The resulting sensor combines the advantages of GO, Pd and PB nanoparticles and show good sensitivity and excellent electrocatalytic ability.

This modified electrode was characterized by several techniques including scanning electron microscopy (SEM), energy dispersive X–ray spectroscopy (EDX), and cyclic voltammetry (CV).

The sensor showed significantly better electrocatalytic activity for the reduction of hydrogen peroxide in comparison with the single GO/PGE, PB/GO/PGE and Pd/Go/PGE modified electrodes. This was attributed to the synergistic effect of PB, Pd and GO nanoparticles. Also, this proposed sensor demonstrated an overall high level of performance for the analysis of H_2O_2 using hydrodynamic amperometry in the concentration range from 0.2 µM to 0.5 mM and detection limit of 0.049 µM with good stability, repeatability, and selectivity.

Keywords: *Prussian blue, Hydrogen peroxide reduction, Electrocatalysis, graphene oxide, Pd nanoparticles*

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Synthesis and electrochemical charactristics of NiTi alloy nano composite inorder to use in supercapacitor

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Abstract

Full density NiTi samples with a composition of Ti-50 wt% Ni are fabricated using hot isostatic pressing (HIP), followed by the HPT process at room temperature, with an applied pressure of 6 GPa for 10 turns. The nanostructural analysis reveals that the HIP-processed samples with a B2-NiTi phase evolve into significant grain refinement after HPT process and an interwoven B2-B19′ nanocrystalline/amorphous structure formed, leading to increased hardness in these samples. We demonstrate the efficient synthesis and its capacitive performance was calculated by cyclic voltammetry and charge–discharge cycling in 6M KOH solution. It is found that the NiTi samples with nafion and PTFE solution electrode exhibits superior capacitive performance with high capability at about 500 F g^{-1} at 2 A g^{-1}, excellent rate capability, and enhanced electrochemical stability with 91.7% retention after 800 continuous charge-discharge cycles even at a high current density of 2 mA cm^{-2}.

Keywords: Nano composite, Nickel, Titanium, Supercapacitor

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Investigation of Metoclopramide tablet prohibiting effect on mild steel corrosion in 0.5 M phosphoric acid environment

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Abstract

In this study, we investigated the effect of Metoclopramide as corrosion inhibitor for mild steel (MS) in 0.5 M phosphoric acid solution by electrochemical measurements such as tafel polarization and electrochemical impedance spectroscopy. The inhibition efficiency was found to grow with increasing inhibitor concentration. Metoclopramide showed 97% inhibition efficiency at concentration of 300 ppm. Adsorption of the inhibitor follows Langmuir adsorption isotherm. The effect of temperature on corrosion rate in absence and presence of these drug was studied too. Some thermodynamic parameters were computed from the effect of temperature on corrosion and inhibition processes. Surface characterization techniques (FTIR and SEM) are used to ascertain the nature of the protective film, as well.

Keywords: *Corrosion Inhibitor, Potentiodynamic Polarization, Electrochemical Impedance Spectroscopy, Adsorption isotherm, Mild steel, Metoclopramide*

Conductometric study of complexation reaction of Dibenzo-24-crown-8 with Ce^{3+} cation in some non-aqueous solvents and their binary mixture

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Abstract

Pedersen first discovered the complexation of crown ethers with alkali metal ions [1]. Crown ethers are one of the most widely studied family of host compounds in the field of supramolecular chemistry, involving non-covalent interactions [2]. The main characteristic of these compounds is the complexation of their ether oxygens with various ionic species. Formation of a complex between a macrocyclic ligand and a cation, depends on many factors including: the relative size of the cation and the crown cavity, cation charge and type, nature of counter anion, number and type of donor atoms, substituents at the crown molecule, electron density of the crown cavity, the crown ether ring flexibility, and also the effect of solvent [3,4]. One of the techniques which is used for study of complexation process is conductometry [5]. This technique is a sensitive and inexpensive method with a simple experimental arrangement for such investigations [6]. In the present work, the complex formation between of dibenzo-24-crown-8 (DB24C8) with Ce^{3+} cation in acetonitrile (AN), methanol (MeOH), tetrahydrofuran (THF) and also in the binary mixtures of acetonitrile-methanol (AN-MeOH), acetonitrile-tetrahydrofuran (AN-THF) and tetrahydrofuran-methanol (THF-MeOH) was studied at various temperatures using conductometric method. The conductance-mole ratio data show that the stoichiometry of the complex which is formed between the macrocyclic ligand and the rare earth metal cation is 1:1 [M:L]. The stability constant of the $(DB24C8.Ce)^{3+}$ complex at each temperature, was determind using a computer program, GENPLOT. The obtained results show that the stability order of the complex at 15°C and 35°C in pure non-aqueous solvents is: THF > AN > MeOH and in the case of the mixed solvent solutions, the stability constant of the complex, changes with the nature and also composition of solvent systems. The standard thermodynamic quantities (ΔH_c° and ΔS_c°) of the complexation reaction were evaluated by the temperature dependence of formation constant,

using the van't Hoff plots. The results obtained in this study, show that the values of thermodynamic of the complexation reaction is influenced by the nature and composition of the binary mixed solvent solutions.

Keywords: *Dibenzo-24-crown-8, Ce^{3+} cation, Non-aqueous solvents, Conductometry*

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Coupling of microextraction and voltammetry techniques for the determination of hemin in human serum samples

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Abstract

Extra concentrations of hemin (ferriprotoporphyrin) are toxic since it may intercalate in lipid membranes and catalyze the formation of hydroxyl radicals and the oxidation of low density lipoproteins, damage mitochondrial DNA of hepatocytes, inhibit cytochrome P450-catalyzed reactions of human liver microsome, cause the oxidation of membrane components which may promote cell lysis and death (1, 2). So, determination of hemin concentration is of importance. However, a sample preparation step seems to be inevitable prior to the determination due to the complexity of the biological samples. Dispersive liquid–liquid microextraction (DLLME) is a very simple and rapid method for the extraction and separation of various analytes from complex samples (3). Ionic liquids (ILs) are green solvents comprised of asymmetric organic cation and organic or inorganic anion, so are liquids which represent a new class of non-aqueous but polar solvents with high ionic conductivity (4). In the present work, an ammonium-based task-specific ionic liquid containing salicylate as anion was synthesized and used for the extraction of hemin Hemin is extracted into the ionic liquid after interaction with the anion of the ionic liquid. Voltammetric determination followed the extraction process. For this purpose, the IL-rich phase separated from the sample was placed on the surface of a glassy carbon electrode with the help of nafion and ethanol. In this way, the IL was used as both extracting solvent (due to its polarity and water-immiscibility) and electrode modifying agent (due to its ionic structure). The peak current obtained from the electrochemical reduction of hemin was used as the analytical signal correlated to the concentration of hemin. Different experimental parameters affecting both the extraction and electrochemical processes were optimized. Under the optimized conditions, a linear concentration range of 0.020-2.60 μM with a detection limit of 3.16×10^{-3} μM was obtained. The

presented methodology was successfully applied to the determination of hemin in human serum samples indicating its applicability to complex media.

***Keywords**: Hemin, Ionic liquids, Microextraction, Voltammetry*

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Electrochemical oxidation of polybutadiene/organoclay nanocomposite by silver (II)

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Abstract

Electrochemically generated Silver (II) was used for mediated electrochemical oxidation (MEO) of vulcanized polybutadiene/organoclay nanocomposite (BRN). X-ray diffraction (XRD) pattern and transmission electron microscopy (TEM) pictures verified intercalated organoclay/Cloisite 20A morphology in the BRN matrix. Atomic force microscopy (AFM) revealed that surface roughness of BRN samples were considerably enhanced after oxidation. Scanning electron microscopy (SEM) micrographs showed that weak boundary layer (WBL) on the rubber surface was clearly removed after 600 seconds, further oxidation led to surface degradation due to creation of holes and cracks.

Keywords: *Polybutadiene, Organoclay nanocomposite, Silver(II), Mediated electrochemical oxidation, Characterization.*

Introduction

Surface modification of Polybutadiene/organoclay nanocomposites by appropriate method for applications such as adhesion improvement is important in rubber industry [1]. MEO method as a clean surface modification technique has some advantages such as availability in low temperature and pressure, reversibility of oxidizing ion and high oxidation efficiency. These advantages make MEO as an effective method for surface oxidation of different polymers in the last years [2]. Increase in surface roughness and enhancement in adhesion properties by removing the impurities and different additives (WBL) from the surface without degrading the surface is the major aim in rubber surface modification [3]. Therefore, in this study, silver (II) ion was generated as mediator to oxidize the PB rubber surface. Then its surface roughness and morphology were studied before and after different oxidation times.

Methods

Based on ASTM 3189-06, BRN was formulated, vulcanized and cut into 1×3 cm^2 dimension with of 1 mm thickness. For producing silver(II), catholyte was prepared from nitric acid and deionized water with a concentration of 10 Normal. Anolyte was prepared from 0.5 Molar solution of silver nitrate in 6 Normal nitric acid media.

Results and discussion

Figure 1 illustrates the XRD pattern and TEM image of BRN sample. The characteristic diffraction peak , which was observed at 2θ = 1.50 (The d-spacing of Cloisite 20A calculated from Bragg's law was found to be 62.2 Å larger than pure cloisite 20A (d001=24.3 Å)) and TEM image indicated intercalated structure in the BRN matrix.

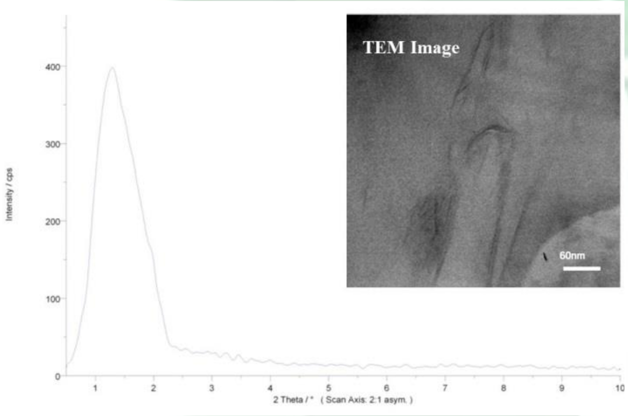

Fig11. XRD pattern and TEM image of BRN sample.

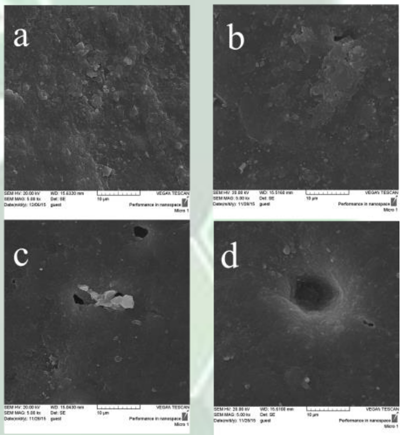

Fig 12. SEM micrographs of BRN surface a) before and after oxidation b) 300, c) 600, and d) 1200 sec of oxidation.

Obtained surface roughness parameters by AFM showed that maximum height of roughness increased from 155 nm to 316, 393 and 451 nm after 300, 600 and 1200 seconds of oxidation by silver(II), respectively. Figure 2 shows the SEM micrographs for top views of the examined rubbers before and after oxidation by silver (II) for 300, 600 and 1200 sec. As obvious, BRN surface had heterogeneous morphology before oxidation due to existence of WBL. The SEM micrographs clearly show that the WBL has almost completely been removed till 600 sec of oxidation but after that surface degradation was occurred due to creation of holes and cracks.

Conclusion

XRD pattern and TEM results revealed intercalated organoclay/cloisite 20A morphology in the BRN matrix. AFM presented surface roughness increased after oxidation. SEM micrographs shows that surface morphology changed clearly and WBL was removed completely after 600 seconds, further oxidation led to surface degradation.

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Voltammetric determination of tetracycline at the surface of poly (thionine)-modified carbon nanotube paste electrode

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Abstract

Tetracylines (TCs) produced by Streptomyces spp. are a large family of antibiotics used in human and veterinary medicine due to their broad-spectrum activity against most Gram-positive and Gram-negative bacteria (1). When tetracycline drugs are administered by laymen, as in most cases, correct dosages and withdrawal periods are unlikely to be observed. This raises concerns that animal tissue intended for human consumption might be contaminated with residues of TCs (2). Herein, a simple, rapid, accurate and sensitive electrochemical sensor is described for the determination of trace amounts of tetracycline based on a poly (thionine) film which is effectively shuttle electrons between the analyte and the base electrode. Generally, the preparation of conducting films by electropolymerization of a monomer which itself was a redox mediator has been demonstrated to enhance the sensivity of the electrochemical sensor (3). In the present work, electropolymerization of thionine on the surface of a carbon nanotube paste electrode provided a chemically modified electrode which responded linearly to the concentration of tetracycline, shifted the peak potential of tetracycline negatively and increased the peak current. Electrochemical behavior of tetracycline at the surface of poly(thionine)-modified carbon nanotube paste electrode was fully characterized using cyclic voltammetry and chronoamperommetry. Moreover, the effect of different experimental parameters including pH, on the electrochemical current of tetracycline was evaluated. Under the optimized conditions, the proposed electrode showed linear dependence of peak current with the concentration of tetracycline within the range of 0.50-20.0 µM with the detection limit of 0.46 µM. Finally, tetracycline tablet and urine samples were analyzed for tetracycline with the presented method using standard addition. The obtained recoveries indicated the accuracy and applicability of the method.

Keywords: *Tetracycline, Poly (thionine), Carbon nanotube paste electrode, Voltammetry*

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Electrochemical synthesis of Ni nanostructures on paper electrode for simultaneous sensing of dopamine, tryptophan and ascorbic acid

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Abstract

In this work we used a simple strategy for simultaneous determination of dopamine-hydrochloride (Dph), tryptophan (Trp) and ascor-bic acid (AA) by electrochemical synthesis of conductive Ni nanostructures (band gap of 1.0eV) on the surface of multiwalled carbon nanotube nanocomposite modified paper electrode (NiNPs/MWCNT/PE). Scanning electron microscopy (SEM), electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and differential pulse vol-tammetry (DPV) were used to characterize the performance and microstructure of the sensor. The diffusion coefficient (D) and the kinetic parameters such as electron transfer coefficient (α) and catalytic rate constant (k) for Dph, Trp and AA were also determined using electrochemical approaches [1]. The cyclic voltammetry method showed Dph, Trp and AA oxidation reaction with irreversible characteristics was diffusion-controlled at low scan rates. Under the optimized experimental conditions Dph, Trp and AA give linear response over the range of 0.008 - 70.0 µM, 0.006–50.0 µM and 0.01.0–40.0 µM, respectively.The lower detection limits were found to be 0.23 for Dph, 0.10 for Trp and 0.79 nM for AA. The modified electrode showed good sensitivity and stability by better response than to other reported papers [2-3].The practical application of the modified electrode was demonstrated by measuring the concentration of Dph, Trp and AA in blood serumand pharmaceutical samples.

***Keywords**: Electrochemical deposition, Ni nanostructures, Dopamine-hydrochloride, tryptophan and ascorbic acid, Nanomolar sensor*

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Chloride voltammetric Sensor Based On Aminated Carbon Nanoparticles

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Introduction

Nano-carbon based electrodes e.g. based on carbon nanotubes, carbon nanofibers, graphene, or carbon nanoparticles are of interest in electrochemical processes due to their often highly active surface characteristics and their ease of functionalisation. The modification of functional groups at carbon surfaces provides an important tool for achieving chemical selectivity [1]. Chloride ion concentration is an important parameter for various biological and environmental applications. Chloride is a key parameter of water quality and salinity. In mechanical industries chloride is a major contributor to corrosion of metal components in steam-generating systems. Chloride is also one of the major contributors to reinforcement corrosion in concrete, especially for structures near sea water or which are exposed to deicing salt. The chloride ion concentration inside the reinforced concrete has been linked to the corrosion process and it is therefore highly desirable to be able to detect the chloride ion concentration level. Thus, keeping in view these applications, the development of a long-term and reliable chloride ion sensor is of great importance [2]. In this study, the surface functionalized aminated carbon nanoparticles have been prepared and characterized. A novel, inexpensive, highly simple, and disposable sensor for the determination of chloride ions has been developed. It is based on the systematic shift of the voltammetric peak potential of a Hg(II) species in presence of chloride ions. Differential pulse voltammetry has been applied for sensitive determination of chloride ions in real samples. The disposable character and simplicity of the device provides an interesting alternative to the most frequently used potentiometric method.

Methods

Voltammetric experiments were performed using a Metrohm Computrace Voltammetric Analyzer model 797 VA. A conventional three-electrode. The modification of glassy carbon electrode has been performed by casting method. The modified electrode has been used for voltammetric measurements.

Results and Discussion

Morphology and structure of the resultant product were characterized by SEM, FT-IR spectroscopy and electrochemical techniques (Electrochemical Impedance Spectroscopy and cyclic voltametry). It was observed that the voltammetric peak of a Hg(II) species at the surface of GCE/ CNP-NH_2 electrode shifts when chloride is added to the sample. The systematic shift of the peak potential of a Hg(II) is related to the amount of chloride. The potential shift increase with chloride concentration from 10^{-7} M to 0.1 M, and a linear relationship between peak potential and the logarithm of chloride concentration was obtained in this concentration range (figure 1).

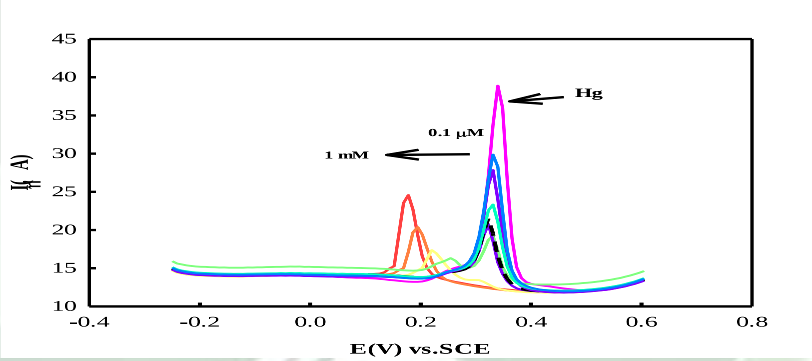

Fig 1. Differential pulse voltammograms of 1.0×10^{-5} M Hg in a batch containing different concentrations of chloride ion. Scan rate 50 mVs^{-1}.

