ARTICULOS PUBLICADOS

LGAC: **Detección y Remoción de Contaminantes del Medio Ambiente**

La productividad de esta línea de investigación en cuanto a artículos publicados durante el periodo 2012-2017 fue de 26 artículos científicos.

A continuación se da el detalle de los artículos publicados:

1) Zapata-Fernández, J. R.; Gochi-Ponce, Y.; Salazar-Gastélum, M. I.; Reynoso-Soto, E. A.; Paraguay-Delgado, F.; Lin, S. W.; Félix-Navarro, R. M.* Ultrasonic-assisted galvanic displacement synthesis of Pt-Pd/MWCNT for enhanced Oxygen Reduction Reaction: effect of Pt concentration, *Int. J. Hydrogen. Energy*, **2017**, 42(15) 9806-9815.

2) Silva-Carrillo, C.; Reynoso-Soto, E. A.; Paraguay-Delgado, F.; Alonso-Nuñez, G.; Felix-Navarro, R. M.* Synthesis of PtNPs/MWCNT Functionalized with 4-Mercaptophenylboronic Acid for an Electrochemical Sensor of Fructose, *J. Electrochem.Soc.* **2017**, 64(4), B86-B91.

3) Quiroa-Montalván, C. M.; Gómez-Pineda, L. E.; Álvarez-Contreras, L.; Valdez, R.; Arjona, N.; Oropeza-Guzmán, M. T. Ordered Mesoporous Carbon Decorated with magnetite for the detection of heavymetals by square wave anodic stripping voltammetry. *J. Electrochem.Soc.* **2017**, 164(6), B304-B313.

4) Trujullo-Navarrete, B.; Haro-Vázquez, M. P.; Félix-Navarro, R.M.; Paraguay-Delgado, F.; Alvarez-Huerta, H.; Pérez-Sicairos, S.; Reynoso-Soto, E. A.* Effect of Nd^{3+} doping on structure, microstructure, lattice distortion and electronic properties of TiO$_2$ nanoparticles. *Journal of Rare Earths*, **2017**, 35(3), 257-270.

5) Lin, S. W.; Corrales-López, K. A.; Perez-Sicairos, S.; Félix-Navarro, R. M. Preparation, characterization and application of PS/ SPEES–PES UF membranes for removal of ppm Cd^{2+} from aqueous media. *Polymer Bulletin*, **2017**, DOI 10.1007/s00289-017-1979-1.

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INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 42 (2017) 9806–9815

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journal homepage: www.elsevier.com/locate/he

Ultrasonic-assisted galvanic displacement synthesis of Pt–Pd/MWCNT for enhanced oxygen reduction reaction: Effect of Pt concentration

J.R. Zapata-Fernández [a], Y. Gochi-Ponce [a], M.I. Salazar-Gastélum [a],
E.A. Reynoso-Soto [a], F. Paraguay-Delgado [b], S.W. Lin [a],
R.M. Félix-Navarro [a,*]

[a] Centro de Graduados e Investigación en Química, Instituto Tecnológico de Tijuana, Apdo. Postal 1166, 22000 Tijuana, BC, Mexico
[b] Centro de Investigación en Materiales Avanzados, S.C., Laboratorio Nacional de Nanotecnología, Miguel de Cervantes 120, CP. 31136 Chihuahua, Chih., Mexico

ARTICLE INFO

Article history:
Received 15 November 2016
Received in revised form
27 January 2017
Accepted 8 February 2017
Available online 23 March 2017

Keywords:
Pt–Pd catalyst
Sonication-assisted reaction
Galvanic displacement
ORR
PEMFC

ABSTRACT

The most important issue for proton exchange membrane fuel cells (PEMFC) is the catalyst which is predominantly Pt-based materials. The simple and fast galvanic displacement (GD) method is a novel alternative does not require any surfactants, additive reagent, or post-treatment in the synthesis of bimetallic materials. The parameters investigated were Pt concentration and sonication in GD bath, finding that both play a key role in the physicochemical features, and thereby, modifying the performance of the catalysts towards the oxygen reduction reaction (ORR) activity. The materials obtained by GD were studied using TGA, ICP-OES, TEM and evaluated as catalysts for ORR in acidic media. Among all synthesized catalysts, highly dispersed $Pt_{10}Pd_{90}$/MWCNT synthesized by GD in sonication, exhibited the highest electrocatalytic activity and H_2O_2 was not detected, showing as a promising catalyst for the use in PEMFC applications.

Introduction

During the last few decades, proton exchange membrane fuel cells (PEMFC) had become an attractive power source due to their high energy conversion efficiency and low emission for vehicles and portable applications [1]. Research on PEMFC technology involves several scientific fields such as simulation, engineering and synthesis of new materials [2–4]. It is well known that the ORR taking place at the PEMFC cathode is kinetically slower than hydrogen oxidation at the anode, thereby several catalysts have been studied to address this limitation [5–7]. The synthesis of new materials requires the control of structure and morphology, because these are the key factors that have a great influence on the kinetics of the electrochemical reactions involved. The current approaches are broadly classified into Pt-based metals in order to study the relationship between size and support of the platinum particles upon electrocatalytic activity, and non-Pt metals catalysts to analyze different alternatives to enhance the ORR

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* *Corresponding author*. Fax: +52 664 6 23 4043.
E-mail address: rmfelix2003@yahoo.com.mx (R.M. Félix-Navarro).

http://dx.doi.org/10.1016/j.ijhydene.2017.02.057

Journal of The Electrochemical Society, **164** (4) B86-B91 (2017)
0013-4651/2017/164(4)/B86/6/$37.00 © The Electrochemical Society

Synthesis of PtNPs/MWCNT Functionalized with 4-Mercaptophenylboronic Acid for an Electrochemical Sensor of Fructose