Conclusion

The covalently modification of carbon nanoparticles with ethylene diamine functional groups is demonstrated. The new carbon nanoparticle substrate is versatile and can be employed for sensitive and selective determination of chloride ions. Nowadays, the development of alternative methods for chloride determination in waters is very interesting due to the problems associated to potentiometric methods, generally used in routine determinations. This work describes the successful development of a low cost method for the detection of chloride ion, which is based on the shift measurement of voltammetric peak potential of mercury, when this ion is present in a solution.

***Keyword**: Carbon Nanoparticle, Covalenty Modification, Voltametry Sensor, Chloride.*

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Antioxidant Investigation of Marjoram using Aminated Carbon Nanoparticles/Glassy Carbon Modified Electrode

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Introduction

Development of new methods for determination of antioxidants in natural compounds has received considerable interests in recent years. Various methods such as chromatography, spectrophotometry and capillary electrophoresis (CE) have been developed for this purpose. These techniques are limited by poor accuracy or the need for expensive instrumentation with high operating costs. Among the various reported methods, electrochemical techniques are often preferred because of their high selectivity, rapid detection, low cost and their lack of a substantial sample preparation setup [1]. Marjoram belongs to the mint family. Flowers and leaves are the parts of the plant are used in medicinal preparations. Marjoram is packed with vitamins and minerals, that gives the following health related properties: anti-microbial, anti-septic, anti-inflammatory, anti-depressant, anti-viral and antioxidant. Gallic acid is a natural antioxidant that not synthesized in the human body [2]. It has reported that the main compound responsible for antioxidant properties of Marjoram is Gallic acid. In this study, glassy carbon electrode has been modified by using Alginate/CNP-NH_3^+ bilayer. The formation of bilayer is based on electrostatic interaction between two components. The modified electrode has been studied using cyclic voltammetry, electrochemical impedance spectroscopy (ESI) and scanning electron microscopy (SEM). The modified electrode has been employed for determination of gallic acid. The gallic acid has been used as standard for antioxidant properties of Marjoram.

Method

Voltammetric experiments were performed using a Metrohm Computrace Voltammetric Analyzer model 797 VA. To evaluate the electrochemical sensing ability of the Alginate/CNP-

NH_3^+ through Gallic acids, modification of glassy carbon electrode has been performed by casting method. First 10 μL of alginate solution was casted on the GCE surface and dried in the air to evaporate solvent. Then 10 μL of CNP-NH_3^+ suspension was casted on the GCE surface and dried in the air to evaporate solvent too. The modified electrode has been used for voltammetric measurements.

Result and discussion

A glassy carbon electrode modified in situ with bilayer of alginate/CNP-NH_3^+, and the ability of electrode for sensing in Marjoram was investigated. Differential pulse voltammetry has been employed as a sensitive method for determination of gallic acid that exists in Marjoram using standard addition.

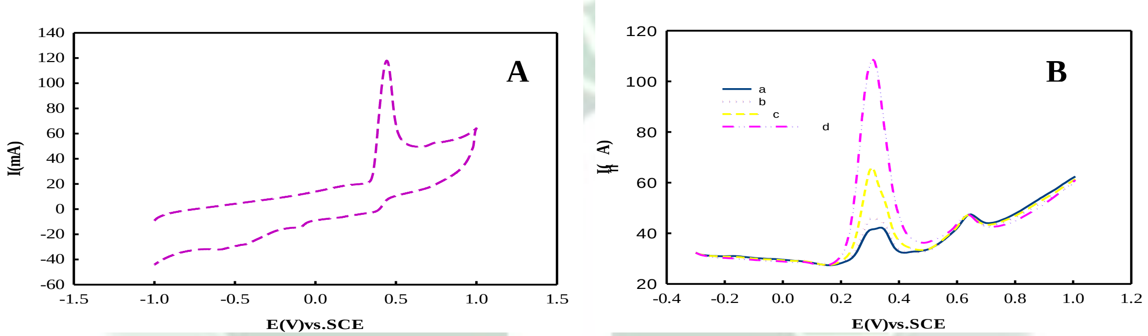

Figure 1.(A) Cyclic voltammograms of 1 mM GA in phosphate buffer of pH= 3 at the surface of GCE/Alginate/CNP-NH_3^+, Scan rate is 100 mV/s. (B) Differential pulse voltammograms of the methanol extracts of Marjoram (a), in presence of 5 μM (b),50μM (c) and 500μM(d) GA solution in phosphate buffer of pH= 3 at the surface of GCE/Alginate/CNP-NH_3^+, Scan rate is 50 mV/s.

Currents versus GA concentration shows linear relationship from 0.5 μM to 0.1 mM with the correlation coefficient equal to 0.99 and limit of detection for modified electrode is: 0.43 μM

Conclusion

The present study demonstrates an excellent approach for the development of a voltammetric sensor for investigating antioxidant properties of some herbs such as Marjoram.

Keywords: *Marjoram, Ascorbic acid, Gallic acid, Modified electrode, Voltammetry, Antioxidant*

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Electrophoretic deposition of uniform graphene oxide thin film on porous silicon substrate

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Abstract

In present work, a uniform thin film of graphene oxide (GO) was deposited on porous silicon (PS) substrate. GO was successfully synthesized using the modified Hummer's method and was efficiently deposited onto photo-electrochemically etched PS substrate using electrophoretic deposition (EPD) technique. The morphology and structural properties of synthesized and deposited layer was investigated using field emission scanning electron microscopy and Raman spectroscopy. The results showed that high surface area of porous structure facilitated deposition of GO. Thus, a uniform and high quality thin film of GO was deposited on PS substrate.

Keywords: *Porous silicon, Photo-electrochemical etching, Graphene oxide, Electrophoretic deposition*

Introduction

Due to their extremely large surface-to-volume ratio and enhanced physical properties, porous structure is materials of interest in many applications. Also, graphene and graphene oxide (GO) few layers have attracted much attention due to their superior properties in variant fields[1]. Although, porous structures are suitable substrates for deposition of GO, but there are few reports on this research area. In this paper, GO thin film was deposited on porous silicon (PS) substrate using electrophoretic deposition (EPD) technique. EPD is a low temperature deposition technique that does not require sophisticated physical conditions such as vacuum and high pressure. Moreover, deposition of few layers of charged GO is possible by this technique.

Methods

PS substrate was synthesized using photo-electrochemical etching technique. In this method, n-type silicon wafer (with sheet resistivity of $0.6\ \Omega \times cm$) was cut into 1 cm×1 cm square and was used as anode in electrochemical etching cell. The electrolyte was a mixture of HF (38-40%) andC_2H_5OH (96%) with the volume ratio of 1:4. The etching current density was fixed at 20 mA/cm^2 and the etching process was carried out in 30 min. A 100 W tungsten lamp was placed on top of the cell with a distance of 20 cm for illuminating Si substrate during etching process. Freshly prepared PSi sample was used as a substrate material for deposition of GO using EPD technique. In this method, the electrolyte was colloidal GO flakes in water suspension. A modified Hummer's method with sonication time of 2 h was used for preparing GO flakes. Morphological and structural characteristics of deposited layer were investigated using field emission scanning electron microscopy (FESEM) and Raman spectroscopy.

Results and Discussion

Fig. 1 (a) shows FESEM micrograph of successfully deposited GO layer with high uniformity on porous substrate using EPD technique. Fig. 1 (b) demonstrates Raman spectra of bared PS and GO/PS samples. The peaks at 520 cm^{-1} and 950 cm^{-1}correspond to the phonon vibration in PS and the distinctive peaks at 1350 cm^{-1} and 1600 cm^{-1} are related to GO thin film. The first order of the zone boundary phonons is only observed as a peak at~1350 cm^{-1}, named D-band. The G-band is a result of the doubly degenerate zone center E_{2g} mode and represents the in-plane vibration mode of sp^2 hybridized carbon atoms (the E_{2g} phonon of C sp^2 atoms)[2]. The height of the D band directly depends on the number of the sp^3 carbon atoms of graphene surface. The intensity ratio (I_D/I_G) obtained from Raman spectroscopy showed that the deposited GO thin film consists of oxygen functional groups.

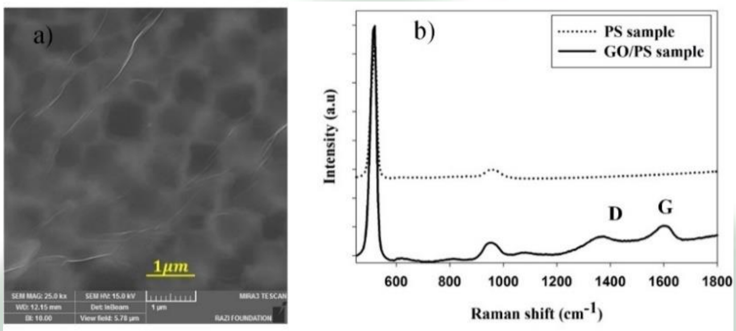

Fig.1 (a) FESEM micrograph of GO few layer on PSi substrate and (b) Raman spectra of GO/PS and bared PS samples using excitation laser with wavelength of 532 nm

Conclusions

High quality and uniform GO thin film was successfully deposited on PS substrate using EPD technique. Raman spectroscopy showed existence of GO by indicating a peak at ~1350 cm^{-1} which is related to sp^2 carbon atoms in the surface. Moreover, the intensity ratio (I_D/I_G) of 0.85 confirmed the existence of GO thin film on porous structure.

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Electrochemical determination of acetaminophen by carbon paste electrode modified with Nickel-Cobalt salen complexes encapsulated in nano zeolite NaX

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Introduction

Acetaminophen (AC) is a combination of drugs, which are commonly used to treat pain and fever. The liquid chromatography [1] and spectrophotometry [2] analytical techniques have been developed for AC quantification. But, these methods are often expensive and usually need to pretreatment or toxicity solvents [3]. AC is an electro-active compound; therefore electrochemical technique for the determination of AC drew a lot of attention in the last few years due to its simplicity, low cost, high sensitivity and selectivity [3,4]. In this study, a type of carbon paste electrode using Ni-Co salen complexes encapsulated in nanozeolite NaX was prepared and was used for electro-catalytic oxidation of AC in biological samples.

***Keywords**: acetaminophen, cyclic voltammetry, salen complex, nano zeolite*

Method

Nanozeolite NaX with molar composition of 5.5 Na_2O:1.0 Al_2O_3:4.0 SiO_2:190 H_2O, in our laboratory. Ni-Co/NaX was prepared by using the ion-exchange method. The metal complex was encapsulated in zeolite by using the flexible ligand method [5]. The modified carbon paste electrode was fabricated using graphite, paraffin oil and Ni-Co salen/NaX.

Results and discussion

Electrocatalytic behavior of AC at bare CPE, Ni-Co salen/NaX/CPE have been investigated by cyclic voltammetry (CV) and presented in Fig. 1. As can be seen, no current was obtained with these electrodes in the absence of AC. The anodic current for electrooxidation of AC at the surface of Ni-Co salen NaX/CPE was greater than that at the surface of bare CPE. As a result, this improvement in the oxidation current demonstrates that incorporation of Ni-Co salen NaX onto a CPE enhances the electrochemical signal of AC electrooxidation.

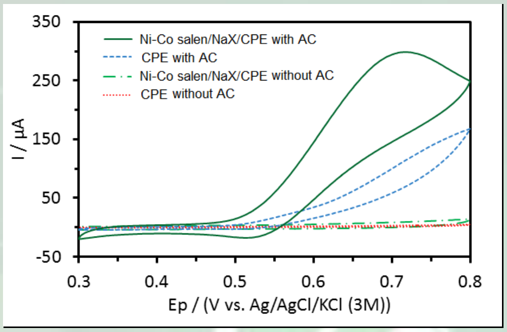

Fig. 1. Cyclic voltammograms of bare CPE and Ni-Co salen/NaX/CPE in the absence and presence of 9.0 mM acetaminophen in 0.1 M buffer phosphate solution (pH=3) at the scan rate of 25 mV s^{-1}.

Conclusion

In this study, a modified electrode was prepared with Ni-Co salen complexes encapsulated in nano-zeolite NaX. This composite showed superior electrocatalytic activity toward AC due to the existence of a synergetic effect which could be attributable to the interaction of Ni-salen and Co-salen and/or formation of binuclear salen complexes through the lattice oxygen of the zeolite host. The obtained results show that the modified electrode can enhanced the oxidation of AC by a catalytic process through a decrease in over potential versus bare CPE.

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Fabrication of an electrochemical EGFR immunosensor using BSA-templated Pb nanocluster as a biocompatible signaling probe

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Abstract

Detection of epidermal growth factor receptor (EGFR) is of paramount importance in medical sciences, since it has significant application in cancer diagnosis, drug development, and therapy monitoring[1]. In this work we introduce a new probe for the development of a sensitive, and selective sandwich-type electrochemical EGFR immunosensor. To design the immunsensor, we employed streptavidin-coated magnetic beads (MB) as a platform for immobilization of the biotinylated primary antibody (Ab_1), and utilized a newly synthesized bovine serum albumin (BSA)-templated Pb nanocluster (Pb_{NC}@BSA), conjugated to secondary antibody (Ab_2), as a signaling probe. After sandwiching the target protein between primary and secondary Ab, we dissolved Pb_{NC}@BSA into an acid, and recorded square wave anodic stripping voltammetric (SWASV) signal of the Pb ions as an analytical signal for quantification of the EGFR. The immunosensor responded linearly towards EGFR within the range of 0.4 ng/mL to 35 ng/mL, with a detection limit of 8 pg/mL. The immunosensor showed a good sensitivity, selectivity, stability, and reproducibility, and proved suitable for direct measurement of EGFR in human serum samples. We also used the as-synthesizd Pb_{NC}@BSA as a fluorescence label for *in vitro* bioimaging of cancerous HeLa and non-cancerous HUVEC cells. In addition, we investigated cytotoxicity of Pb_{NC}@BSA to cancerous and healthy cells, the results of which show that Pb_{NC}@BSA has considerable cytotoxicity to cancerous cells while exhibits subtle cytotoxicity to healthy cells. Thus, Pb_{NC}@BSA as a metal-based signaling probe is a biocompatible fluorescent probe for live cell imaging, with possible theraputic applications.

Keywords**:** *EGFR, Electrochemical sandwich immunosensors, BSA templated Pb nanocluster, Cell imaging, Cytotoxicity*

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Nickel salen NaX nanozeolite modified carbon paste electrode as ascorbic acid electrochemical sensor

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Introduction

Ascorbic acid (AA) is a water-soluble vitamin found in biological systems [1]. Different analytical techniques have been advanced for determination of AA such as liquid chromatography [2] and spectrophotometry [3]. Due to its biological importance, it is essential to develop rapid, selective and sensitive method for its routine and reliable determination in various matrices [1]. Electrochemical technique for the determination of AA represented a lot of attention in the last few years due to its simplicity, low cost, high sensitivity and selectivity [1]. In this study, a type of carbon paste electrode using Ni-salen complexes encapsulated in the NaX nanozeolite was prepared and was used for determination of AA by differential pulse voltammetry (DPV) technique.

Keywords: *Nickel salen, NaX nanozeolite, Modified CPE, Ascorbic acid*

Method

Nanozeolite NaX with molar composition of 5.5 Na_2O:1.0 Al_2O_3:4.0 SiO_2:190 H_2O [4]. Ni/NaX was prepared by using the ion-exchange method and the metal complex was encapsulated in nanozeolite by using the flexible ligand method [5]. The modified carbon paste electrode (Ni-salen-X/CPE) was fabricated using Ni-salen/NaX, graphite and paraffin oil. The electrochemical experiments were performed using a potentiostat/galvanostat SAMA500 electroanalyzer system.

Results and discussion

The XRD pattern of the synthesized nanozeolite NaX is recorded and the crystallization products matched the characteristic peaks of NaX at 2θ values of 7.2°, 10.2°, 12.5°, 16.1°, 21.7°, 24.0°

27.1°, 30° and 34.3°. The crystalline size (*D*) of synthesized NaX zeolite was also calculated using Debye-Scherrer equation and was obtained to be about 58 nm.

Fig. 1A shows electrocatalytic oxidation of AA at bare CPE and Ni-salen-X/CPE by cyclic voltammetry (CV) method. The anodic current for electrooxidation of AA at the surface of Ni-salen-X/CPE was greater than that at the surface of bare CPE. As a result, this improvement in the oxidation current demonstrates that incorporation of Ni-salen-X onto a CPE enhances the electrochemical signal of AA electrooxidation. Fig. 1B displays DPVs with increasing AA concentration leading to a linear increase in the anodic peak current.

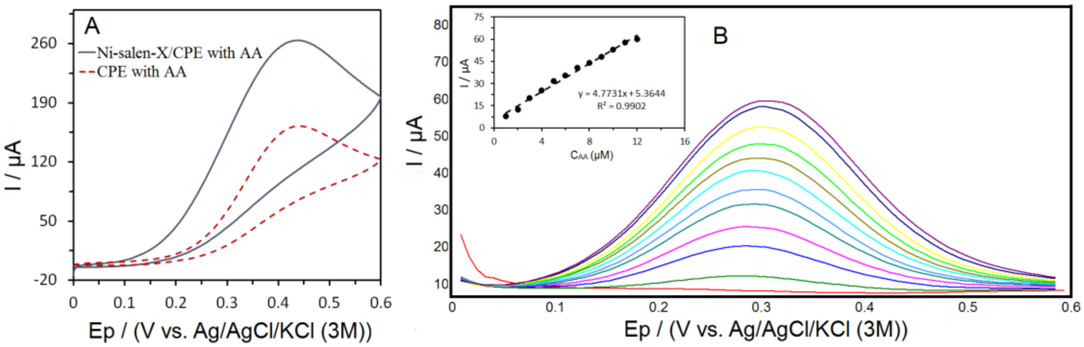

Fig. 1. (A) Cyclic voltammograms of bare CPE and Ni-salen-X/CPE in the presence of 5.0 mM AA in 0.1 M PBS (pH=3) at 20 mV s^{-1}. (B) DPV for different concentration of AA in the Ni-salen-X/CPE surface. Inset in B shows calibration curve.