Carolina Silva-Carrillo,[a,*] Edgar Alonso Reynoso-Soto,[a] Francisco Paraguay-Delgado,[b] Gabriel Alonso-Núñez,[c] and Rosa María Félix-Navarro[a,z]

[a] *Centro de Graduados e Investigación en Química. Instituto Tecnológico de Tijuana, Tijuana B. C. 22000, México*
[b] *Centro de Investigación en Materiales Avanzados. Chihuahua, México*
[c] *Universidad Nacional Autónoma de México, Centro de Nanociencias y Nanotecnología, Ensenada B. C. 22800, México*

Platinum nanoparticles (PtNPs) on multi-wall carbon nanotubes (MWCNT) were functionalized with 4-mercaptophenylboronic acid (4MPB) for electrochemical detection of fructose. The composite nanomaterial was characterized by physicochemical techniques such as TGA and TEM, and electrochemically using the $[Fe(CN)_6]^{3-/4-}$ as channel ion. Experimental values indicate that this sensor presents high sensitivity and selectivity for electrochemical detection of fructose with the sensitivity of 2.794×10^{-5} A mM^{-1} in a range of 2.5 to 10 mM using cyclic voltammetry and sensitivity 8.65 Ω mM^{-1} in range of 0.5 to 10 mM using electrochemical impedance spectroscopy.

Manuscript submitted September 2, 2016; revised manuscript received January 12, 2017. Published January 24, 2017.

Sugars are an important part of a human diet, altogether they are called nutritive sweeteners, and are sugars that originate from natural sources, such as fruits and honey, or from added sugars, mainly sucrose or high-fructose syrup.[1] Sugars that are consumed daily, added for nutrition or during the preparation of foods, sugar are the major contributor of calories to the daily diet. Increased consumption of added sugars has led to calls for renewed public nutrition information including more detailed nutrition labels.[2] Diabetes is one of the most common metabolic disorders in the world and its prevalence in adults has been increasing in the last decades. Growth in urbanization has prompted dramatic life style changes particularly in developing countries.[3,4] Reports show that in 2013 the number of adults with diabetes reached 382 million around the world.[4]

Although fructose is a carbohydrate that is used by diabetic patients, there are reports that indicate that fructose consumption might be a contributing factor to the development of obesity and the accompanying metabolic abnormalities observed in the insulin resistance syndrome.[5–7] Therefore the detection and quantification of fructose and carbohydrates using practical methods are very important. Many studies are being made in this field employing glucose-oxidase[8,9] and d-fructose dehydrogenase[10,11] for glucose and fructose determination respectively. The enzymatic sensors show low detection limits, high sensitivity and selectivity, but the most serious problem with this type of sensors is the lack of stability due to the intrinsic nature of the enzyme.[12] For this reason, in recent years non-enzymatic sensors have been developed for carbohydrate detection.[13] Boronic acid derivatives have being employed in the development of carbohydrate detection systems, since its well known that boronic acid polyols form reversible covalent interactions with 1, 2 and 1, 3 diols, such as fructose and glucose in aqueous and non-aqueous systems.[12–14] The importance of the use of boronic acid is the relatively low toxicity and unique interactions with diols. These kind of sensors have been studied for carbohydrate determination by UV-Vis spectroscopy,[15,16] fluorescence spectrometry,[15,17] electrochemical methods[18,19] and by surface plasmon resonance.[20]

In recent years, the interest of incorporating nanomaterials for carbohydrate determination is growing. Sensors based on nanomaterials offer some important advantages due to their small size and high surface area/volume ratio, which allows an increase in the response signals, better catalytic activity and faster movement of the analyte on the sensor surface.[21–24]

Electrochemical sensors based on nanomaterials offer efficient transfer of electrons improving the recognition of analytes unlike macro-scale materials.[25–27] These sensors provide an unexpensive alternative, they are easily fabricated and have the ability to detect analytes in real time, which is of particular importance in the detection of dynamic concentration levels in biological systems. The core of this research was to prepare a nanomaterial based on PtNPs on MWCNT (PtNPs/MWCNT) and it functionalization with 4-mercaptophenylboronic acid for its use as electrochemical sensor of fructose.

Experimental

Reagents.—All chemicals were purchased from Aldrich and used without further purification. Cetyltrimethylammonium bromide (CTAB, $C_{19}H_{42}BrN$, 98%), sodium borohydride ($NaBH_4$, 96%), sodium citrate tribasic dehydrate ($C_6H_5Na_3O_7 \ . \ xH_2O$, 99%), potassium hexachloroplatinate (IV) ($K_2PtCl_6 \ . \ H_2O$, 98%), 4-mercaptophenylboronic acid ($HSC_6H_4B(OH)_2$, 90%), potassium ferricyanide (III) ($K_3Fe(CN)_6$, 99%), sodium phosphate dibasic (Na_2HPO_4, 98%) and sodium phosphate monobasic (NaH_2PO_4, 99%). Sulfuric acid (H_2SO_4, 97%), nitric acid (HNO_3, 70%) and 2-propanol (C_2H_8O, 99%) were purchased from Fermont. All aqueous solutions were prepared with Milli-Q water (18 M Ω, Millipore). The MWCNT used in this work were obtained by the spray pyrolysis technique as reported Alonso et al.[28] and purified with a mixture of concentrated H_2SO_4/HNO_3 acids (3: 1) before being modified with PtNPs.[29]