Conclusion

In this study, a NaX nanozeolite was synthesized and modified electrode was prepared with Ni-salen complexe encapsulated in NaX. This composite showed superior electrocatalytic activity toward AA and decrease in over potential versus bare CPE.

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A Highly Selective Sensor for 5-Aminosalicylic acid using carbon paste electrode modified by MWCNT/ molecular imprinted polymer

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Abstract

In this work, electrooxidation behavior of drug 5-Aminosalicylic acid using multi wall carbon nanotube/ Poly methacrylic molecular imprinted polymer modified carbon past electrode (MWCNT/MIP-CPE) was investigated. The electrochemical behavior of the MWCNT/MIP-CPE for detection of 5-Aminosalicylic acid was investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The surface feature of the modified electrode MWCNT/MIP-CPE was characterized by scanning electron microscopy (SEM). The MIP and non-imprinted polymers (NIP) were synthesized using 5-ASA as a template, methacrylic acid (MAA) as a monomer, ethylene glycol dimethacrylate (EGDMA) as a cross-linker and 2-Azobisisobutyronitrile (AIBN) as an initiator. All effective factors in this experiment and the interactions between them were optimized in six factors and five levels by Design Expert software Version 7. Based on the software, minimum number of required runs was 33. In these runs, polymers were synthesized quite carefully. All carbon paste electrodes were modified by synthesized polymers and electrochemical measurements were performed in scan rate and pH levels that optimized by the software and responses were examined by ANOVA Analysis Method. A dynamic linear range of 10-500µM was obtained. The detection limit of the sensor was calculated as 4.6µM. As other imprinted materials, one of the main functions of the proposed MWCNT/MIP-CPE was to improve the selectivity of electrochemical sensors. Thus, this sensor was used successfully for the 5-Aminosalicylic acid determination in a commercial pharmaceutical formulation and human serum.

Keywords: *functional multi-walled carbon nanotubes, molecularly imprinted polymer, 5-amino salicylic acid, non-imprinted polymer, differential pulse voltammetry*.

Results and discussion

The analyte was preconcentrated on the surface of the modified electrode for 20 min. After removing the electrode from the solution, it was rinsed with water and was transferred to the electrochemical cell containing phosphate buffer solution at pH 6.0. Fig.1 shows the cyclic voltammograms acquired for the electrochemical response of 0.5 mM of 5-ASA at the CPE, NIP/CPE, MIP/CPE and MWCNT/MIP-CPE in phosphate buffer solution with pH 6.0. It was observed that the peak current at MWCNT/MIP-CPE is much higher than all of the other electrodes. Thus, with respect to the possible interference in the determination of dopamine (DA), Ascorbic Acid (AA), Uric Acid (UA), Acetaminophen (AC) and catechol (CA) were determined as structural analogues and 5-ASA were investigated as coexisting interference. As shown in Fig. 2, DA, AA, UA, AC and CA with the extremely similar structure, don’t show any interfering effect on response of 5-ASA

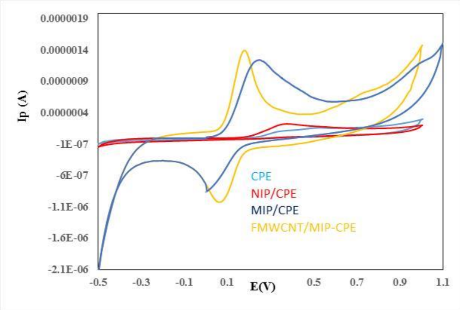

Fig.1:The cyclic voltammograms acquired for the electrochemical response of 0.5mM 5-ASA at the CPE, NIP/CPE, MIP/CPE and FMWCNT/MIP-CPE in phosphate buffer solution 0.1 M with pH 6.0

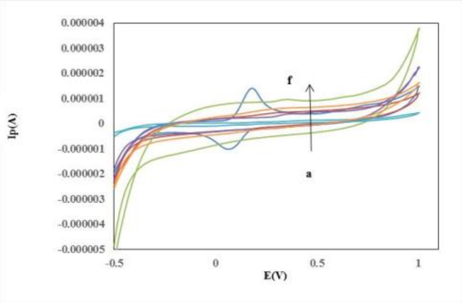

Fig.2: cyclic voltammograms of the 0.5mM dopamine, Ascorbic Acid, Uric Acid, Acetaminophen, Catechol and 5-Aminosalicylic acid by MWCNT/MIP-CPE (a-f).

Determination conditions: phosphate buffer solution 0.1 M pH 6.0 , scan rate: 60 mVs^{-1}

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Investigation of the inhibition effect of Zolpidem for Carbon mild Steel in Chloridric acid

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Abstract

Corrosion of steel is a very big problem and is one of the most important issues in metals science. One of the most widely used steels are mild carbon steels and their corrosion is of the most common form, especially in acid solution. Inhibitors are used to reduce the corrosion attack on metallic materials. Most of the common and commercial inhibitors are toxic in nature and it is very necessary to replace the by environmentally sound inhibitors. The use of pharmaceutical compounds offers interesting possibilities for corrosion inhibition due to the presence of hetero atoms like nitrogen, sulfur and oxygen in their structure. They are particular interest because of the high solubility in water, safe use and high molecular of size [1]. In this research, the corrosion of carbon steel (ST37) in Chloridric acid 1M in the presence of different amounts of Zolpidem as inhibitor was investigated to determine the corrosion parameters. For this purpose, the methods of potentiodynamic polarization, electrochemical impedance spectrometry (EIS) and scanning of electronic microscope (SEM) were used to investigate the mechanism of the samples. The results show that addition of the Zolpidem to Chloridric acid (1M) reduces the corrosion of the carbon steel. Results of polarization reveal that Zolpidem acts as mixed type inhibitor, but dominantly acts as an anodic inhibitor. The outcome of potentiodynamic polarization and electrochemical impedance spectroscopy show that increasing the amount of inhibitor up to a 300 ppm increase the inhibition efficiency. Furthermore, the adsorption of Zolpidem inhibitor on the alloy surface obeys the Langmuir absorption isotherm, and its performance on controlling of mild steel corrosion is attributed to the mechanism of chemical and physical absorption. In the Chloridric acid solution the adsorption prosses is endothermic with an increase in the entropy. After

submerging in acid solution containing inhibitor the results emphasized the results of infrared spectroscopy indicated that the formation of layer in surface of metal.

***Keywords**: Corrosion, Natural inhibitor, Potentiodynamic polarization, Electrochemical impedance spectrometry.*

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Investigation of enhancement dose of the polymer gel include gold nanoparticles in Megavoltage energy with MRI parameter

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Abstract

Background

The use of gold nanoparticles to increase the sensitivity of polymer gels is still controversial. The interaction of photons with gold nanoparticles may lead to an increase in the dose of the polymer gel. In fact, according to the emitted photon energy and atomic number of gold nanoparticles, photon energy less than 0.5 MV could result in photoelectric interaction which in turn might be raise the energy absorbing material.

Materials and methods

While spherical gold nanoparticles with dimensions of approximately 15 nm were prepared using synthesis method, the MAGIC-f polymer gel was prepared with and without gold nanoparticles in the range of 0-60Gy with 6Gy-step (13 groups and 3 samples in each group) and Gama-ray of Co-60 and MRI (1.5Tesla). Using DICOM image in R2-calcuate software was run in MATLAB software, signal intensity was determined on R2(I/T2).

Results

Change of R2 parameter of MAGIC-f with nanoparticle showed that the value of sensitivity in linear range was about 0.15 (1/t) in each Gy. The mean value of standard deviations (in each group) in the linear region was 0.3(1/t) and mean percent of coefficient variation was obtained about 0.1. The correlation coefficient of dose-response parameters in linear regression R2 was estimated around 0.96. The results of R2 parameter sensitivity without gold nanoparticle polymer gel MAGIC-f was obtained about 0.12(1/s) in each Gy compared to the value of 0.15(1/s) for

samples with gold nanoparticles. The comparison between these values demonstrated increasing of %25 for with gold nanoparticle group.

Discussion

This study found that MAGIC-f of with gold nanoparticle may cause increasing of absorbed dose, which can be used by clinicians as well.

Keyword: *geldosimetry- nanoparticle- absorbed dose-MRI*

Voltammetric Determination of Chlorpromazine Hydrochloride at Layered Double Hydroxide Modified Glassy Carbon Electrodes

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Abstract

Chlorpromazine hydrochloride (CPZ) is a phenothiazine drug with an aliphatic side chain, are widely used as therapeutic agents for treating various mental and personality disorders [1]. CPZ is used for controlling psychoses, including mania, schizophrenia, and several disturbed or agitated behavior; it is also used for the relief of nausea, vomiting, preoperative anxiety and intractable hiccups. The characteristics and determination of chlorpromazine were studied by using many methods including chromatography [2], electrophoresis [3], spectrophotometry [4], flow injection analysis [5] and electrochemistry [6]. Layered double hydroxides (LDHs) are a class of ionic lamellar compounds made up of positively charged brucite-like layers with an interlayer region containing charge compensating anions and solvation molecules. The metal cations occupy the centers of edge sharing octahedral, whose vertexes contain hydroxide ions that connect to form infinite 2D sheets. The most widely studied LDHs contain both divalent and trivalent metal cations, a generic formula for these LDHs may be written as; $[M^{2+}{}_{1-x}xM^{3+}x(OH)_2][An^{-}]_{x/n}\cdot zH_2O$, where M^{2+} may be common; Mg^{2+}, Zn^{2+}, or Ni^{2+} and M^{3+} may be common; Al^{3+}, Ga^{3+}, Fe^{3+}, or Mn^{3+}. An^{-} is a nonframework charge compensating inorganic or organic anion, e.g. CO_3^{2-}, Cl^-, SO_4^{2-}, RCO_2^- and x is normally between 0.2−0.4. LDHs may also contain M^+ and M^{4+} cations but these are limited to specific examples such as Li^+ and Ti^{4+}. The chemistry of LDHs is now widely studied and this is in part driven by the use of these materials as precursors for preparing CO_2 adsorbents, catalysts, or directly as ion exchange hosts, fire

retardant additives, polymer/LDH nanocomposites, drug delivery hosts, and as cement additives [7].In this study NiAlLDH was electrochemically deposited on glassy carbon electrode (GCE). The surface morphology and structure was investigated by scanning electron microscopy and Energy-dispersive X-ray spectroscopy methods. Its electrochemical properties were inspected by cyclic voltammetry, chronoamperometry (CA), differential pulse voltammetry (DPV) and electrochemical impedance spectroscopy (EIS). The modified electrode was used for determination of CPZ in alkaline media (0.1 M NaOH). In optimum conditions the linear range of the proposed electrode was 1×10^{-3} - 1×10^{-9} M, with the detection limit of 1 nm. The electrode response stability in the presence of CPZ was determined with CA which was good. The response of the electrode in the presence of three important interferences i.e. dopamine, ascorbic acid and uric acid was obtained, which there was no considerable interfering effect. Finally, this electrode was used for determination of CPZ in a 50 mg CPZ tablet, which the recovery was 109%. According to ease of preparation, low cost, stability and wide linear range this electrode can be a good candidate for determination of CPZ.

***Keywords**: Layered double hydroxide, NiAlLDH, Glassy carbon electrode, Chlorpromazine, Electrochemical determination*

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Polyaniline Nanotubes- Reduced Graphene Oxide Composite for High Performance Supercapacitor

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Abstract

Supercapacitors (SCs), as high power density energy storage resources, have recently attracted considerable attention[1, 2]. Among the vast majority of supercapacitive materials, polyaniline (PANI) with different morphologies[2] has been considered as one of the active materials due to its intrinsic high redox active-specific capacitance and flexibility[3, 4]. In this work, we report a supercapacitor fabricated from PANI rectangular nanotubes that was chemically synthesized by a simple and convenient method. This special shaped PANI composited with graphene oxide prepared with the Hummer method, and then GOES reduced to RGO to compose PANI-RGO composite. The obtained composite was drop-casted on a glassy carbon electrode (GCE) as a current collector. The structural analysis and morphological investigations revealed the formation of PANI rectangular tubes. PANI/RGO supercapacitor possesses a specific capacitance of 855 F/g at 1 A/g current density. The rate capability of the electrode tested at different current densities from 1 to 20 A/g shows an good specific capacitance of 586 F/g at a current density of 20 A/g. The capacitance retention over the long-term galvanostatic charge/discharge (CD) cycles was evaluated and the electrode was found to retain 81% of its capacitance even after 5000 cycles.

Keywords: *Supercapacitor, Polyaniline nanotube, High capacity, RGO, High rate.*

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Effect of supercritical water on redox cycle capability of iron oxide during decomposition of formic acid

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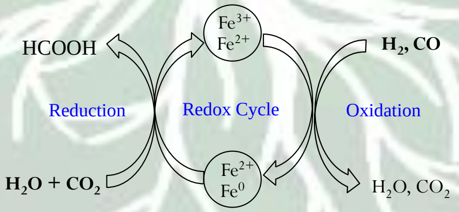
Abstract

Formic acid (FA) has great potential as an in situ source of hydrogen, because it offers high energy density, and can be safely handled in aqueous solution. In the current study, decomposition of formic acid ($H_2+CO_2 \leftarrow HCOOH \rightarrow CO+H_2O$) was investigated in the supercritical water (W) medium over iron oxide nanoparticle in order to shift the conversion toward more hydrogen production through water-gas shift reaction ($CO+ H_2O \leftrightarrow H_2+ CO_2$). This reaction can be accelerated through the redox mechanism ($Fe^{+3} \leftrightarrow Fe^{2+}$) in which supercritical water has a positive effect on this cycle. The effects of parameters (temperature, water density and FA/W ratio) were investigated on the catalyst structure and gas composition. From X-ray diffraction (XRD), electron diffraction (ED) analysis of catalyst as well as gas chromatographic analysis (GC) of gas composition (CO, CO_2, H_2, CH_4), it was revealed that water pressure has positive effect on stability of catalyst and modification of selectivity toward more H_2 production. The pathway of the reaction can be seen at the following.



Keywords: *Redox cycle, Iron oxide, Supercritical water, Formic acid.*

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Electrochemical characterization of cobalt infiltrated $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ cathodes of IT-SOFCs

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Abstract

Nano-sized cobalt oxide decorated $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) cathode was investigated as a promising cathode for intermediate temperature solid oxide fuel cells (IT-SOFC). To characterize the polarization resistance (R_p) of the infiltrated and non-infiltrated cathodes, an equivalent circuit was fitted onto the electrochemical impedance spectroscopy (EIS) data. Compared to pure LSCF, the high frequency polarization resistance decreased significantly as much as 87% at 600 °C by presence of cobalt oxide nano-particles.

Keywords: *IT-SOFC, Electrochemical Impedance Spectroscopy, Cobalt oxide nano-particle, LSCF*

Introduction

Solid oxide fuel cell (SOFC) is an eco-friendly energy conversion device with notable efficiency. The high materials cost is the main drawback of this device which impedes commercialization of the SOFC technology. Many researches have been conducted to reduce the operating temperatures of SOFCs which enables selection of lower cost materials. Slow oxygen reduction kinetics in cathode electrode and consequently high polarization resistance are the major outcome of reduction in working temperature. LSCF is an excellent choice for cathode materials in IT-SOFCs due to its high electrocatalytic activity and good ionic and electronic conductivities. Performance enhancement has been reported through surface modification of the LSCF cathode by impregnation of nano-sized catalysts. In the present study, the effect of presence of cobalt oxide (Co_3O_4) nano-catalyst on the electrochemical performance of the LSCF cathode has been investigated [1].

Method

Symmetric cells with two identical LSCF cathodes on the both side of a $Zr_{0.92}Y_{0.08}O_2$ (YSZ) electrolyte were used. The LSCF ink was painted on the YSZ pellet with a $Ce_{0.8}Gd_{0.2}O_2$ buffer layer between them. The LSCF cathode was infiltrated by 0.6M cobalt nitrate solution followed by calcination at 500 °C for 1 h. The impedance spectroscopy data were collected by a PARSTAT 2273 Potentiostat in the frequency range of 10 mHz to 100 kHz with a signal amplitude of 10 mV at 600 °C. The distribution and morphology of cobalt oxide nano particles was characterized by a high resolution scanning electron microscope (Tescan).

Results and discussion

Figure 1 shows the micrograph of a cobalt infiltrated cathode which shows uniform distribution of Co_3O_4 nano particles with a mean particle size of 50 nm on the surface of LSCF grains (indicated by arrows). Figure 2a shows the impedance curves for the LSCF cathodes with and without Co-infiltration at 600°C. An equivalent circuit of $R_sL(Q_HR_H)(Q_LR_L)$ was fitted to the impedance data to obtain polarization resistances at high and low frequency ranges. Symbols are experimental data and lines are the fitted results. R_s is the ohmic resistance of the system, L is the inductance related to the testing fixture and R_H and R_L correspond to the polarization resistances of the high and low frequency arcs [2]. Figure 2b shows that the reduction in R_H is about 87% while the reduction in R_L is negligible (~3.3%). In general, high frequency arc is related to the polarization resistance of the charge transfer process in which the electron transfer between the gas species and backbone surface is the limiting factor. After firing, cobalt nitrate transforms to cobalt oxide (Co_3O_4) nano-particles with a spinel structure consisting of Co^{+2}, Co^{+3} and oxygen ions. The oxidation state of the cobalt ions can be changed in the oxide structure for some reasons such as temperature fluctuation. Variation in the Co^{+3}/Co^{+2} ratio, caused by the modification of the oxidation states, provides enough electrons to accelerate oxygen reduction reaction resulting in a significant drop in the low frequency section of the polarization resistance. The low frequency arc is associated with the mass transfer processes such as oxygen atomization and gas diffusion. The slight decrease in the R_L may be attributed to better oxygen adsorption and dissociation at LSCF/nano-particles interface [3].

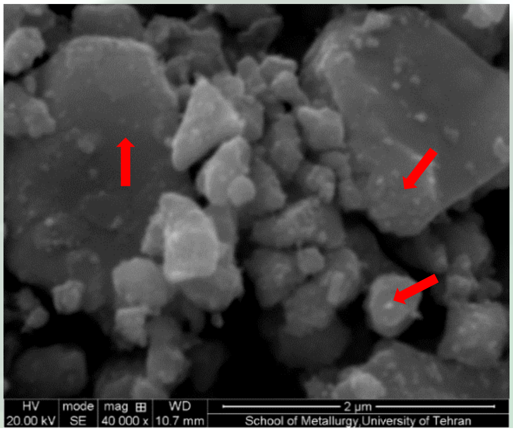

Figure 13: SEM image of the cobalt infiltrated LSCF cathode.