Synthesis of PtNPs/MWCNT.—The synthesis of PtNPs supported on MWCNT was carried out by a microemulsion method. The microemulsion dispersion used in this study were shaped by CTAB and 2-propanol as continuous phases and water. Higher than stoichiometric amounts of sodium borohydride and sodium citrate tribasic were needed to reduce the platinum precursor thoroughly in order to obtain the platinum nanoparticles. The procedure is described in detail: 20 mg of MWCNT were dispersed for 20 min by ultrasound in 40 mL of the microemulsion solution in a three-necked round-bottom flask. In a second vessel, 10 mL of the microemulsion solution were mixed with 5 mL of 0.1 mM aqueous solution of K_2PtCl_6. This mixture was then added to the MWCNT microemulsion and heated at 60°C at constant stirring. After 10 min a mixture of 10 mL of microemulsion solution and 5 mL of 39 mM aqueous solution of the reducing agents were added to the MWCNT-K_2PtCl_6 microemulsion mixture and was left to react for 2 hours at 60°C at constant stirring. After this time the PtNPs/MWCNT nanomaterial was separated from the dispersion by filtration using a regenerated 0.4 μm nitrocellulose membrane and the hybrid material was washed with acetone and deionizad water. The procedure was repeated several times in order to eliminate remaining

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[*] Electrochemical Society Student Member.
[z] E-mail: rmfelix@tectijuana.mx

Journal of The Electrochemical Society, **164** (6) B304-B313 (2017)
0013-4651/2017/164(6)/B304/10/$37.00 © The Electrochemical Society

Ordered Mesoporous Carbon Decorated with Magnetite for the Detection of Heavy Metals by Square Wave Anodic Stripping Voltammetry

C. M. Quiroa-Montalván,[a,z] L. E. Gómez-Pineda,[b,c,z] L. Álvarez-Contreras,[d] R. Valdez,[a] N. Arjona,[a,*] and M. T. Oropeza-Guzmán[a,b,z]

[a]*Centro de Investigación y Desarrollo Tecnológico en Electroquímica, Unidad Tijuana, Tijuana B.C., C.P. 22444, Mexico*
[b]*Tecnológico Nacional de México, Instituto Tecnológico de Tijuana, Tijuana, B.C., C.P. 22500, Mexico*
[c]*Universidad Autónoma de Baja California, Escuela de Ciencias de la Ingeniería y Tecnología, Tijuana, B.C., C.P. 21500, Mexico*
[d]*Centro de Investigación en Materiales Avanzados S.C. (CIMAV), Laboratorio Nacional de Nanotecnología, C.P. 31136 Chihuahua, Mexico*

In this work, oxidized ordered mesoporous carbon (OMC-OXI) decorated with magnetite (OMC-OXI-Fe) was synthesized via a soft template technique in combination with a solvothermal method. The OMC-OXI-Fe was characterized by Raman spectroscopy, X-ray diffraction, nitrogen adsorption-desorption, scanning electron microscopy and thermal gravimetric analysis, indicating that the material keeps the OMC structure. The prepared material was used as an electrochemical sensor for the single and combined detection of Cd(II), Cu(II), Hg(II), and Pb(II) ions by square-wave anodic stripping voltammetry (SWASV). The electrochemical results showed that incorporation of magnetite did not modify the charge transfer properties, and maintained the available surface area for the metal ion detection. OMC-OXI-Fe presented a very favorable sensitivity (145.75 μA mg^{-1} L) and LOD (1.57 μg L^{-1}) for Pb(II), while the responses to Cu(II), Cd(II) and Hg(II) were much lower. These results indicated that the magnetic properties of the modified electrode increased the individual sensitivity for Pb(II) detection and maintained the capacity of simultaneous detection for the studied heavy metal ions. The combination of magnetic mesoporous carbon and electrochemical pulse techniques is a suitable and practical alternative method for the electrochemical detection of hazardous metallic ions in water for human use.

Manuscript submitted February 8, 2017; revised manuscript received April 4, 2017. Published April 27, 2017.

Pollution by heavy metals related to the wastewater discharge to the environment has a toxic effect on diverse living organisms, natural ecosystems, and human health, even at low concentrations. Heavy metals such as cadmium, mercury, and lead are toxic elements for the human body because they are considered as persistent, bioaccumulative, and non-degradable.[1] Based on this, research is focused on the development of sensors capable of detecting metals at very low concentrations.[2–6]

Analytical methods as colorimetric analysis, UV-vis spectrometry, atomic absorption spectrometry, atomic fluorescence spectrometry and ion chromatography are the most common ways to determine metal ions.[7–14] Some drawbacks of these methods such as time-consuming, do not allow in-situ measurement because of their complex operation procedures, high cost and in most cases, the analysis require sample pretreatment. In this context, electrochemical methods offer several advantages such as portability, high sensitivity, good selectivity, easy operation procedures, short analysis time, and low cost instrumentation.[15–19] Furthermore, they offer a real-time analysis and can determine the presence and concentration of different metal ions simultaneously.[20,21] This is an advantage because several heavy metal ions coexist together in wastewater.

The anodic stripping voltammetry (ASV) is the most used electrochemical technique for heavy metal analysis, being capable of analyzing ionic traces of heavy metals. ASV involves an electrochemical pre-concentration stage of metal ions, followed by the quantification of the accumulated species, and further dissolution of those ions obtaining the signal of interest.[19,22–24] For many years mercury-based electrodes were utilized for ASV owing to their high sensitivity and reproducibility, but due to the toxicity of mercury and problems related to its handling and final disposal, new environmentally friendly materials have replaced it. Recently, new materials have been developed as an alternative to the determination of heavy metals by ASV, such as modified electrodes based on carbon nanotubes,[25–27] nanostructured magnesium silicates,[28] functionalized mesoporous silica,[29] clusters of mesoporous $MnFe_2O_4$ nanocrystals,[30,31] and electrodes with a thin film of bismuth modified with a mixture of gold nanoparticles-graphene-cysteine,[21] among others.