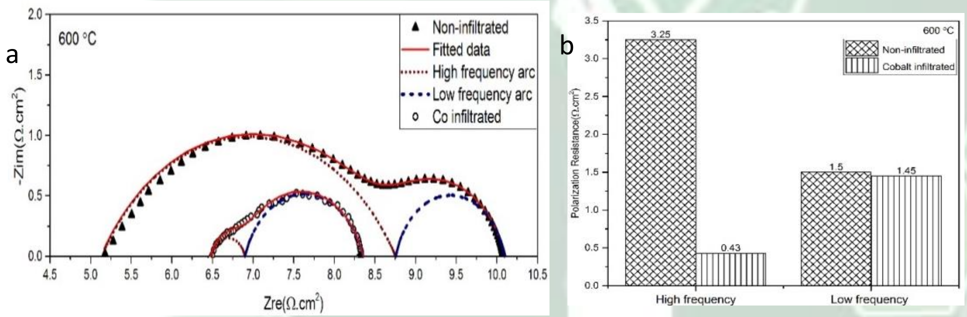

Figure 2: a) Impedance curves, b) Polarization resistances at non-infiltrated and cobalt infiltrated LSCF cathodes.

Conclusion

The impedance spectra of the infiltrated and non-infiltrated cathode were successfully divided into two separable arcs by a proposed fitting circuit. Considerable decrease in R_H in the LSCF cathode prompted with Co_3O_4 nano-particles was observed.

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Role of deviation from Li stoichiometry in synthesis of $LiFePO_4$ cathode material

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Abstract

Olivine-structured $LiFePO_4$ was successfully synthesized by co-precipitation method as the cathode material for Li-ion battery application. In this study, deviation from nominal stoichiometry of $LiFePO_4$ and its effects on the final phase composition and powder particle morphology have been investigated using X-ray diffraction (XRD) and high resolution scanning electron microscopy (HRSEM), respectively. The XRD results revealed that the molar composition of Li : Fe : PO_4 = 1.25 : 1 : 1 in the precipitation stage is the proper stoichiometry for achieving single phase $LiFePO_4$ with orthorhombic crystal structure after calcination at 700°C under reductive atmosphere. Scanning electron microscopy studies confirmed formation of ultra-fine spherical particles of $LiFePO_4$ phase for the above sample.

***Keywords**: Lithium-ion battery, Cathode materials, $LiFePO_4$, Sarcopside*

Introduction

$LiFePO_4$ also known as LFP is one of the most promising candidates for using as the cathode material in lithium ion batteries. LFP shows a well-defined potential for $LiFePO_4 \rightarrow Li^+ + FePO_4 + e$ reaction at 3.45 V versus Li/Li^+, with 170 $mA.h.g^{-1}$ as its theoretical capacity (1) Meanwhile, possibility of preparing pure LFP phase increases the chance for reaching to a cathode material with desirable properties (2). Based on the literature (2) Li deficiency results in the formation of a homogeneous solid solution of Sarcopside ($Fe_3(PO_4)_2$), at which, Li deficiency results in the formation of Li vacancies, with simultaneous conversion of Fe^{2+} to Fe^{3+} to maintain the Coulomb charge neutrality of compound, which eventually results in electrochemical performance drop off.

On the other hand, excess in lithium normally results in Li_3PO_4 impurity phase segregation, with no detrimental effect on the electrochemical properties (3). So it is crucial to prevent formation of Sarcopside in synthesis of $LiFePO_4$.

In the present work, $LiFePO_4$ phase was synthesized via co-precipitation route and the effects of off-stoichiometric Li mole percent on the characteristics of the final products have been investigated systematically.

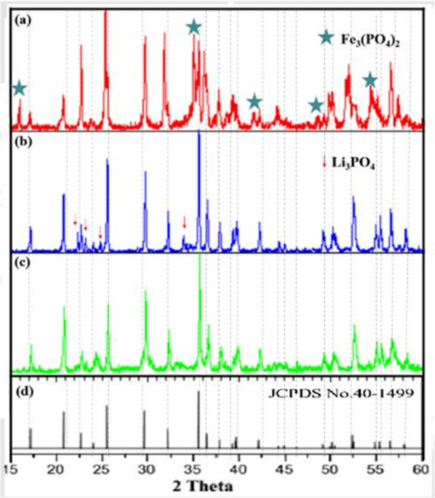
Method

$LiNO_3$, $FeSO_4.7H_2O$ and $NH_4H_2PO_4$ (all Merck, Germany) were used as starting materials and ammonia as pH controller. The relative molar composition of precursors was controlled at Li: Fe: PO_4 = xLi : 1 : 1 with a xLi equal to 1, 1.20 and 1.25. At each certain value of xLi, the obtained precipitate is filtered off and rinsed and then thermally heat treated in the tube furnace under protective gas (N_2-5%H_2) at 700℃ for 8 hours.

The phase composition of prepared powder was characterized by X-ray diffraction (Philips PW-1730 diffractometer) using Cu-K_α radiation. High resolution Scanning electron microscopy (Tescan MIRA3) was used to investigate the morphology of the powders. Inductively coupled plasma (ICP) analysis was used to determine the chemical composition.

Results and discussion

Fig. 1 shows the XRD patterns of the samples processed under different molar compositions of Li: Fe: PO_4. It is shown in Fig. 1a that a solid solution of $Fe_3(PO_4)_2$, known as sarcopside, is formed due to the Li deficiency in the sample processed at a molar composition of Li: Fe: PO_4 = 1: 1: 1. According to the literature, only 6.8% Li deficiency is pretty enough for sarcopside formation (3). Based on the ICP results, Li loss during precipitation is about 20% so at the molar composition of Li: Fe: PO_4 = 1.20: 1: 1, pure $LiFePO_4$ phase with an orthorhombic structure has been formed, as can be seen in Fig. 1b. Fig. 1c shows that by increasing Li stoichiometry up to a molar ratio of Li : Fe : PO_4 = 1.25: 1 : 1, in addition to the formation of main phase (LFP), a second phase of Li_3PO_4 is formed. Figure 2 shows that Li excess or deficiency has no significant effect on the particles morphology.



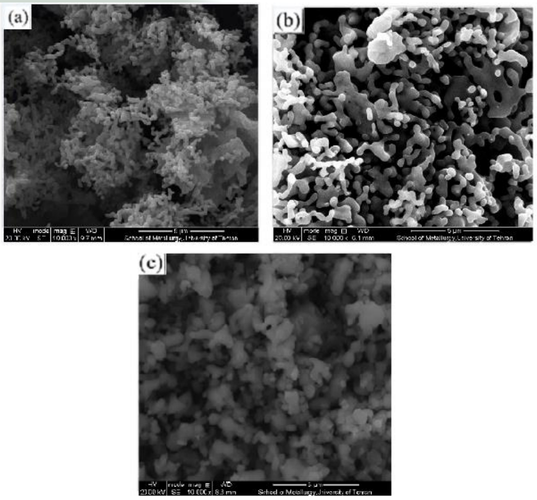


Figure 1- XRD patterns of LFP prepared with various precursor compositions, (a) Li: Fe: PO_4, (b) 1.20Li: Fe: PO_4, (c) 1.25Li: Fe: PO_4 and (d) reference pattern of LFP. The dashed lines indicate the peaks assigned to LFP.

Figure 2- HRSEM images of LFP prepared with various precursor compositions, (a) Li: Fe: PO_4, (b) 1.2Li: Fe: PO_4 and (c) 1.25Li: Fe: PO_4.

Based on XRD and SEM results, the difference in the formation of impurities in the experiments with excess or deficiency of lithium implies that the energy of formation of the iron antisite defect on Li site is small, while that of Li on iron site is large, so that this defect cannot be formed during the synthesis process with excess Li (3).

Conclusion

Pure olivine $LiFePO_4$ can be successfully prepared via co-precipitation method by molar composition of Li : Fe : PO_4 = 1.20: 1 : 1 in aqueous solution. XRD and HRSEM results confirm formation of pure phase with spherical morphology.

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Synthesis of Arrayed Aluminum Oxide Templates by Hard Anodization and DC Electrodeposition of Co Nanowires

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Abstract

In recent years particular attention has been paid to one dimensional nanostructures for example nanotubes, nanodots and more important nanowires. Reason of these attention is application of these materials in nanodevices [1, 2], sensors and magnetic devices with high capacity especially [3,4]. Electrodeposition into ordered aluminum oxide templates is one of applicable methods to synthesis of these nanostructures. In addition to the electrodeposition parameters, structure of templates effect on properties of them directly and indirectly. Innovation of porous alumina return to 1950 that was only one step anodization but synthesis ordered aluminum oxide template is introduced by Masuda at 1995 [5]. This mild anodization almost do in sulfuric, oxalic or phosphoric acid at certain voltage 25, 40 and 195 volt respectively. Chu, et al [6] could anodize at same mild anodization condition in sulfuric acid at 70 volt as hard anodization to produce template [7]. Also Woo Lee et al, did hard anodization in oxalic acid at voltages 3 time more than normal voltage and introduced diameter modulated templates that have large potential to use nanotechnology.

High purity Al foils (99.999 wt. %) were used substrates to fabricate highly ordered AAO templates using anodization process. The Al foil was cleaned and electropolished and anodization was done under a constant cell potential in a 0.3 M oxalic acid electrolyte at 0° C. However Al layer is removed to reach template and then pore widening was done in Phosphoric acid 5% at 32°C. As last step, the Gold layer was coated on the bottom of template. Co nanowires were then DC electrodeposited at room temperature into the nanoporous AAO templates in a three-electrode cell at 1.1 V, where a platinum plate acts as a counter-electrode and $Ag/AgCl_3$ as

reference electrod. The electrolyte consisted of 0.1 M $CoSO_4 \cdot 7H_2O$, and 30 g/L boric acid for Ni nanowires. Scanning electron microscopy (SEM) were used to investigate the morphology. Magnetic loops were measured by vibrating sample magnetometer (VSM).

Wave form figure 1a includes 80 V for 600 s and an 130 V for1200 s. As presented in figure 1a, first current increase then decrease and increase again and to be constant finally. Firstly anodizing includes two solution and oxidation reactions that cause to growth of oxide layer. This layer is stable and integrated as barrier layer that causes to increase resistance and decrease current to minimum amount. Gradually cracks are created and the oxide layer growth by those reactions as stable condition. This is a general growth behavior for the formation of porous-type aluminum oxide films meaning that the oxide film comprises two layers: (1) a thin barrier or compact film on aluminum and (2) porous aluminum oxide film. Current density increases at the beginning exhibiting the formation of the barrier layer until a peak value is achieved where the pore initiation takes place. At the end, a plateau is achieved because the barrier layer thickness becomes constant at the bottom of the pores. To interpret this behavior, one has to consider the formation and dissolution of oxide layer in respect to the applied electrical field or anodizing potential. Under the anodizing conditions of the experiments, the growth rate of the oxide layer exceeds its dissolution rate, leading to the formation of a barrier type layer right on the substrate at the bottom and a porous-type layer at the top. The process of the development of pores requires the interaction between the electrolyte and surface and is currently understood using the so-called field-assisted dissolution (FAD) hypothesis which describes the initiation and propagation of pores at the barrier layer. Current increase by increasing voltage at 1.3 V/s to 80 volt and barrier layer has resistance in return of this increasing at primary times but after some minutes resistance is broken by increasing of crack and slope of current is increased. Barrier layer restores itself at constant 80 V gradually and in result current decrease to a constant current. This behavior is repeated when voltage increase to 130 V at 0.04 V/s.

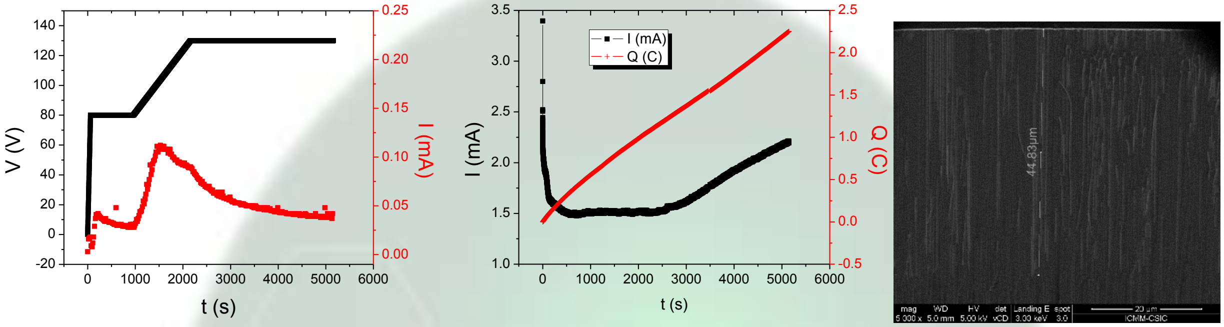

Fig 1. Hard anodization V-t and I-t curves (a), electrodeposition I-t and Q-t curves (b) and SEM image of nanowires in template.

Figure 1b shows I-t curves of electrodeposition of cobalt nanowires into templates that was explained. Figure 1c is SEM image of these nanowires into template that shows almost of pores are filled. It can be seen diameter of nanowires as modeled on template is about 90 nm and length is 44 µm. Also distance between pores is about 100 nm. Figure 2 shows magnetic hysteresis loops for Co nanowire into template at perpendicular (90°) and parallel (0°) between magnetic field and nanowire axis. In parallel state, coercively and squareness are more than perpendicular sate. It shows that easy axis for magnetization in this nanowire is perpendicular with axis of nanowires.

	Hc (Oe)	Squ %
0	371	17.9
90	97	2.3

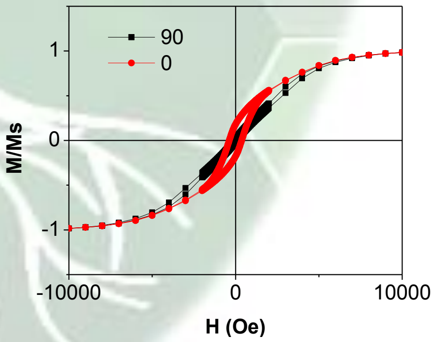

Fig 2. Magnetic hysteresis loops measured by VSM

***Keywords**: Arrayed Aluminum Oxide Templates, Hard Anodization, Electrodeposition, Nickel Nanowire and Magnetic propertie.*

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Photocatalytic performance of Mg-doped TiO2 nanoparticle for photocatalytic degradation of some environmental pollutants under UV light in aqueous solution

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Abstract

In this research Mg-doped TiO2 nanopowders were synthesized by the sol–gel method. The Mg-TiO2 photo-catalyst was prepared using Titanium tetra-iso propoxide and Magnesium sulfate as the dopant precursors. Rhodamine B, Nonylphenol ethoxylates 6 mol, Pseudoephedrine hydrochlorid, and Nicotine were used to study the photocatalytic performance of the Mg doped TiO2 under UV irradiation. The synthesized samples were characterized by x-ray diffraction, x-ray photoelectron spectroscopy, Transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and Photoluminescence (PL). The photocataltic degradation show that after 60, 90, 120, and 120 of irradiation time with UV light, 99%, 98%, 98% and 98% of rhodamine B, Nonylphenol ethoxylates 6 mol, Pseudoephedrine hydrochloride, and Nicotine were decomposed by Mg-doped TiO2 sample, respectivly.

Keywords: *Mg-doped TiO2; Photocatalytic degradation; Sol-gel method; environmental pollutant.*

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Photocatalytic degradation of phenylephrine hydrochloride in aqueous solutions by synthesized SnO_2-doped ZnO

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Abstract

ZnO and SnO_2-doped ZnO nanoparticles were prepared by a sol–gel method for the first time. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to characterize the ZnO and SnO_2-doped ZnO samples. Advanced oxidation processes (AOPs) have proved very effective in treatment of the various hazardous organic pollutants such as surfactants and pharmaceuticals in water. The photocatalytic degradation of drug phenylephrine hydrochloride (PHE) was studied as model organic pollutant. Under UV exposure the process was investigated with ZnO and SnO_2-doped ZnO. The degradation was studied under different conditions including irradiation time, pH, catalyst concentration, phenylephrine hydrochloride concentration and potassium peroxydisulfate as an oxidant. The experimental results indicated that maximum degradation (99.4±1.0%) of drug occurred with SnO_2-doped ZnO catalyst. The results demonstrated that photodegradation efficiency of SnO2-doped ZnO was significantly higher than that of undoped ZnO.

Keywords: *SnO_2-doped ZnO, phenylephrine hydrochloride, potassium peroxydisulfate, photocatalytic degradation.*

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Investigation of Over Potentials in a Short Stack with Integrated Humidifier and Water Separator Using EIS

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Abstract

In this study, for the first time, a cascade type 4 cells stack with integrated humidifier, water separator and internal manifolds was designed, fabricated and tested. The diagnostic test was conducted by EIS. The effects of dead end mode of the stack impedance spectra are studied. The results suggested that ohmic resistance of the single cell decreased with increasing current density due to the greater effect of hydration of membrane.

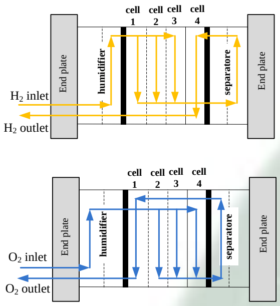
Keywords: *Cascade type stack, Electrochemical Impedance Spectroscopy, Dead-end Operation.*

Introduction

EIS can be utilized to optimize fabrication of membrane electrode assembly (MEA) [1]. EIS has also been applied to measure the ohmic resistance of the fuel cell [2], to optimize the FC operating conditions [4], and to investigate the effect of contamination [4-5]. Even though much more efforts have been made to diagnose the PEMFC performance by applying EIS, most of studies have concentrated on single cells with small or partially medium active areas [6]. In addition, only limited works have been done with PEMFC stacks, especially with large active areas [6]. In this study, for the first time, a cascade type stack with integrated humidifier and water separator and internal manifolds was designed, fabricated and tested. In this test, the impedance spectra of each cell and the stack are plotted simultaneously.

Experimental investigation

Figure 1 shows a schematic drawing of the proposed design for a PEMFC stack which is not equipped with any hydrogen or oxygen recirculation devices.



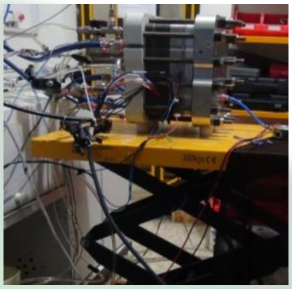
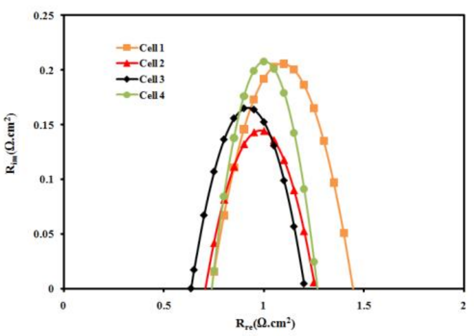


Figure 1: Schematic illustration of the proposed PEMFC stack design.

Figure 2: Dead-end stack with liquid separators, humidifiers and cell voltage monitoring cables.

Dead end mode

One of the important priorities in our test was to use Kikusui impedance meter that has the ability to measure the electrochemical impedance of each cell and the stacks, simultaneously. The electrochemical impedance spectra of each single cell are shown in Figure 3. As a result, the water content of membrane in the first stage of oxygen is higher than the second stage and the ohmic resistance of cell 1 is higher than the others. The generated water increases by enhancing the current density and the hydration level of the membrane. Consequently, the ohmic resistance decreases slightly in cells 2, 3 and 4. Indeed, the ohmic resistance of cell 1 decreases dramatically which is attributed to the similar hydration level of this cell to the first stage cells (Figure 3).



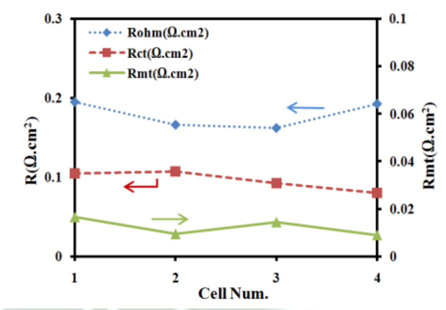


Figure 3: AC impedance spectra of the each single cell at output current densities (i=500

Figure 4: The dependence of the ohmic resistance (R_{Ω}), the charge transfer resistance (R_{ct}) and the mass transport resistance (R_{mt}) of the each single

mA/cm^2 ,T=70 ºC.) cell

The changes in HFR, R_{mt}, R_{ct} of each cell at output current density 500 mA/cm^2 and operating temperature of 70 ºC obtained from the proposed equivalent electrical model are shown in Figure 9. At low current density (Figure 4.), the reduction rate of oxygen is high denoted by the charge transfer resistance (R_{ct}). Moreover, the O_2 mass transfer resistance to reaction interface increased by the enhancement of current density.

Conclusions

The results of the electrochemical impedance suggested that gas operating mode had major effects on electrochemical impedance of the stack. When the stack was tested in dead end mode, the charge transfer resistance of the stack decreased significantly. In addition, this mode affected the mass transfer resistances slightly. Moreover, the current density could play an important role in the electrochemical impedance in the dead end mode. The ohmic resistance of the single cells decreased by increasing the current density due to more the hydration of the membranes. Moreover, higher ORR would lead to a gradual decrease in the charge transfer resistance of the stack at higher current density. The AC impedance diagnosis of stack could provide researchers with some useful information about the FC stack, especially in the dead end cascade type stack which its mode evaluation was more complicated.

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Mathematical Modelling of Cyclic Voltammogram and Linear Sweep Voltammogram for Cathode of Polymeric Fuel Cell

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Abstract

Voltammetry is one of the electrochemical methods used to test the electrode processes of fuel cells, generally in two forms of cyclic voltammetry (CV) and linear sweep voltammetry (LSV). Based on the results of especially two mentioned methods, many information about structure and performance of fuel cell catalyst layer can be obtained. These information include electron transfer kinetic, electrochemical active surface area, activity and stability of catalyst layer [1]. Solvation and oxidation of platinum as the most practical catalyst metal are important processes which influence on the reduction of oxidant and stability of platinum in the cathode of polymer exchange membrane fuel cell (PEMFC). These two processes are responsible for coverage percentage of catalyst area by oxidized materials (PtO_n), which prevents the operation of oxygen reduction reaction (ORR) and therefore the activity of catalyst decreases [2].

In this study, the typical model of cyclic voltammogram and linear sweep voltammogram for the cathode of PEMFC are investigated. For these purpose, the mechanism and kinetic of solvation and oxidation of platinum and the effect of structural parameters were assayed. In order to mathematical modelling, the Butler–Volmer equation and a series of electrochemical fundamental equations with considering desirable boundary conditions were used. Furthermore, the effect of environmental parameters such as temperature, humidity, size of nanoparticles and amount of catalyst loading on outcoming current caused by scan of potential between 0 – 1.2 volts with different scan rates were investigated and the results were compared with the experimental data. The obtained results showed that relative humidity increased the rate of surface oxidation and therefore decreases the activity of catalyst. However, increment of

temperature of cell and nanoparticles size of catalyst lead to increase the catalyst activity as observed by experiments [3, 4].

***Keywords**: Mathematical Modelling, Cyclic Voltammogram, Linear Sweep Voltammogram, Platinum Catalyst, PEMFC*

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The effect of Ni doped ZnO in carbon substrate of platinum electrodeposited electrode for methanol oxidation reaction in low temperature methanol fuel cell system

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Abstract

nowadays, methanol fuel cell systems has been attracted research activities to investigate for facilitating methanol oxidation reaction. One of activities is concentrated on improving electrocatalysts. ZnO and its derivatives can be used as additive in electrode substrate. In this work, a simple low temperature hydrothermal method has been used for synthesis of different morphologies of ZnOand 1-20% molNi doped ZnOnanostructures.After preparation additive it was inserted electrode substrate as paste. Then platinum was electrodeposited by cyclic voltammetry on substrate of electrode. Prepared electrodes was investigated for methanol oxidation reaction in three electrode half-cell system.The electrochemical methods like as linear sweep voltammetry was used for studying of the content of Ni/ZnO in substrate of electrode effect on methanol oxidation reaction. According our results, by increasing the Ni concentration in electrode, the current density is increased. Studies of cyclic voltammetry using providedmodified electrodes showed a significant reduction in anodic over voltage compared to bare electrodewas observed. Best response was obtained in terms of the current enhancement, overvoltage reduction, and reversibility improvement of the methanol oxidationreaction under experimental conditions by modified electrode with 20% Ni doped ZnOnanoparticles.

Keywords: *Methanol fuel cell, Platinum electrodeposited electrocatalyst, Ni/ZnO nano particles, Methanol oxidation reaction*

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Design and Development of Electrochemical Nanosensor based on Carbon Ceramic Electrode modified using Molecular Imprinted Membrane for Determination of GALLIC ACID

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Abstract

Gallic Acid (3,4,5–trihydroxybenzoic acid) (GA) is one of the main natural phenolic components. It is extensively used in tanning, ink dyes, manufacturing of paper, food industry, and drug trimethoprim in the pharmaceutical industry [1, 2]. Rapid and accurate detection of GA is of great interest to analytical chemistry because it has not only strong anti-mutagenic, anti-carcinogenic, and anti-oxidant activities but also potential health effects which have been found recently [3]. In past years, various methods have been applied to determine GA, such as flow injection analysis [4, 5], resonance light scattering [6], thin–layer chromatography [7], reversed phase high-performance liquid chromatography [8], and electrochemical method [9,10]. With regard to the conducted surveys, no MIP-based chemical sensor has been presented so far for determination of GA. However, MIP has been used to separate GA from aqueous samples. In the present study, a sensitive electrode is developed to determine GA in very low concentrations. MIP, containing recognition sites for GA, is synthesized by electropolymerization of aniline on carbon ceramic electrode in present of GA. For optimization of separation and determination of GA in solutions, operational parameters include pH solution, pre-concentration time of nanosensor in GA solution and solution temperature was chosen and optimized via central composite design. Using Design–Expert 8.0.2 software, a complete CCD matrix include 20 experiments was designed. The optimal conditions for determination of GA nanosensor were solution pH= 3.62, accumulation time=45 min and 45 °C as solution temperature. In order to confirmation of improvement the nanosensor performance due to creation an molecular imprinted membrane (MIM) on carbon

ceramic electrode (CCE) in determination of GA, DPV of four different electrode such as CCE, multiwall carbon nanotube modified CCE (MWCNT/CCE), electropolymerized MWCNT/CCE in absence of GA (ENIM) and in presence of GA (EMIM) was measured based on these optimum conditions. The mentioned electrodes were separately immersed into a 1.0 mM GA solution with the pH of 3.62 at 45 ˚C for 60.0 min until GA accumulated on the electrodes. After accumulation of GA molecules on the electrodes, they were washed with a water-ethanol (50% v–v) solution and displaced to a phosphate buffer solution with the pH of 7.0. Their DPVs are depicted in Fig 1. As it can be seen, there is no significant reduction current for GA on CCE (curve a) and ENIM/MWCNT/CCE (curve c). Indeed, CCE and ENIM/MWCNT/CCE have no capability for trapping and accumulating of GA. On the other hand, by comparing DPVs of CCE (curve a) and MWCNT/CCE (curve b), it can be conclude that cathodic peak current is increased due to the presence of MWCNT. It seems that a possible reason for the increase of current is the presence of MWCNT in the electrode structure; MWCNT has a larger surface area and higher conductivity than graphite. However, EMIM/MWCNT/CCE (curve d) is considerably indicate the current for reduction of GA. Thus, the prepared electrode is able to trap GA molecules. Under optimal experimental conditions, DPVs of EMIM/MWCNT/CCE was recorded to estimate the lower limit of detection and the linear range of GA. As expected, the reduction peak current increased upon the increase of GA concentration. Fig 2 clearly indicates that the plot of the reduction peak current against the GA concentration was linear in the range of 10–500 µM. According to the method mentioned in Skoog et al. (1998), the lower detection limit, C_m, was calculated 6.5 µM by using the equation $C_m=3s_{bl}/m$, where s_{bl} is the standard deviation of the blank response and m is the slope of the calibration plot (0.006 µA µM). The average voltammetric peak current and the precision estimated in terms of the coefficient of variation for repeated measurements (n = 15) of 6.5 µM GA at the EMIM/MWCNT/CCE were 0.295 ± 0.007 µA and 2.4 %, respectively.

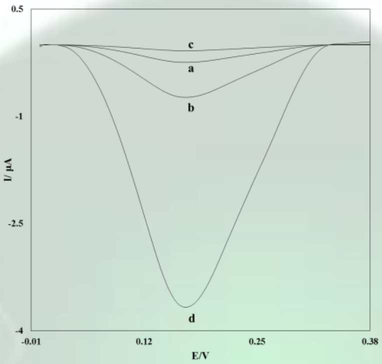

Fig 1. Differential pulse voltammogram analysis of electrodes a) bare CCE, b) MWCNT/CCE, c) ENIM/MWCNT/CCE, and d) EMIM/MWCNT/CCE incubated in 1.0 mM GA solution for 60 min at 45 °C.

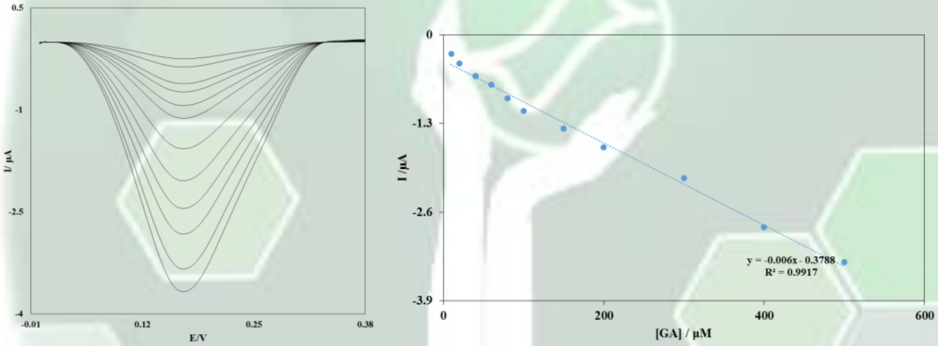

Fig 2. Differential pulse voltammograms of EMIM/MWCNT/CCE in a 0.1 M phosphate-buffered solution (pH 7.0) containing different concentrations of GA. Insets show the plots of the electrocatalytic peak current as a function of GA concentration in the range of 10-500 µM.

Keywords: *Electro polymerization, Gallic Acid, Nanosensor, Molecular Imprinted Membrane.*

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Determination of Cloxacillin Residues using Design and Development of the Electrochemical Nanosensor based on Molecular Imprinted Polymer

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Abstract

Cloxacillin is an antibiotic useful for the treatment of a number of bacterial infections. It is semisynthetic and in the same class as penicillin [1]. Numerous Methods have been described for determination of Cloxacillin in food samples by Reversed-Phase High-Performance Liquid Chromatography, FT-NIR spectroscopy and electrochemistry. Electrochemical analysis is more attractive due to its simplicity, high sensitivity, fast response and relatively low cost [2]. On the other hand, molecularly imprinted polymers (MIPs) are tailor made materials with selective recognition properties toward a chosen guest molecule or related compounds similar to that displayed by antibodies but without their experimental restrictions. These materials are prepared by the polymerization of a suitable monomer and a cross-linker agent in the presence of a template molecule [3]. Since, the application of electropolymerization for synthesis of MIP to determination of cloxacillin residues in milk and animal tissue has not previously been reported. The aim of this work is development a procedure for separation and determination of Cloxacillin in dairy products based on electropolymerization of aniline layer on carbon ceramic electrode for creation of MIP. Firstly, a multiwall carbon nanotube modified carbon ceramic composite was prepared via sol gel. Next, presented composite was prepared into carbon ceramic electrode. The surface electrodes were coated with electropolymerization by a layer of molecular imprinted polymer from polyaniline. Electropolymerization was preformed out in presence of Cloxacillin through applying potential in range of -0.2 to 1.1 V, at scan 6 cycles. The specialty site for Cloxacillin was created in surface after extraction of Cloxacillin inside polymeric matrix. The

morphology of electrode coated with molecular imprinted polymer was studied by scanning electronic microscopy (Fig 1). Separation and determination of accumulated Cloxacillin on surface electrode was optimized by changing parameters include pH solution, accumulation time and temperature. The high anodic signal was obtained when presented nanosensor was allocated in solution include 1.0 mM Cloxacillin and 0.1 M phosphate buffer with pH= 3.8 and 35 °C for 95 min.

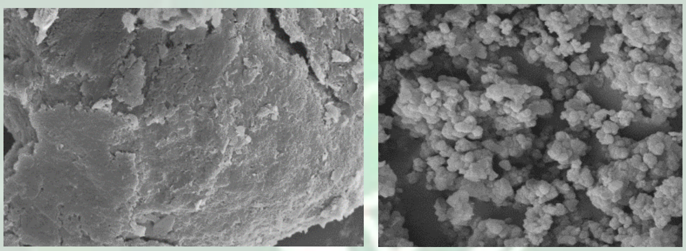
a b

Fig 1. SEM images of electropolymerized electrode (a) in absence and (b) in presence of Cloxacillin

The electrochemical behavior of proposed sensor was evaluated in different concentration of Cloxacillin, which their DPVs depicted in Fig 2 and its linear range and detection limit obtained 120 – 600 nM and 48.0 nM, respectively.

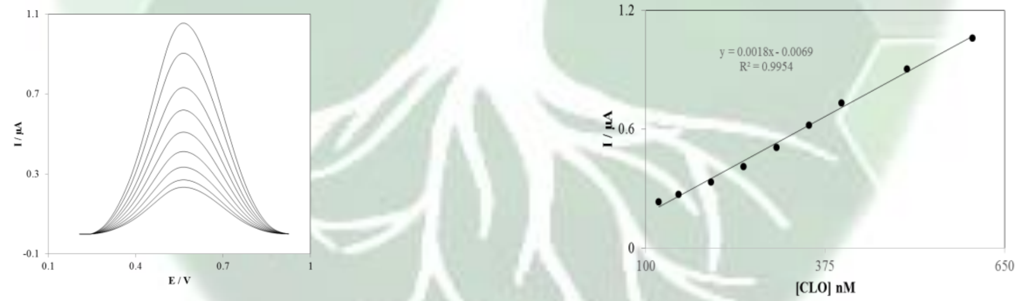

Fig 2: Differential pulse voltammograms of MIP/MWCNT/CCE in a 0.1-M phosphate-buffered solution (pH 7.0) containing different concentrations of Cloxacillin. Insets show the plots of the electrocatalytic peak current as a function of Cloxacillin concentration in the range of 120–600 nM

Keywords: *Cloxacillin, Dairy, Electrochemical sensor, Molecular Imprinted Polymer.*

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Development of a carbon ceramic electrode for determination and separation of tert-Butylhydroquinone in Edible Oils using molecular imprinted Polymer

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Abstract

Tert-buthyl hydroquinone (TBHQ), a phenolic antioxidant used as a food additive, and its metabolite 2-tert-butyl-1,4- benzoquinone (TBQ) was cytotoxic in human monocytic leukemia U937 cells. Both compounds induced caspase activity towards DEVD-MCA as a substrate and the cleavage of poly (ADP-ribose) polymerase in cells. The inhibition of monooxygenation activity was accompanied by redox cycling due to the tert-butylquinone produced during BHA metabolism, as measured by increased NADPH and oxygen consumption or hydrogen peroxide and superoxide anion production [1]. Accordingly, there is a need for a method to assess and determination of particular drug. Electrochemical sensor may serve the purpose due to its relative simplicity, selectivity, low-cost and fast response time [2]. On the other hand, molecularly imprinted polymers (MIPs) are tailor made materials with selective recognition properties toward a chosen guest molecule or related compounds similar to that displayed by antibodies but without their experimental restrictions [3]. Molecularly imprinted polymer (MIP) were synthesized of TBHQ (template), methacrylic acid as functional monomer, ethylene glycol dimethacrylate as cross-linking agent and 2,20- azobisisobutyronitrile as initiator . Then, the MIPs were used to modify the carbon ceramic paste electrode (CCE). In the present study, an electrochemical nanosensor based on molecular imprinted polymer has been designed and developed for separation and determination of TBHQ antioxidant in edible oil. The MIP synthesized by Methacrylic acid as a functional monomer, Ethylene glycol dimethacrylate as cross linker, 2,2-azobis(2-methyl propionitrile) as initiator and TBHQ has been used as template. In the next stage Multiwall carbon Nano tube, Graphite, MIP and SiO_2 solution used for making carbon ceramic

electrode. The effect of different parameters such as, solution temperature and time for pre-concentration of TBHQ on electrode surface, also MIP and MWCNT amounts in preparation of electrode were investigated and optimized with statistical method of the Central Composite Design (CCD). Optimized condition determined as MWCNT=7.0 mg, MIP= 11 mg, Temp=32 °C and time of 12 minutes. Under optimal experimental conditions, DPVs of MIP/MWCNT/CCE was recorded to estimate the lower limit of detection and the linear range of TBHQ. As expected, the oxidation peak current increased upon the increase of TBHQ concentration. Fig 1 clearly indicates that the plot of the reduction peak current against the GA concentration was linear in the range of 20–950 µM. According to the method mentioned in Skoog et al. (1998), the lower detection limit, C_m, was calculated 7.1 µM by using the equation $C_m=3s_{bl}/m$, where s_{bl} is the standard deviation of the blank response and m is the slope of the calibration plot (0.0013 µA µM). The average voltammetric peak current and the precision estimated in terms of the coefficient of variation for repeated measurements (n = 15) of 7.1 µM TBHQ at the MIP/MWCNT/CCE were 0.295 ± 0.007 µA and 2.4 %, respectively. Finally, performance of proposed procedure was evaluated to separation and determination of TBHQ in different edible oil Table 1.