The ordered mesoporous carbon (OMC) has attracted great attention due to its unique physical and chemical properties such as a highly ordered porous structure, elevated surface area, a narrow porous size distribution in the range of mesoporous, high electrical conductivity, and great chemical, mechanical and thermal stability. These properties make the OMC, an excellent material to be used in catalysis,[32,33] energy storage,[34] pollutant adsorption,[35,36] and as electrochemical sensors.[25,37–39] The OMC employed as modified electrode has been applied in the electrochemical analysis of organic molecules.[37–40] However, there are few reports focused on electroanalytical applications for testing traces of heavy metals.[41,42] OMC may contain favorable sites for electron transfer.[43] The incorporation of Fe_3O_4 into the structure promotes the electron transfer[44] and provide electrostatic attraction.[45] This approach can increase the accumulation efficiency toward ionic metals improving the selectivity and sensitivity of the OMC modified electrode for the analysis by anodic stripping voltammetry.

The square-wave voltammetry (SWV) is an attractive electrochemical technique because it employs pulsed potentials allowing an excellent sensitivity, a fast analysis and the suppression of background currents,[46] which can greatly enhance the electroanalytical response of several organic molecules. In addition, SWV separates selectively the electrochemical response of different species. Hence, the square-wave anodic stripping voltammetry (SWASV) can substantially diminish the limits of detection ($<$100 mg L^{-1}) compared with the simple ASV, which is enough sensitive usually above 100 mg L^{-1}.

In this work, ordered mesoporous carbon electrodes with large surface area and excellent electronic and electrochemical properties were synthesized via a soft template technique. Moreover, the OMC was functionalized incorporating carboxylic groups, followed by the addition of iron oxide magnetic nanoparticles to improve its physicochemical properties. These carbon-based materials were characterized by X-ray diffraction, Raman spectroscopy, Brunauer–Emmett–Teller (BET) methods, and scanning electron microscopy. In addition, they

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[*] Electrochemical Society Member.

[z] E-mail: vasco_quiroa@yahoo.com.mx; cquiroa@cideteq.mx; gopile@tectijuana.mx; luis.gomez53@uabc.edu.mx; oropeza1@yahoo.com

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JOURNAL OF RARE EARTHS, Vol. 35, No. 3, Mar. 2017, P. 259

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Effect of Nd^{3+} doping on structure, microstructure, lattice distortion and electronic properties of TiO_2 nanoparticles

Balter Trujillo-Navarrete[1], María del Pilar Haro-Vázquez[2], Rosa María Félix-Navarro[1], Francisco Paraguay-Delgado[3], Henry Alvarez-Huerta[1], Sergio Pérez-Sicairos[1], Edgar Alonso Reynoso-Soto[1,*]

(1. Institute Technology of Tijuana (ITT), Blvd. Alberto Limón Padilla, P.O.B 1166. Tijuana B.C. México; 2. University Autonomous of Baja California (UABC), Roadway University 14418, P.O.B 22390, Tijuana B.C. México; 3. Investigations Center of Advanced Materials (CIMAV). Miguel de Cervantes 120. P.O.B 31109, Chihuahua, México)

Received 25 June 2016; revised 30 September 2016

Abstract: Doped and undoped TiO_2 nanoparticles were prepared by Stöber method and thermally treated at 600 ºC. The effect of Nd^{3+} ion on the structure and microstructure of anatase-phase TiO_2 nanocrystals was studied by Rietveld refinement method using X-ray powder diffraction data. Bond lengths, bond angles, and edges distances were analyzed. The phase formation was confirmed by high-resolution transmission electron microscopy. The adjustment of Ti–O bond length induced by the addition of Nd^{3+} ions, reduced the octahedral distortion and altered the octahedral array in the anatase-phase TiO_2 nanocrystal. The changes of structure and microstructure were mainly observed for TiO_2 nanoparticles doped with 0.1 at.% of Nd^{3+} ions and attributed to the cationic substitution of Ti^{4+} ions which promoted changes in the density of states and gap band of TiO_2. The dopant insertion resulted in a better structural stability of the nanocrystals that enhanced their charge transference and photocatalytic efficiency.

Keywords: neodymium; TiO_2 nanoparticles; microstructure; lattice distortion; photocatalytic activity; optical properties; Rietveld refinement; rare earths

Titania nanoparticles doped with rare earth (RE) elements have applications in the degradation of persistent contaminants and dye-sensitized solar cells (DSSC). Several changes are attributed to the RE dopant in the nanocrystal, e.g., size, microstrain, specific surface area, and band gap. The modifications involve complex interactions between the RE dopant and their surrounds in the TiO_2 lattice like charge, orbital ordering, and distortions. Where, the analysis of microstructural and structural parameters is essential for the understanding of the charge transference in the photocatalytic activity or the photovoltaic performance.

The anatase-phase TiO_2 structure shows an array of empty and full octahedrons. The addition of RE^{3+} ions changes the octahedral array in the matrix of Ti^{4+} ions. It may happen in two routes: (i) the occupation of a cationic interstitial site, which is an empty octahedron generated from the arrangement of six occupied octahedrons or (ii) the cationic substitution in body-centered (BC) or face-centered (FC) positions[1]. In both substitutions, an REO_6 octahedron replaces a TiO_6 octahedron if the coordination number is six like Ti^{4+}.

For trivalent Nd (effective ionic radius of 6-coordinate Nd^{3+} is 0.098 nm), the difference in bond length between the axial Ti–O bond and the Nd–O bond is approximately 0.04 nm from their effective ionic radii[2,3] or taking the experimental value reported in perovskites structures[4,5]. Therefore, the insertion of NdO_6 octahedron may cause structural deformations that adjust Ti–O bond lengths, O–Ti–O bond angles and O–O distances in the unit cell altering Ti–O–Ti bond angles and Ti–Ti distances between adjacent octahedrons in the anatase-phase TiO_2 lattice.