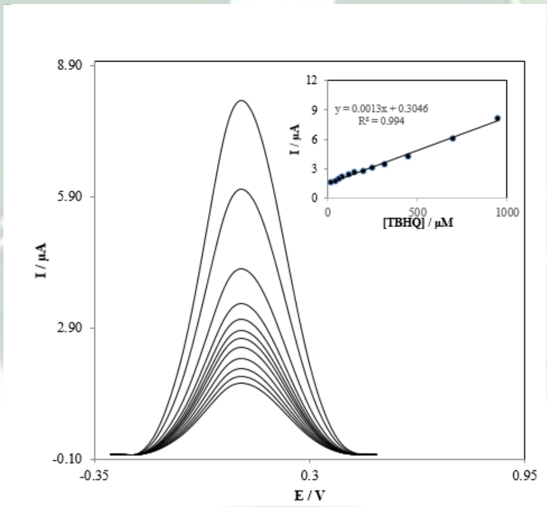

Fig 1. Differential pulse voltammograms of MIP/MWCNT/CCE in a 0.1 M phosphate-buffered solution (pH 7.0) containing different concentrations of TBHQ. Insets show the plots of the electrocatalytic peak current as a function of TBHQ concentration in the range of 20-950 µM.

Table 1: Determination and recovery results of TBHQ in edible oil using DPV calibration plots and with the nanosensor (MIP–MWCNT–CCE)

Sample	Initial found (µM)	Added (µM)	Found (µM)	Recovery (%)
Sesame Oil	*	40.0	40.5	101.25
		60.0	59.8	99.66
		80.0	81.2	101.5
corn oil	124.8	40.0	163.9	99.45
		60.0	185.2	100.2
		80.0	203.12	99.1
Sunflower oil	177.75	40.0	216.54	99.4
		60.0	240.1	101.25
		80.0	253.64	98.4
Colza Oil	276.5	40.0	319.2	100.8
		60.0	333.6	99.13
		80.0	365.8	102.6

***Keywords**: Molecular Imprinted Polymer, Tert- Butyl Hydroquinone, nanosensor, Edible Oil.*

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Electrolyte free and flexible micro-supercapacitors based on PET fabric

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Abstract

The present research developed a new electrolyte free and flexible micro-supercapacitor (MSC) based on polyethylene terephthalate (PET) fabric as a new kind of wearable electronic device. Laser scribing, based on its ability regarding to pattering and reducing at the same time is used as a reduction source on the thermally sensitive underneath such as polymer or textiles. The as-prepared laser patterned devices (rGO-GO-rGO) show good electrochemical performance without the use of any external electrolyte (Figure 1). Due to the uncertainty in the measurement of the exact mass of the laser reduced active electrode material, we will mostly report the capacitance values in area density mF/cm^2 units. In comparison, a well-designed recently reported, inkjet-printed carbon supercapacitor, with inter-digitated electrode structure and similar electrode thickness showing that the performance of our device without external electrolyte is in the same range as reported for other systems. The electrochemical performances show the almost good activity of devices without any electrolytes. The capacitance is measured in different scan rates from 5 mv/s up to 40 mv/s.The interaction between the trapped water and GO layers is a key to the ionic conductivity observed here. At low concentration, H_2O molecules bind to GO sheets via strong intermolecular interaction (hydrogen bonding); as the water content increases, the active sites on GO sheets get saturated, and the excess water molecules become free to rotate and diffuse. The protons, which are the species here taking part in ionic conduction, come from the hydrolysis of the functional groups (carboxyl, sulfonic and/or hydroxyl) present on GO, and the resulting protons can move via Grotthuss Mechanism, which is hopping via hydrogen bonding network, or even freely migrate in the hydronium form (H_3O^+) within the intralayer spaces.

Keywords: *Wearable, Supercapacitor, Reduced graphene oxide, Laser, Polyethylene terephthalate*

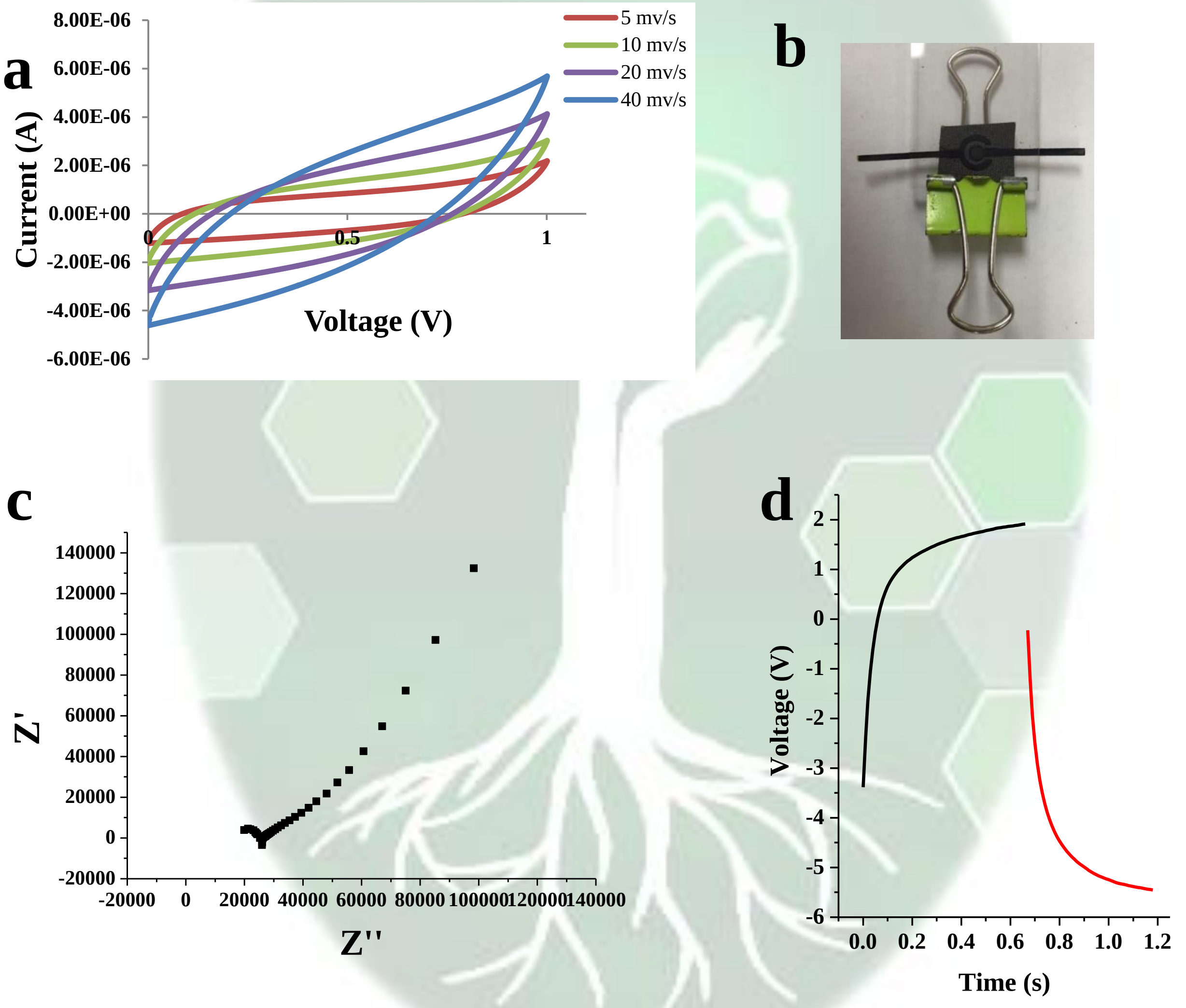

Figure 1. Electrochemical performance of flexible micro supercapacitor without using any external electrolytes. A) CV curves of device in different scan rates, b) Photograph of microsupercapacitor device, c) EIS curve and d) charge-discharge behavior

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Design and Development of a Nanostructure Sensor for Determination of L-Dopa with MIP and Carbon Ceramic Composite

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Abstract

Parkinson’s disease is an age related neurological non-genetic disorder associated with the progressive degeneration of dopamine containing component of the nigro-striated neurons and the subsequent loss of dopamine in the corpus striatum which affects the mobility and control of the muscular system skeletal [1]. L-Dopa ([3-(3, 4-dihydroxylphenyl)-L-alanine] is a medication used to treat Parkinson's disease [2]. This is an unusual amino acid, an important neurotransmitter, and has been used for the treatment of neural disorders such as Parkinson’s disease [3]. Accordingly, there is a need for a method to assess and determine a particular drug. Electrochemical sensor may serve the purpose due to its relative simplicity, selectivity, low-cost and fast response time [4]. The application of MIPs in electrochemistry is rather recent and was directed to combine their intrinsic properties to selected electrochemical reactions, in order to improve the response of the electrode [5]. MIP based sensors compared to natural receptors have several advantages such as suitable (proper or accurate) selectivity, high robust and reusable, and is less expensive to prepare [6]. Therefore, use of MIP modified electrodes has been considered by the researchers [7]. In previous work, we optimized preparation condition of the MIP based carbon paste electrode for determination L-Dopa [8]. This study presented the ability of MIP/MWCNT/ carbon ceramic electrode for determination of L-Dopa in solution. Moreover, comparison between performance of different four electrodes including CCE, MIP/CCE, MWCNT/CCE and MIP/MWCNT/CCE in measurement of L-Dopa was carried out. Molecularly imprinted polymer were prepared using L-Dopa as template, methacrylic acid as functional monomer, ethylene glycol dimethacrylate as cross linker and 2,2–azobis (2–methyl propionitrile) as initiator. The MIP was embedded in the multi walled carbon nanotube modified carbon ceramic electrode (MWCNT–CCE), which acted as the selective recognition element and pre–concentrator agent for L-dopa. The effect of different factors such as MIP and MWCNT amounts at preparation of electrode, also pH of pre-concentration solution and time of L-dopa accumulation on oxidation current of accumulated L-dopa at electrode surface were investigated and optimized with Central Composite Design. The optimum conditions for construction of MIP based sensor including 0.01 g MIP and 0.01 g MWCNT, also best condition for accumulation and pre-concentration of L-Dopa on sensor surface were found to be solution pH of 2.38 duration 14.5 min. The results showed that MIP/MWCNT/CCE has enough capability for accumulation and trapping of L-Dopa molecules available in solution. The linear response range and detection limit were found to be 0.5 to 450.0 nM and 0.13 nM, respectively using the differential pulse voltammetry method (DPV). The results showed that the proposed sensor is highly selective, sensitive with a fast response for L-Dopa analysis.

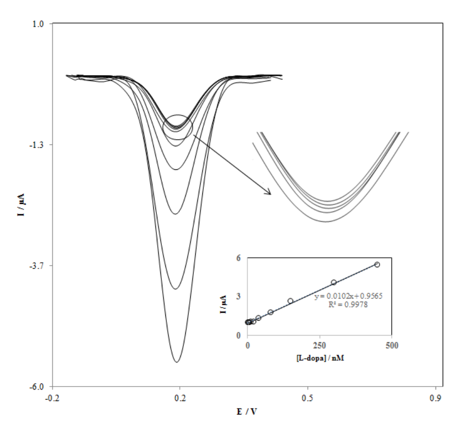

Fig 1: Differential pulse voltammograms of MIP/MWCNT/CCE in a 0.1-M phosphate-buffered solution (pH 7.0) containing different concentrations of L-Dopa. Insets show the plots of the electrocatalytic peak current as a function of L-Dopa concentration in the range of 0.5–450 nM

Keywords: *Molecularly Imprinted Polymer, Nano–sensor, L-dopa, Carbon ceramic electrode, Central Composite Design.*

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Highly defective mesoporous carbon toward fabrication of efficient electrochemical sensors

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Abstract

The presence of structural defects significantly alters the properties of carbon nanostructures. The results of recent literature have confirmed that the vacancy defects can serve as favorable sites for the electron transfer as well as adsorption sites which are beneficial for fabrication of energy storage and electrochemical sensing devices. For example, improved heterogeneous electron transfer rate toward electrochemical reaction of ferrocenemethanol [1], oxygen [2], and nitrate [3] was reported at the surface of defective nanocarbon based electrodes. Also the results of theoretical efforts predicted the favorable adsorption of Li^+, Na^+, Ca^{2+} ions on the defective sites of graphene sheets [4-6]. Generally, structural defects were induced by chemical treatments and ion irradiation [7,8]. In this paper, preparation of a highly defective mesoporous carbon (DMC) via a facile mass producible method for electrochemical sensing applications was reported. The synthesis of DMC with desired structural defects was conducted using nanosilica as hard template, sucrose as a carbon source, and KNO_3 as a defect causing agent. During carbonization process, the oxygen gas released from the decomposition of KNO3, which was coated on nanosillica template, reacts with carbon atoms and provides a highly defective mesopores carbon. Raman spectroscopy was used to evaluate defect density while porous structure and surface morphology of synthesized materials were investigated with N_2-adsorption/desorption, XRD, SEM and TEM techniques. Cyclic voltammetry and electrochemical impedance spectroscopy studies were performed on fabricated renewable mesoporous carbon paste electrode (MCPE). The optimal effective heterogeneous rate constant for ferri/ferrocyanide redox probe at the surface of highly defective mesoporous carbon was determined as $0.42\ cms^{-1}$ which is about 145, 75 and 50 fold faster than graphite, MWCNT and graphene, respectively. It is worth mentioning

that the obtained K_0 (0.42 cmS^{-1}) at the surface of highly defective mesoporous carbon presented in this work is higher than those of other reported carbon based electrodes such as edge plane HOPG (0.10 cmS^{-1}), 50 SWCNT (0.003 cmS^{-1}), 51 and glassy carbon (0.029 cmS^{-1}) [9-11]. Moreover, the study of CVs of different redox species verified the excellent electrochemical performance of the synthesized highly defective nanocarbon. The favorable electroanalytical behavior of highly defective mesoporous carbon toward fabrication of electrochemical sensors were further explored by study the CVs of some important biological and environmental species such as ascorbic sacid, uric acid, dopamine, paracetamol, hydroquinone, and Bisphenol A. The experimental findings are valuable for design and fabrication of efficient carbon based electrochemical sensing devices.

Keywords: *Structural defect; mesoporous carbon; electrochemical sensing; paste electrode*

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Design and Development of a Nano sensor Modified by Molecularly Imprinted Polymers for Determination of Thiourea at Industrial Media

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Abstract

Thiourea (TU) as an organic additive is most commonly used in industrial processes of copper electro refining from acidified copper sulfate solutions. TU affects the structure of deposited cathodes via the mechanism of electrolytic reduction processes. Smooth and pure copper is obtained in case the reagent is in a proper concentration. An insufficient amount of a smoothing reagent has an equally detrimental effect that causes the nodulation phenomenon of the cathode. Since TU is consumed during electro refining by co-deposition with copper, it must be added to the electrolyte in a continuous way. Therefore, it is desirable to be able to measure the reagent concentration in the electrolyte [1]. In food industries, TU is known as a toxic and hazardous, and these effects seem to arise from a disturbance of carbohydrate metabolism that may be harmful for humans. Furthermore, TU has also been screened as allergenic and carcinogenic factors [2]. Different analytical techniques such as UV–Vis spectrophotometry, UV reflectance spectrometry, infrared spectrometry, chemiluminescence, Raman spectroscopy, chromatography and electrochemical methods [3] have been reported for the determination of TU in various samples. Electrochemical methods are suitable for determination of low levels of TU because of their high sensitivity and selectivity and inexpensive instrumentation. Development of various modified electrodes to achieve higher selectivity and sensitivity has been of interest, but there are few reports so far on the determination of TU using modifiers. Moreover, molecularly imprinted polymers (MIPs) are tailor made materials with selective recognition properties toward a chosen guest molecule or related compounds similar to that displayed by antibodies but without their experimental restrictions [4]. The MIPs were used to modify the carbon ceramic paste electrode

(CCE). In the present study, an electrochemical nanosensor based on MIP has been designed and developed for separation and determination of TU in industrial waste of Sarcheshmeh copper Inc. Co. The MIP synthesized by Methacrylic acid as a functional monomer, Ethylene glycol dimethacrylate as cross linker, 2,2-azobis(2-methyl propionitrile) as initiator and TU has been used as template. In the next stage Multiwall carbon Nano tube, Graphite, MIP and SiO_2 solution used for making carbon ceramic electrode. The effect of different parameters such as, solution pH and time for pre-concentration of TU on electrode surface, also MIP and MWCNT amounts in preparation of electrode were investigated and optimized with statistical method of the Respond Surface Methodology (RSM). Optimized condition determined as MWCNT=3.3 mg, MIP= 12.3 mg, pH=8.0 and time of 26 min. Under optimal experimental conditions, DPVs of MIP/MWCNT/CCE was recorded to estimate the lower limit of detection and the linear range of TU. As expected, the oxidation TU signal increased upon the increase of TU concentration. Fig 1 clearly indicates that the plot of the reduction peak current against the TU concentration was linear in the two range of 0.05–5.0 nM and 50 -1100 nM. According to the method mentioned in Skoog et al. (1998), the lower detection limit, C_m, was calculated 0.12 pM by using the equation $C_m=3s_{bl}/m$, where s_{bl} is the standard deviation of the blank response and m is the slope of the calibration plot (0.2883 µA nM). The average voltammetric peak current and the precision estimated in terms of the coefficient of variation for repeated measurements (n = 15) of 0.12 pM TU at the MIP/MWCNT/CCE were 0.295 ± 0.007 µA and 2.4 %, respectively.