In polyhedral structures, the distortion of octahedrons can be measured using the bond angles variance $\sigma^2_{\theta(\text{oct})}$ and the mean quadratic elongation $\langle\lambda_{(\text{oct})}\rangle$[6]. For polymorphs TiO_2, Meagher and Lager reported both parameters showing that the anatase phase is the most distorted among TiO_2 phases because it is sharing the higher number of edges[7]. The addition of the Nd^{3+} ion can adjust the structural distortion in the polyhedral array of the anatase phase TiO_2. The understanding of this evidence can contribute to explaining modifications in the microstructure of doped TiO_2 nanoparticles.

Furthermore, the effect of RE^{3+} ions on the microstructure of nanocrystalline anatase-phase TiO_2 samples has been reported in detail[8–11]. However, the structural distortion due to RE^{3+} such as Nd^{3+} is yet being studied in details. The role of RE^{3+} ions in the improvement of electronic transport properties of these

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Foundation item: Project supported by Consejo Nacional de Ciencia y Tecnologia or National Council of Science and Technology (CONACYT, 175925)

* **Corresponding author:** Edgar Alonso Reynoso-Soto (**E-mail:** edgar.alonso@tectijuana.mx; **Tel.:** +52 664 6233772)

DOI: 10.1016/S1002-0721(17)60909-8

Polym. Bull.
DOI 10.1007/s00289-017-1979-1

ORIGINAL PAPER

Preparation, characterization and application of PS/SPEES–PES UF membranes for removal of ppm Cd^{2+} from aqueous media

S. W. Lin[1] · K. A. Corrales-López[1] ·
S. Perez-Sicairos[1] · R. M. Félix-Navarro[1]

Received: 26 January 2017 / Revised: 7 March 2017 / Accepted: 13 March 2017

Abstract Ultrafiltration membrane prepared from hydrophobic polymers like polysulfone or polyethersulfone (PES) suffers heavy membrane fouling during cross-flow filtration. Inclusion of hydrophilic polymer like SPEES in the membrane will increase the hydrophilicity of the membrane surface, this in turn would slow down the membrane fouling process and thus prolong the service life time of the polymeric membrane. This work involves the fabrication and characterization of nine KC-series ultrafiltration membranes containing various weight percent of sulfonated polymer (SPEES) via phase-inversion process; basic characteristics of these membranes like pure water flux, water content, surface charge density, molecular weight cut-off were determined. Application of KC-series UF membranes, containing various amounts of hydrophilic polymer [sulfonated polyetherethersulfone/polyethersulfone (SPEES/PES)], for the removal of Cd^{2+} in ppm concentrations from aqueous media via cross-flow filtration operation was investigated. Rejection of Cd^{2+} from the feed containing 50 ppm in Cd^{2+} and 100 ppm in polyacrylic acid sodium (225 kDa) salt achieved ~100%.

Introduction

Research and development works on membrane technology for industrial, environmental and domestic applications have been going on for few decades [1, 2]. The demands for membrane separation systems are growing rapidly each year in areas of oil/water, hydrogen/oxygen, gas, pesticide, eater vapor lithium ion, protein, etc. [3–9]. In spite of the success of the membrane technology, all of the

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✉ S. W. Lin
sl388@AOL.COM

[1] Centro de Graduados e Investigación en Química, Instituto Tecnológico de Tijuana, 22500 Tijuana, B.C., Mexico

Energy 109 (2016) 446–455

Contents lists available at ScienceDirect

Energy

journal homepage: www.elsevier.com/locate/energy

Evaluation of Pt–Au/MWCNT (Multiwalled Carbon Nanotubes) electrocatalyst performance as cathode of a proton exchange membrane fuel cell

M. Beltrán-Gastélum [a], M.I. Salazar-Gastélum [a], R.M. Félix-Navarro [a, *], S. Pérez-Sicairos [a], E.A. Reynoso-Soto [a], S.W. Lin [a], J.R. Flores-Hernández [b], T. Romero-Castañón [b], I.L. Albarrán-Sánchez [b], F. Paraguay-Delgado [c]

[a] *Centro de Graduados e Investigación en Química, Instituto Tecnológico de Tijuana, Blvd. Alberto Limón Padilla s/n Col. Otay Tecnológico, Tijuana, B. C. 22510, Mexico*

[b] *Instituto de Investigaciones Eléctricas, Ave. Reforma 113 Col. Palmira, Cuernavaca, Morelos, 62490, Mexico*

[c] *Centro de Investigación en Materiales Avanzados SC (CIMAV), Ave. Miguel de Cervantes 120 Complejo Industrial Chihuahua, Chih, CP 31136, Mexico*

ARTICLE INFO

Article history:
Received 10 February 2016
Received in revised form
5 April 2016
Accepted 28 April 2016

Keywords:
PEMFC
MWCNT
Oxygen reduction reaction
Bimetallic
Nanomaterial
Electrocatalyst

ABSTRACT

A comparative study between Pt–Au/MWCNT and Pt/C (commercial) as cathodic electrocatalyst of H_2/O_2 fuel cell is performed. Pt–Au/MWCNT is synthesized using the reverse microemulsion method and this procedure is scaled-up in order to prepare membrane-electrode assemblies for fuel cells with an active area of 9 cm^2. Those electrocatalysts are characterized by both physicochemical techniques and electrochemical measurements to evaluate their catalytic activity for ORR (Oxygen Reduction Reaction). In the half-cell study, Pt–Au/MWCNT show higher kinetic current density as cathodic electrocatalyst compared with Pt/C. Likewise, in a fuel cell hardware the maximum power density is significantly higher for Pt–Au/MWCNT cathode (625 mW cm^{-2} at 0.426 V) when compared with Pt/C anode (355 mW cm^{-2} at 0.499 V).

1. Introduction

One of the main concerns of the last decades has been the demand for efficient energy sources to supply energetic requirements worldwide [1]. Energy sources based on petroleum and hydrocarbon are the most employed to satisfy the population energetic demand [2]. Nevertheless, two main adverse effects are implied: (a) Petroleum is limited and it is anticipated that the availability of this source will decrease [3]; (b) Most hydrocarbons contribute significantly to pollution generation, increasing the concentration of the greenhouse effect gases. Furthermore, gases such as NO_x and SO_x are also involved either in oil refinery or energy generation process from hydrocarbon sources [4].