Finally, performance of proposed procedure was evaluated to separation and determination of TU in industrial electrolyte of Sarcheshmeh copper Co. (Table 1).

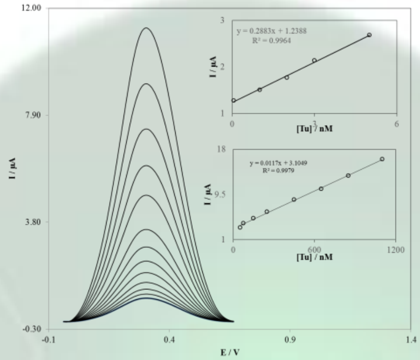

Fig 1. Differential pulse voltammograms of MIP/MWCNT/CCE in a 0.1 M phosphate-buffered solution (pH 7.0) containing different concentrations of TU. Insets show the plots of the electrocatalytic peak current as a function of TU concentration in the range of 0.05-1100 nM.

Table 1: Determination and recovery results of TU in industrial electrolyte using DPV calibration plots and with the nanosensor (MIP–MWCNT–CCE)

Initial found (nM)	Added (nM)	Found (nM)	Recovery (%)
155.1	10.0	168.6	102.1
	20.0	173.9	99.3
	50.0	208.65	101.7
	100.0	251.21	98.51

***Keywords**: Thiourea**,** Determination, Molecular Imprinted Polymer, Nanosensor, Carbon Ceramic Electrode.*

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Comparison of Electroless and Electrodeposition of Pd-Ag Alloy on hydrogen separation performance

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Abstract

In the work presented here, palladium-silver membrane has been prepared by Electroless and Electro-deposition methods on porous stainless steel (PSS) substrate. The PSS substrate was washed with acetone and rinsed with distilled water, afterwards chemically cleaned using a 10% sodium chloride solution at 55°C and finally rinsed with distilled water. In Electroless deposition, the Pd-Ag alloy was fabricated by ethylene glycol as a new reducing agent and polyol process at 120°C for 10 minutes. In electrodeposition, the membrane was prepared using cyclic voltammetry and chronopotentiometry technique from alkaline solution containing tetraamminepalladium (II) chloride monohydrate, silver chloride and ammonium hydroxide at room temperature. The Electrodeposition carried out in the potential range of -1V to +1 V vs.

The morphology of resulted alloy on PSS was analyzed by the scanning electron microscopy (SEM) and the phase structures of the coatings were examined by an X-ray diffractometer (XRD). The surface compositions were analyzed with an energy dispersive spectrometer (EDS) as well as hydrogen permeation analysis. The hydrogen separation tests confirmed the membrane coated by Electroless method is more highly selective towards hydrogen compared to other ones prepared by electro-deposition which could be attributed to the formation of dense and homogenous microstructure with finely divided powder and nano-sized pores as it could not be achieved in electro-deposition. Furthermore, the results showed that, 77:23 is the optimum ratio of Pd to Ag in both methods. The hydrogen separated gas of the optimized Pd/Ag membrane

showed the purity as much as 63.57% and 68.26% at 60°C and 120°C respectively for the electrodeposited membranes whereas it was equal to 99.9903% and 99.9936% at 60°C and 120°C respectively in the case of Electroless deposited membranes. SEM images of a typical Pd/Ag alloy coatings at PSS substrate in both methods is presented in Fig. 1. Also, the EDS analysis results are illustrated in Fig. 2.

***Keywords**: Pd-Ag membrane, Electroless, Polyol process, Electro-deposition, hydrogen separation*

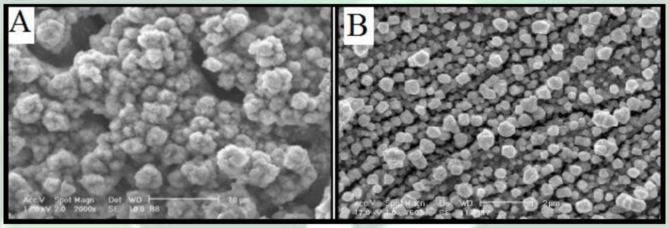
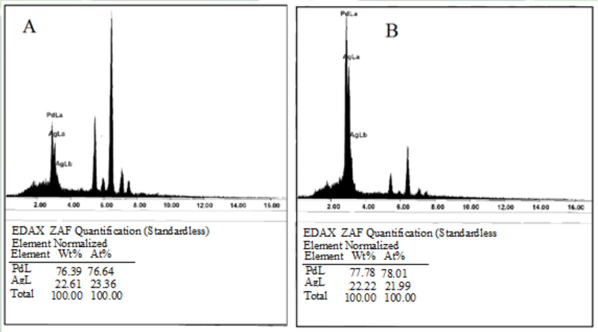


Fig.1. SEM images of a typical Pd/Ag alloy coatings at PSS substrate: membrane resulted from (A) Electroless, and (B) electrodeposition method



EDAX ZAF Quantification (Standardless)
Element Normalized

Element	Wt%	At%
PdL	76.39	76.64
AgL	22.61	23.36
Total	100.00	100.00

EDAX ZAF Quantification (Standardless
Element Normalized

Element	Wt%	At%
PdL	77.78	78.01
AgL	22.22	21.99
Total	100.00	100.00

Fig.2 . The EDS analysis results of the final Pd/Ag coatings: membrane resulted from (A) Electroless, and (B) electrodeposition method

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The effect of electrochemical deposition solution's pH on prepared platinum electrocatalystcharecteristic for oxygen reduction reaction in low temperature fuel cell systems

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Abstract

Nowadays, the fuel cell role in energy resources has been explicated more. At these systems, many activities are focused on improving sluggish oxygen reduction reaction at cathode especially in low temperature systems. Platinum is common electrocatalyst has been used in low temperature fuel cell systems for oxygen reduction reaction (ORR). Various methods have been used for preparing platinum electrocatalyst at cathode. One of these methods is electrochemical deposition method. The platinum is electrodeposited from electrochemical deposition solution. In this process, various parameters have effect on performance of prepared electrocatalyst. In this work the pH of electrochemical deposition solution effect on properties of electrodeposited platinum for ORR was studied. The pH of electrochemical deposition solution in presence of Britton-Robinson Buffer(0/04 M H_3PO_4 H_3BO_4; CH_3COOH +Xmm 0/2M NaOH) is varied from 8 to 11. For doing electrochemical electrodeposition cyclic voltammetry method(scan rate 100 and potantioal -0.25 -1.25)was used in a conventional three electrodesystem.The electrochemical methods like as linear sweep voltammetry and cyclic voltammetry were used for studying the fabricated electrodes for ORR at sulfuric acid solution (2.5 M) saturated with oxygen gas. According our results, the pH of electrochemical deposition solution affects on characteristic of electrodeposited platinum as electrocatalyst for oxygen reduction reaction. It has been shown the optimum result is related to buffer solution with pH 9.

***Keywords**: low temperature fuel cell; oxygen reduction reaction; platinum electrocatalyst; electrodeposition; Britton-Robinson Buffer.*

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Electroanalysis Determination of Nitrite Ions Using Nano Zeolite Modified Carbon Paste Electrode

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Abstract

The determination of nitrite concentration, especially for drinking water quality, wastewater treatment, for the food industry , dyes, bleaches, fertilizers as well as for medicinal purposes and for the control of remediation procedures, is of rapidly increasing interest[1-2]. Nitrite ions are critical precursors in the formation of nitrosamines, many of which have been shown to be carcinogens and harmful on our environment [3]. Nitrite ions are used as food preservatives against food poisoning microorganisms such as clostridium botulinum[4]. The nitrite salts are known to occur in high quantity in soil and ground waters. Then, determination of nitrite has received substantial attention. several methods have been developed to determination nitrite, which are laborious to perform or require chemical reagents , the electrochemical approaches are favorable due to the rapid response, low costs and simple operation in compare of other methods [5]. In this research nano zeolite-modified electrodes have been developed for the determination of nitrite ions. Zeolite-supported electrocatalysts can be subjected to improve the performance of the electrocatalytic responses with reduced overpotentials and increased electroanalysis signals allowing low detection limits and high sensitivities. The used nano ZSM-5 zeolite was synthesized as literature [6]. Graphite powder and *ferrous* chloride ,phosphoric acid, and sodium nitrite used in this work were also purchased from Merck. Electrochemical experiments were carried out using a potentiostat/galvanostat (Auto Lab PG 302 N). An Ag|AgCl|KCl (3M) electrode as reference electrode, a platinum wire as the auxiliary electrode and carbon paste electrode modified with nano zeolite as the working electrode were used. Approppariated ammount of synthesized nano zeolite was lightly ground and immersed to 10 ml 1 M $FeCl_2$

solution for 3 h. Then the solid was dried. The 30% (W/W) Fe^{2+}-zeolite to graphite powder paste was made by mixing the given quantity of Fe^{2+}-zeolite and graphite powder in diethyl ether and the solvent was evaporated by stirring a mixture. Then paraffin was blended by hand mixing and the resulting paste was inserted in the bottom of a glass tube. The electrical connection was implemented by a copper wire fitted into the opposite opening of the glass tube. For the comparission the unmodified carbon paste was prepared. Obtained results show that proposed modified carbon paste electrode can used for couantitative determination of nitrite inos with detection limit $1.45*10^{-6}$ M and the catalytic rate constant for this process was calculated as $2.75*10^{3}$ M^{-1} s^{-1} (Fig 1).

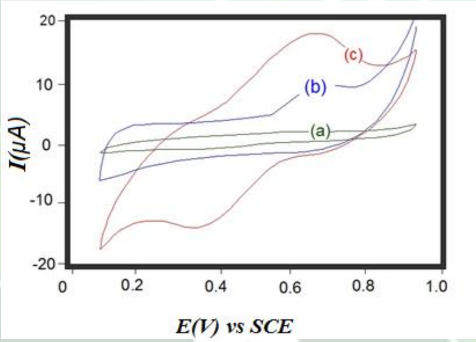

Figure 1, Cyclic voltammograms of (a) CPE in the absence and (b) Zeolite/CPE (c) Fe/Zeolite/CPE in the presence of nitrite in phosphate buffer The scan rate was 10 mV s^{-1}.

Keywords**:** *Nitrite ion, Electrocatalytic determination, Nano-zeolite, Voltammetry*

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Hydrogenation effect of furan ring of methylene tanshinone quinone on its one-electron reduction potential

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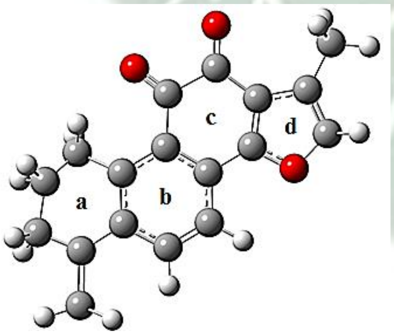
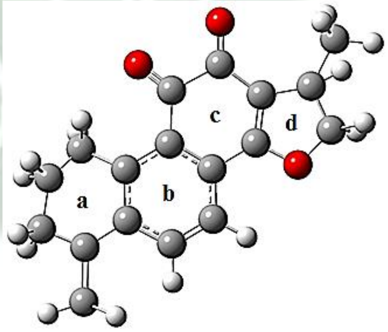
Abstract

Electron transfer processes form the main feature of chemical, biochemical and particularly electrochemical reactions. Theoretical calculation is a practical model for prediction of reduction potential of irreversible reactions or those for which the experimental measuring of that index is not easy (1). The one-electron reduction potentials of methylene tanshinone quinone (A) and methylene dihydrotanshin quinone (B) have been calculated in DMSO in the present work. All structures have been optimized at the B3LYP/6-311G++(d,p) level by the Gaussian 09 program package (2). The one-electron reduction potentials of quinones are calculated as follow:

$$E_{NHE}\left({}^{Q}/{}_{Q^{\cdot-}}\right) = E_{NHE}\left({}^{P-BQ}/{}_{P-BQ^{\cdot-}}\right) + \frac{\Delta G^{*}_{Sol}}{F} \qquad (1)$$

Where, E_{NHE} (p-BQ/P-BQ$^{\cdot-}$) is the reduction potential of para-benzoquinone (P-BQ) in DMSO and F is the Faraday constant (3). The estimated values of reduction potential for A and B are equal to, -0.778 V and -0.836 V, respectively. In fact, hydrogenation of d ring lead to the increase in the reduction potential of quinone A.





(A) -0.778 V **(B) -0.836 V**

Keywords: *Quantum mechanics, Methylene tanshinone quinone, Reduction potential*

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Investigation of the isomerization effect on diospyrin one-electron reduction potential

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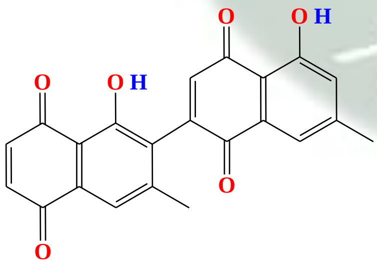
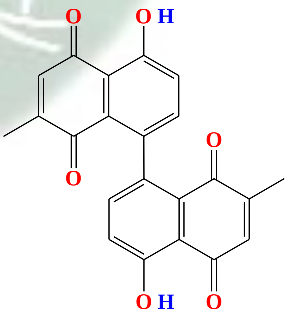
Abstract

Quinone reduction is very important in electrochemistry, biological energy saving and organic reactions. Our knowledge about quinone reduction potentials is so important in understanding the nature of their chemical reactions for designing new electronical materials and evaluating their biological activities. The calculation of reduction potential of quinones by the means of theoretical methods is an appropriate approach for solving experimental measurement problems (1, 2). The one-electron reduction potentials of diospyrin (A) and martinon (B) have been calculated in DMSO at the B3LYP/6-311G++(d,p) level in the present work. The one-electron reduction potentials of quinones ware calculated on the base of following equation:

$$E_{NHE}\,\left({}^{Q}/_{Q^{\cdot -}}\right)= E_{NHE}\,\left({}^{P-BQ}/_{P-BQ^{\cdot -}}\right) + \frac{\Delta G^{*}_{Sol}}{F} \qquad (1)$$

Where, E_{NHE} (p-BQ/P-BQ$^{\cdot -}$) is the reduction potential of para-benzoquinone (P-BQ) in DMSO and F is the Faraday constant (3). The estimated values of reduction potential for A and B are equal to, -0.222 V and -0.397 V, respectively. Isomerization leads to the increase in the reduction potential of related quinone (A).





(A) -0.222 V **(B) -0.397 V**

Keywords: *Electrochemistry, Quinones, Para-benzoquinone, Reduction potential*

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Fabrication of Novel Modified Glassy Carbon Electrode for Determination of Toxic Phenol

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Abstract

Phenol and a considerable number of its derivatives are important toxic compounds and are extensively used in several industrial processes such as plastics, dyes, pesticides, papers, and petrochemical products. It is also produced in our body during food intake. As a result, phenols are often detected in water, soil and sediment samples. Phenol is used in the cleaning process of bacteria and fungi and for the treatment of sour threat as a paste and solution in medicine due to its disinfectant properties. Phenol today is not only threating the human health but also is a major source of pollutant, thus, it carries a potential risk for usage. Owing to their poor biodegradability, high toxicity and ecological aspects, phenol should be determined quantitatively when the sample is analyzed by sensitive analytical methods [1]. Phenol can be bind onto an electrode surface thus a polymerization process takes places on the modified electrode surface. The binding of phenol on the electrode surface enable us to determine phenol at very low concentrations. Voltammetric techniques require a small amount of sample volume thus help us to determine phenol and its derivatives [2]. Recently, metal nanoparticles have paid much attention due to their enhanced catalytic properties in various chemical reactions. Many reports established that the metal nanoparticles had high yields in catalyzing due to their smaller size (1-100 nm), and they possess unique exhibit unique physical, chemical and electronic properties which are different from the bulk materials, and it can be used to construct novel and enhanced sensing devices, particularly, electrochemical and biosensors [3]. In this work, we tried to develop a specific sensor electrode for the determination of phenol by modifying GCE surface using $CoFe_2O_4$ nanoparticles and (14E)-4-((E)-4-(2-hydroxybenzylideneamino)phenoxy)-N-2-

hydroxybenzylidenebenzenamine (see fig. 1). After the modification process, the electron transfer becomes easier and faster. For the calibration curve, a series of standard phenol solution between 1.0×10^{-3} M and 1.0×10^{-8} M was prepared. By using this calibration method, the amount of phenol was determined as 8.33×10^{-5} M in natural decayed leaves. Detection limit was obtained as low as 1.0×10^{-8} M. By using this developed sensor electrode one can easily quantitatively determine phenol at very low concentrations. This study was successfully applied to the real samples for phenol determination.