Hence, new sustainable energy sources such as solar [5], wind [6], geothermal [7], hydro [8] have emerged as an alternative to supply the energetic requirements of the mankind and have gained importance in recent years. Renewable energies have the advantage of producing clean energy on site, but lack the capability to produce steady power as the resource will vary according to the weather conditions. Batteries, capacitors and fuel cells are ideal companions to renewable energies and can complement these technologies as they supply electricity during intermittent energy production. The most efficient way to convert hydrogen back to electricity is via fuel cells, which can be defined as a device that generate electrical energy from a chemical [9] or biochemical [10] reaction. Fuel cells are efficient, clean, and noise free energy generators that convert the chemical energy of a fuel and oxidant into electricity. The fuel cell consists of an anode and cathode, where the oxidation of the fuel and reduction of the oxidant take place, respectively. Both electrodes are typically made of a catalyst layer on top of a gas diffuser, and separated by an electrolyte where the ion exchange occurs to complete the reaction.

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* Corresponding author. Tel.: +52 6646233772.
E-mail address: rmfelix@tectijuana.mx (R.M. Félix-Navarro).

http://dx.doi.org/10.1016/j.energy.2016.04.132

Journal of The Electrochemical Society, **163** (5) G37-G43 (2016)
0013-4651/2016/163(5)/G37/7/$33.00 © The Electrochemical Society

Electrochemical and Spectrometric Studies for the Determination of the Mechanism of Oxygen Evolution Reaction

M. I. Salazar-Gastélum,[z] S. W. Lin, G. E. Pina-Luis, S. Pérez-Sicairos, and R. M. Félix-Navarro[z]

Centro de Graduados e Investigación en Química, Instituto Tecnológico de Tijuana, Tijuana B.C. 22000, México

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A novel study of the oxygen evolution reaction (OER) mechanism at different anode materials is shown using the two approaches: electroanalytical and spectroscopic. For first time, new evidence is provided for electroanalytical approach which consists of using chronoamperometric curves, to obtain Tafel plots at different detection times. Besides, intermediates of OER (e.g. $^{\bullet}$OH) were detected and quantified indirectly by fluorescence spectroscopy. This technique detects the formation of 7-hydroxycoumarin in situ from the reaction between coumarin and $^{\bullet}$OH. Among all anode materials tested, only SnO_2-Sb_2O_5 and boron doped diamond (BDD) electrodes showed the typically Tafel slope value of 120 mV dec^{-1}, associated with a primary water discharge as determining step, where $^{\bullet}$OH is the main active intermediate. The potential that provide the best detection of $^{\bullet}$OH in several electrolytes for these two electrodes were identified. This spectroscopic studies support the evidence of the formation of $^{\bullet}$OH as the rate determining step (RDS) in the OER mechanism.

Manuscript submitted October 1, 2015; revised manuscript received December 26, 2015. Published January 21, 2016.

In recent years, electrochemical research has mostly focused on pollutant degradation, evaluating different electrochemical methods,[1–4] and process designs[5] to remove trace amounts of organic compounds in wastewater. Among the several electrochemical methodologies reported, electrochemical oxidation has provided a path to total mineralization of pollutants.[6] However, this process strongly depends on the both the medium being treated and electrode materials chosen for their ability to form strong oxidants.[7] Among the known oxidant species, $^{\bullet}$OH has attracted much attention because of its high oxidizing power, which is a highly desirable feature for the destruction of toxic organic contaminants.[8] In addition, $^{\bullet}$OH is well recognized as potent reactive oxygen species in biological systems which is known to cause oxidative stress and other physiological complications in living organisms. Therefore, numerous researchers have reported on the $^{\bullet}$OH generation.[8–11] Methods for $^{\bullet}$OH generation includes Fenton or Electro-Fenton process,[12] radiation of TiO_2 photocatalyst in aqueous media,[9] and polarization at high anodic potentials.[13] Consequently, polarization at high anodic potentials can lead to mineralization of organic compounds via electrochemical oxygen transfer reaction (EOTR). However, the determining step of EOTR can be attributed to anodic discharge of $^{\bullet}$OH to O_2 in the oxygen evolution reaction (OER).[13]

OER is an anodic process in which oxidation of water takes place via the transference of either one electron, leading to the electrogeneration of $^{\bullet}$OH (Reaction 1) or involving two transferred electrons, leading to oxygen evolution (Reaction 2) and production of less powerful oxidants such as O_2, O_3, etc.[14]

$$H_2O \rightarrow \cdot OH + \ H^+ + \ e^- \qquad [1]$$

$$H_2O \rightarrow \frac{1}{2}O_2 + \ 2\,H^+ + 2\,e^- \qquad [2]$$

The rate of OER at given electrode potential depends critically on the nature of electrode materials.[15] PbO_2,[14,16] SnO_2-Sb_2O_5[17] and boron-doped diamond (BDD),[18] are anode materials reported with high overpotentials for oxygen evolution. On the other hand, platinum based-electrodes[19] and dimensionally stable anodes (DSA)[20,21] are electrodes reported with low overpotentials for oxygen evolution. OER is a complex process and is not only a function of overpotential value due to the possibility of different pathway occurring simultaneously. This process depends on several thermodynamics parameters such as electrolyte, temperature, anode material, electrolyte concentration, etc. A large number of reports discuss the mechanistic aspects of OER in terms of Tafel slope values.[11,13,15,19] The discussion of this reaction mechanism of OER is mostly based on the analysis of Tafel slope value, supplemented by spectroscopic studies of the nature of the reaction intermediates.[15]

Several mechanisms differing in molecular details have been proposed for OER.[15,19,21] A generalized mechanism can be stated as follows:

$$S + H_2O \rightarrow S - \cdot OH + H^+ + e^- \qquad [3]$$

$$S - \cdot OH \rightarrow S - OH \qquad [4]$$

$$S - OH \rightarrow S - O + H^+ + e^- \qquad [5]$$

$$2S - O \rightarrow O_2 + 2S \qquad [6]$$

The first step of the generalized mechanism is the discharge of water (Reaction 3) with the generation of S-$^{\bullet}$OH which is the main active intermediate of OER. Depending on the nature of the electro material, a surface rearrangement of the $^{\bullet}$OH could take place resulting in a more stable specie, (Reaction 4). This stable specie is susceptible to electrochemical oxidation (Reaction 5), and subsequently oxygen is released (Reaction 6). Thus, the rate determining step (RDS) of OER mechanism is related to Tafel slope value.[22]

A large number of publications report the Tafel slopes from different materials and electrolytes using linear sweep voltammetry,[10,11,13,20,23] or galvanostatic polarization.[22] Tafel slope values are usually between 30 to 120 mV dec^{-1}.[15] Table I summarizes the Tafel slope values founded in literature for OER. The intermediate Tafel slope values are interpreted in terms of mixed mechanism or of intermediate coverage with adsorbed species,[15] and this phenomenon is associated with the surface rearrangement as the RDS (transformation of the intermediate). Nevertheless, Tafel slope values higher than 120 mV dec^{-1} may result from the presences of species adsorbed that act as barrier for OER,[11] this fact is related with the formation and adsorption of S-$^{\bullet}$OH as RDS.[22] Multiple Tafel slopes can also be observed as function of overpotential where the transitions can be due to (a) changes in the coverage of adsorbed species for the same RDS of the same mechanism, (b) changes in the RDS in the same mechanism, and (c) changes in the mechanism.[15] Under the basis of a generalized mechanism, only changes in the adsorbed species or changes in the RDS are considered for further discussion.

The physicochemical properties of $^{\bullet}$OH makes it possible for these radicals to carry out the mineralization of organic contaminants. However, the concentration of $^{\bullet}$OH is difficult to quantify due to a highly active intermediate and a lifetime of approximately 10^{-9} s.[31] Since

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[z] E-mail: rmfelix2003@yahoo.com.mx; moi6salazar@hotmail.com

Renewable Energy 87 (2016) 31–41

Contents lists available at ScienceDirect

Renewable Energy

journal homepage: www.elsevier.com/locate/renene

Bimetallic Pt–Au nanoparticles supported on multi-wall carbon nanotubes as electrocatalysts for oxygen reduction

R.M. Félix-Navarro [a, *], M. Beltrán-Gastélum [a], E.A. Reynoso-Soto [a], F. Paraguay-Delgado [b], G. Alonso-Nuñez [c], J.R. Flores-Hernández [d]

[a] Centro de Graduados e Investigación en Química, Instituto Tecnológico de Tijuana, Blvd. Alberto Limon Padilla S/N, Tijuana, B. C. 22500, Mexico
[b] Centro de Investigación en Materiales Avanzados S C, Miguel de Cervantes 120, Chihuahua, Chih. 31109, Mexico
[c] Universidad Nacional Autónoma de México, Centro de Nanociencias y Nanotecnología, Km. 107 Carretera Tijuana-Ensenada, Ensenada, B. C. 22800, Mexico
[d] Instituto de Investigaciones Eléctricas, Av. Reforma 113 Col. Palmira, Cuernavaca, Mor. 62490, Mexico

ARTICLE INFO

Article history:
Received 9 February 2015
Received in revised form
7 August 2015
Accepted 27 September 2015
Available online 18 October 2015

Keywords:
Nanomaterials
Nanotubes
Oxygen reduction
Pt:Au electrocatalyst
Fuel cell

ABSTRACT

Platinum-gold nanoparticles supported on multi-wall carbon nanotubes (MWCNT) with various Pt:Au ratios are prepared by microemulsion method for use as electrocatalysts in the oxygen reduction reaction (ORR). The influence of the Pt:Au ratio on the electrocatalytic activity during ORR is investigated in detail. The synthesized nanomaterials are analyzed by different physicochemical techniques. The electrocatalytic activity for oxygen reduction is evaluated using a rotating disk electrode (RDE) system. We report that the activity and oxygen reduction mechanism depends strongly on the Pt:Au ratio; in the case of Pt:Au ratio higher than 0.60, oxygen is reduced to water by a four electron process pathway, while at 0.33 ratio the reaction follows a two-electron-transfer mechanism.

1. Introduction

In recent years, Proton Exchange Membrane Fuel Cells (PEMFC) have received significant attention as one of the most promising power sources for portable electric devices due to high energy density, low temperature operation, simple, easy to handle structure, and the ability to transport and store inexpensive fuel. The oxygen reduction reaction (ORR) is known to be the limiting step in fuel cells due to the slow reaction kinetics at the cathode as compared to the anode. For that reason, ORR continues to be an active field for research. Different experimental and fundamental approaches have been used to focus on understanding the main factors, models and mechanisms for the electrocatalysis of this reaction [1–3]. Depending upon the electrode material and the solution composition [4], the ORR may proceed via two different pathways; a two-electron-transfer process (Reaction 1) or a four-electron-transfer process (Reaction 2), yielding H_2O_2 and H_2O, respectively.

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{1}$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \tag{2}$$

Both reactions are important in different areas of research. The partial oxygen reduction to H_2O_2 is important for environmental applications such as an electro-Fenton process to degrade organic compounds [5]. The direct four-electron pathway is preferable in energy conversion applications for several reasons; one being, the absence of peroxide species that contribute to certain electrode and membrane degradation mechanisms, another being higher operating potentials and current efficiency in the PEMFC [4,6,7].