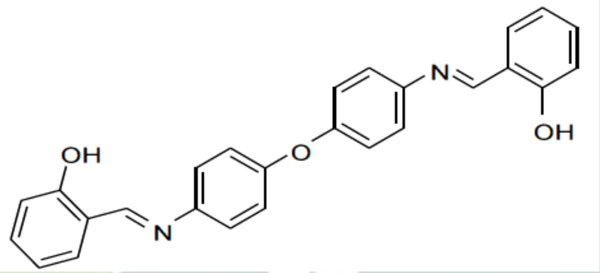

Fig. 1. Chemical structure of (14E)-4-((E)-4-(2-hydroxybenzylideneamino)phenoxy)-N-2-hydroxybenzylidenebenzenamine

Keywords: *Phenol, Glassy carbon electrode, Cyclic voltammetry, Surface modification*

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An Electrochemical Sensor for Hydrazine Based on $CoFe_2O_4$ Nanoparticles: Toward Water Samples

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Abstract

Environmental pollution and food safety are currently a focus of considerations worldwide. Hydrazine is a highly carcinogenic substance and may cause water source contamination, owing to its wide-range applications involved with industrial process. For example, hydrazine can function as corrosion inhibitor, antioxidant, catalyst, reducing agent, photographic developer, rocket propellant, and is frequently used as the starting material for the synthesis of insecticides, explosives, dyestuffs and pharmaceuticals. However, it has adverse effect on health such as brain damage, DNA damage, and creation of blood abnormalities and irreversible deterioration of nervous system. Therefore, humans exposed to hydrazine would bear severe health risk. In this regard, detection of this poisonous substance is of practical importance [1]. Electrochemical methods are practical and attractive because electrochemical instrumentation is usually compact, relatively inexpensive, reliable and sensitive. It is known that at a bare electrode surface, the electrochemical oxidation of hydrazine requires high-overpotential. To improve the detection performance, a variety of nanomaterials have attracted worldwide attention, such as carbon materials, metal nanoparticles, and metal oxides [2]. In particular, the magnetic nanoparticles $CoFe_2O_4$ have attracted great attention due to large specific surface area, low toxicity, and magnetic properties. Most importantly, it can be easily separated from the aqueous samples by an external magnetic field, and has a good auxiliary catalytic property [3]. In this work, we tried to develop a specific sensor electrode for the determination of phenol by modifying GCE surface using $CoFe_2O_4$ nanoparticles and (14E)-4-((E)-4-(2-hydroxybenzylideneamino)benzyl)-N-2-hydroxybenzylidenebenzenamine (see fig. 1). The hydrazine sensor, appeared to exhibit a good

linear range of 1×10^{-6}–7.4×10^{-3} M and a detection limit of (S/N=3) 1.7×10^{-7} M. The selectivity of the modified electrode for hydrazine was studied for a number of ions such as, Na^+, Cl^-, Ca^{+2}, Mg^{+2}, and SO_4^{-2} and biomolecules such as glucose and ascorbic acid. Therefore, modified electrode appears to be a good candidate for the oxidation and quantitative determination of hydrazine.

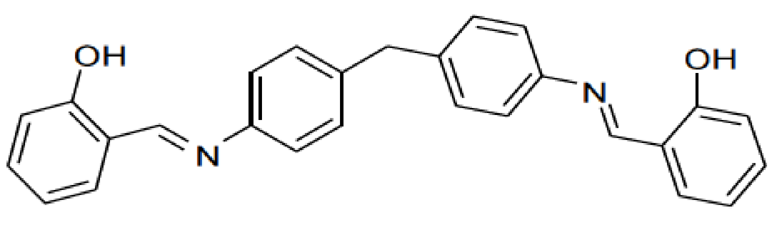

Fig. 1. Chemical structure of (14E)-4-((E)-4-(2-hydroxybenzylideneamino)benzyl)-N-2-hydroxybenzylidenebenzenamine

Keywords: *Hydrazine, Glassy carbon electrode,* $CoFe_2O_4$ *nanoparticles, Surface modification*

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Investigation of variation of porous silicon structure using metal-assisted chemical etching

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Abstract

Metal-assisted etching procedure is an inexpensive, easy, and efficient method to create porous structures which are the potential candidate in photovoltaic industry [1]. Porous structures due to their great applications in optoelectronics, sensors, solar cells has been attracted great attentions [2-5]. In this research metal-assisted etching of silicon in $HF/H_2O_2/H_2O$ mixture was investigated by using Ag nanoparticles as catalyst agents. So we changed the concentration of H_2O_2 relative to HF to creation of various structures and characterization of their properties such as anti-reflection properties. FE-SEM images and etch rate measurements were performed as a function of the etching solution mixture. Depending on the relative amount of HF and H_2O_2, different morphology and structures were resulted. The molar ratio of HF, H_2O_2 is given in table1. The XRD analysis was done to investigate the structure formation and found that the sample which is immersed into an aqueous solution of HF/H_2O_2 and molar ratio (7/0.88) has the best porous structure and shows that the sample3 has a structure similar to the free single crystal wafer because of its peak is sharp and has high intensity. The anti-reflection properties of porous layer was investigated to trapping the sun light and found that the sample2 is the most appropriate one.

Table1. The combination of etching solution and the pore size of silicon wafers

Solution	Molar concentration of HF	Molar concentration of H_2O_2
1	7	0.78

2	7	0.88
3	7	1.01

Keywords: *Silver nanoparticles, HF–H_2O_2 solutions, Assisted etching, Porous silicon*

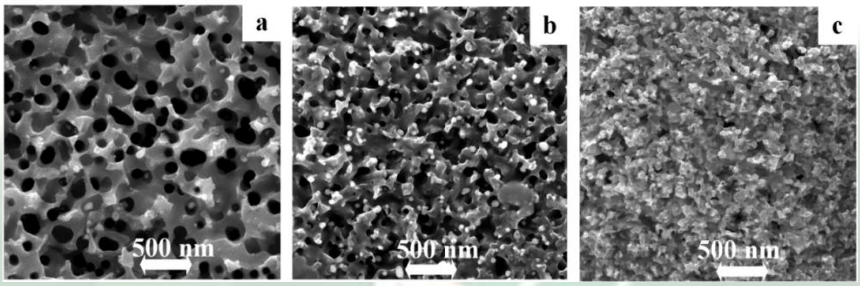

Fig.1. FE-SEM images of p-Si (100) samples after HF-H_2O_2 etching for different concentration of H_2O_2 relative to HF (a)0.78M , (b)0.88M , and (c)1.01M

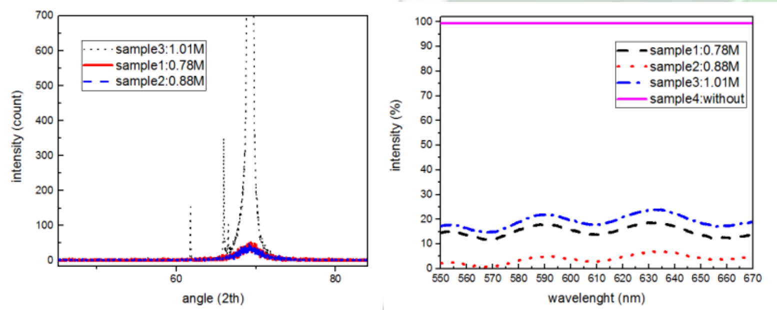

Fig.2. (left) XRD pattern of porous silicon wafers with 0.78M ,(b)0.88M , and (c)1.01M (right) Reflection spectra of etched wafers, (a)0.78M ,(b)0.88M ,(c)1.01M ,and (d)free Si wafer

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Electrochemical oxidation of 2-nitroso-1-naphtol in the presence of sulfinic acids

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Abstract

Electrochemical methods are widely used for the study of electroactive compounds in pharmaceutical forms and physiological fluids due to their simple, rapid, and economical properties [1]. The electrochemical oxidation of 2-nitroso-1-naphtol have been studied in various pH values in aqueous solutions by cyclic voltammetry method. The results showed that in pH 1-9 by increasing pH the peak potential for anodic peak shifts to negative values. And after pH 9 by increasing pH peak potential is independent of pH[2].

Synthesis of different derivatives of 2-nitroso-1-naphtol were carried out by the electrochemical reaction of 2-nitroso-1-naphtol with the arylsulfinic acids. This process was monitored by cyclic voltammetry [3].

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Nano-size Electrolytic Manganese Dioxide synthesis and characterization for sensing applications

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Abstract

Acidic gases, such as HCl, are used as precursors in CVD processes and as etching gases in semiconductor processing. Moreover, CO2 attracts attention as a main source of global warming. Many methods have been developed to detect such acidic gases in environment; in particular, electrochemical sensors have been intensively studied because of their unique features. Several studies [l-3] were made using an acidic-gas sensor based on the amperometry of lead oxide, manganese dioxide, iodine and Platinum oxide, but it is important to develop more reliable amperometric sensors in the industrial purposes. Direct electrode oxidation of HF or HCl is difficult, because of their high redox potentials. So, we have investigated amperometric detection system based on electroactive manganese dioxide to detect the acidic gases. The electroactive manganese dioxide phases used in the work were prepared by electrodeposition, and hence were designated as electrolytic manganese dioxide (EMD). We prepared EMD in an electrolysis cell based on a 300 mL Pyrex beaker in a temperature controlled bath. The anode in the cell onto which the EMD was deposited consisted of two 14 cm^2 titanium sheets interspaces with one similarly sized titanium cathode. The electrolysis current passed through the cell was set to 50 A/m^2. The electrolyte used was based on an aqueous solution of $MnSO_4$ and H2SO$_4$. We select the specific conditions from the literature to achieve highest BET surface area around 50 m^2/g. The bath temperature, $MnSo_4$ and H_2So_4 molarity was chosen to be 90°C, 0.7 molar and 0.5 molar respectively. The EMDs were characterized by electron microscopy studies (Fig 1a.) and XRD (Fig 1b.). The dry electrode ingredients were combined by lightly grinding together a mass mixture of the active material (manganese dioxide), conductive agent and binder using a ceramic

mortar and pestle (5 min). This powder was then made into an ink by adding terpineol in a weight ratio of 40:1 solvent to solid. The ink was sonicated for 30 min until evenly dispersed. Electrode was screen printed on a gas-permeable membrane. Fabricated electrode have been used as working electrode in an miniature sized amperometric three electrode electrochemical cell consisting of Ag/AgCl reference electrode, Pt Counter electrode and Nh4Cl aqueous Electrolyte. The reaction current was expected to depend on the H+ concentration at the electrode surface. We compared the characteristics of sensors made of working electrodes composed of EMD and commercial MnO_2 for detection of HCl. Figure 2 shows the comparison of the sensitivity of the sensors made of commercial MnO2 and EMD based working electrode to the 10 ppm HCl flow with 0.7 Lpm flow rate. The data acquired as it can be seen EMD based sensors are more than 5 time sensitive than their commercial analogous.

Keywords: *EMD, Gas sensor, Amperometry*

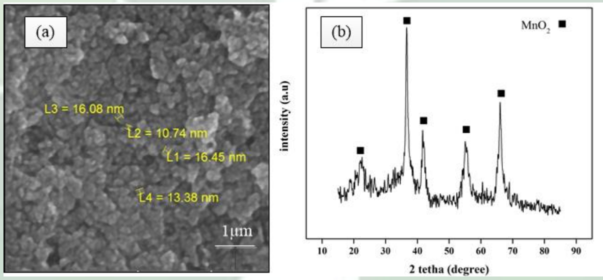

Fig1. Characterization of EMDs by (a) SEM (b) XRD

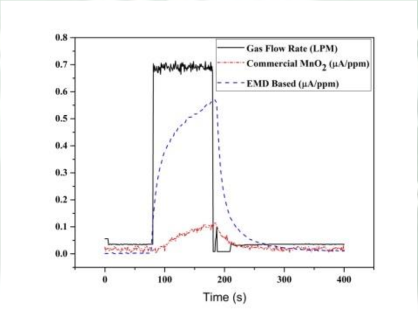

Fig2. Comparison of the sensitivity of the sensors made of commercial MnO2 and EMD based working electrode

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Nanostructure Electrochemical Sensor for Voltammetric Determination of Vitamin C in the Presence of Vitamin B_6: Application to Real Sample Analysis

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Abstract

Vitamins constitute a group of compounds, which are essential to human body for health, nutrition and normal growth, self maintenance and functioning of human and animal bodies[1]. Vitamin C and vitamin B_6 belongs to the water-soluble vitamins [2, 3]. Since these biochemical active molecules can not be synthesized by the human body, small quantities are required in the diet. Leftover amounts of the vitamin leave the body through the urine. That means you need a continuous supply of such vitamins in your diet [4-6]. An electrochemical method has been developed and successfully applied for the simultaneous determination of vitamin C and vitamin B_6 using the carbon paste electrode modified by using ZnO/CuO nanosheets, ionic liquids (N-hexyl-3-methylimidazolium hexafluoro phosphate) and 2-(ferrocenylethynyl)fluoren-9-one. The oxidation peak currents show a linear dependence on the vitamin C concentrations in the range of 4.0×10^{-8} M– 1.0×10^{-3} M with a detection limit of 2.0×10^{-8} M. The diffusion coefficient ($D/cm^2\,s^{-1}=5.38\times10^{-6}$), electron transfer coefficient, ($\alpha=0.28$) and the heterogeneous rate constant, ($k/M^{-1}s^{-1}=2.3\times10^{3}$) for vitamin C were determined using electrochemical approaches. It has been found that, the oxidation of vitamin C at the surface of such an electrode occurs at a potential about 190 mV less positive compared to an unmodified carbon paste electrode. The modified electrode greatly enhanced the electrooxidation reactions of vitamin C and vitamin B_6, and in optimized conditions well-separated voltammetric peaks for sensitive and selective determination of vitamin C and vitamin B_6 appeared using the SWV technique. The proposed method could be applied to the determination of vitamin C and vitamin B_6 in real samples.

Keywords: *Vitamin C. Vitamin B6. ZnO/CuO nanosheets. Ionic liquid. Food analysis.*

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Voltammetric determination of amoxicillin using gold nanoparticles modified glassy carbon electrode

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Introduction

Amoxicillin (AMX) is one of the most frequently used β-lactam antibiotics in the world. Because of therapeutic importance, development of rapid and sensitive methods for clinical monitoring of AMX are important [1]. Different analytical techniques have been applied for determination of AMX such as HPLC [2] and voltametric methods [3-5]. The HPLC method have been often time consuming processes and are usually expensive. In this study, a novel modified electrode is prepared by electrochemical deposition of nano-Au on the surface of a poly(L-methionine) (PMT)-modified glassy carbon electrode (GCE). The nano-Au/PMT/GCE was used as a novel sensor for determination of AMX in biological sample.

Method

Polymerization of L-methionine on the GCE was performed using cyclic voltammetry in an aqueous solution of L-methionine (2.5 mM) and phosphate buffer solution (0.1 M). Nano-Au was electrochemically deposited on the PMT/GCE surface by applying a cathodic potential of –0.23 V for 300 s in $HAuCl_4$ solution (0.5 mM). The obtained nano-Au modified PMT film electrode was washed with deionized water and is namely nano-Au/PMT/GCE.

Result and discussion

The parameters of the L-methionine concentration and pH of the supporting electrolyte solution were optimized by CV methods. Optimum conditions were 2.5 mM of L-methionine and pH of 9. Fig. 1 shows CVs of nano-Au/PMT/GCE in phosphate buffer solution (PBS, pH = 9.00) in the absence an presence of 0.1 mM AMX. No anodic current was observed in the surface of bare

GCE. The anodic current for electrooxidation of AMX at the surface of nano-Au/PMT/GCE was significant. As a result, this improvement in the oxidation current demonstrates that incorporation of nano-Au and PMT onto a GCE enhances the electrochemical signal of AMX electrooxidation.

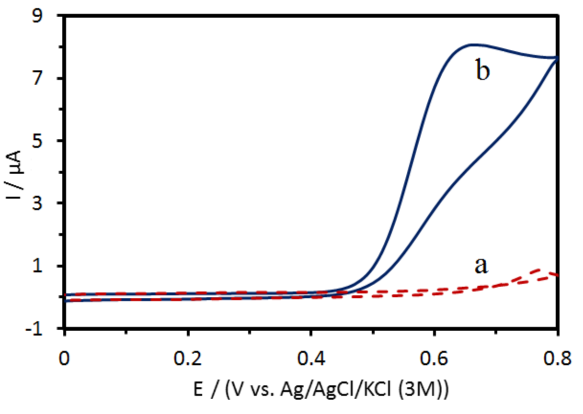

Fig. 1. CVs of nano-Au/PMT/GCE (a) in the absence and (b) presence of 0.1 mM AMX in 0.1 M PBS (pH=9) at 20 mV s^{-1}.

Conclusion

In this study, a novel AMX sensor was fabricated by modification of GCE using nano-Au and poly (L-methionine). The modified electrode showed excellent sensitivity, selectivity, and anti-fouling properties for the voltammetric determination of AMX.

Keywords: *Electrochemical determination, Voltammetry, Amoxicillin, Gold nanoparticle*

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Metal Oxide/Pt Based Nanocomposites as Electrocatalysts for Oxygen Reduction Reaction

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Abstract

Fuel cells have been hailed as an important power source for the future because of their high energy conversion efficiency and low environmental pollution. Fuel cells are attractive power sources for both stationary and electric vehicle applications due to their high conversion efficiencies and low pollution. Many difficulties have prevented the widespread usage of fuel cells including high content of high cost platinum as the most familiar electro-catalyst, oxygen sluggish kinetics caused by CO-like species poisoning effect and the formation of –OH species at +0.8 V, which inhibits further reduction of oxygen.Recently, much of the research work is focused on the system of combining metal oxides to reduce the catalytic loading of the materials (cost reduction), to improve the electrochemical activity for the cathodic reaction and to increase stability.In this study, Pt catalyst was precipitated on Vulcan XC-72R containing 10 wt.% NiO and CoO using $NaBH_4$ as a reducing agent. The prepared catalyst was heat-treated at 400-700 °C. XRD and SEM characterizations were carried out to determine the crystalline phase, particle size and morphology of the catalysts. XRD patterns of sample showed peaks characteristic of Pt (111), (200), (220) and (311). The diffraction peaks are also observed for cubic phases of CoO and NiO. The electrocatalytic activity of electrocatalysts was examined by using cyclic voltammetry techniques. The enhanced electrocatalytic performance and the long-term cycle durability of electrocatalyst are attributed to the strong interaction between Pt, NiO and CoO and the formation of small Pt crystals. Cyclic voltammetry and linear sweep voltammetry were recorded to evaluate ORR performance and electrochemically stability.

***Keywords**: Fuel cells, Oxygen Reduction Reaction, Electrocatalysts, Metal Oxide, Platinum*

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