Although platinum supported on carbon is considered the best electrocatalyst for ORR, it is expensive [8]. The ORR is a type of surface–sensitive reaction in which the type of electrode material strongly affects the catalytic activity [9]. Numerous studies have been carried out in an effort to reduce the amount of platinum and improve the catalytic activity [10]. In the last decade gold nanoparticles (AuNPs) have gained attention for their unique catalytic properties for several reactions, including CO oxidation at low temperature [11]. It is also of particular importance to study the

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* Corresponding author.
E-mail address: rmfelix@tectijuana.mx (R.M. Félix-Navarro).

http://dx.doi.org/10.1016/j.renene.2015.09.060
0960-1481/

Hindawi Publishing Corporation
Journal of Nanomaterials
Volume 2016, Article ID 5783920, 11 pages
http://dx.doi.org/10.1155/2016/5783920

Research Article

Organic Solvent's Effect in the Deposition of Platinum Particles on MWCNTs for Oxygen Reduction Reaction

Carolina Silva-Carrillo,[1] Edgar Alonso Reynoso-Soto,[1] Rosa María Félix-Navarro,[1] Shu Wai Lin-Ho,[1] Aline Díaz-Rivera,[1] Francisco Paraguay-Delgado,[2] José Álvaro Chávez-Carvayar,[3] and Gabriel Alonso-Núñez[4]

[1] *Centro de Graduados e Investigación, Instituto Tecnológico de Tijuana, Apartado Postal 1166, 22000 Tijuana, BC, Mexico*
[2] *Centro de Investigación en Materiales Avanzados, Miguel de Cervantes 120, 31109 Chihuahua, CHIH, Mexico*
[3] *Instituto de Investigación en Materiales, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, 04510 Coyoacán, DF, Mexico*
[4] *Centro de Nanociencias y Nanotecnología, Universidad Nacional Autónoma de México, Km 107 Carretera Tijuana-Ensenada, Apartado Postal 356, 22800 Ensenada, BC, Mexico*

Correspondence should be addressed to Edgar Alonso Reynoso-Soto; edgar.alonso@tectijuana.mx and Rosa María Félix-Navarro; rmfelix@tectijuana.mx

Received 24 July 2015; Revised 9 February 2016; Accepted 14 February 2016

Academic Editor: Xiao-Yu Yang

We reported the synthesis of platinum particles anchored on the surface of multiwall carbon nanotubes (MWCNTs). The synthesis of platinum particles was carried out by microemulsion method using hexadecyltrimethylammonium bromide (CTAB) as surfactant to enhance the dispersion of platinum particles in hexane (C6), heptane (C7), and octane (C8) solutions. The effects of the microemulsion dispersion medium on the synthesis of platinum particles on MWCNTs (MWCNT/Pt) hybrid materials and their catalytic activities of the oxygen reduction reaction (ORR) in $HClO_4$ were investigated. The anchored platinum particles showed good dispersion on carbon nanotubes surface with the average particle sizes of 2.65 ± 0.60, 2.89 ± 0.68, and 0.97 ± 0.29 nm for the dispersion medium of C6, C7, and C8, respectively. The experimental results of ORR experiments indicated a relationship between the size and the dispersion media of the platinum particles; also the catalytic activity of the anchored platinum on MWCNT particles strongly depends on the dispersion medium employed in the microemulsion process.

1. Introduction

A fuel cell is an electrochemical device which converts free energy of a chemical reaction directly into electrical energy [1]. The main advantages of fuel cells are their high efficiency for electricity production of about 60% and practically zero emissions [2]. The cathode compartment is very important for the fuel cell because it is where the oxygen reduction reaction (ORR) takes place. The ORR is a sluggish reaction that consumes about 90% of total Pt content in PEM fuel cells [3]. The sluggish kinetics of the ORR are the main factor affecting the energy conversion efficiency of fuel cells [4, 5]. Improvement of the efficiency of the catalyst by the development of Pt nanoparticles supported on carbonaceous materials with high surface area has been proposed as one of the most effective approaches to reduce the Pt contents with good activity for the ORR [6–8]. Surface oxidation of Vulcan Carbon materials as support for platinum nanoparticles can also increase the hydrophilicity of the surface, which can result in the decrease of gas permeability, as the pores become more likely to be filled with liquid water that can hinder gas transport [9]. Due to their unique electrical and structural properties, carbon nanotubes (CNTs) are an attractive support material for Pt nanoparticles (Pt NPs). Carbon nanotubes have demonstrated the ability to carry large current densities and fast electron transfer kinetics when used for electrochemical applications [10].

Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2016.1157041

(2016) 1–13

Taylor & Francis
Taylor & Francis Group

New method of synthesis of sulfonated polyethersulfone (SPES) and effect of pH on synthetic gray water filtration performance by negatively charged SPES/PS UF membranes

Shui Wai Lin*, Fernando Javier Lopez-Garcia, Sergio Perez-Sicairos, Rosa Maria Felix-Navarro

Centro de Graduados e Investigacion en Quimica del Instituto Tecnológico de Tijuana, Apdo. Postal 1166, Tijuana, B.C., Mexico, Tel. +1 858 581 3765; email: sl388@aol.com (S.W. Lin)

Received 24 February 2015; Accepted 25 January 2016

ABSTRACT

All polymeric membrane-based water purification systems suffer serious membrane fouling problem due to protein adsorption and bacteria attachment. Increasing the negative surface charge density of the membrane will increase its hydrophilicity; this would hinder the colloidal and bacteria attachments. This can be achieved through inclusion of sulfonated group ($-SO_3^-$) as part of the moiety of the polymer that made up of the membrane. In this work, a new method of synthesis of sulfonated polyethersulfone (SPES) is reported. In this method, concentrated sulfuric acid was used as the solvent for polyethersulfone (PES) and also as the source of SO_3(g) when the PES/H_2SO_4 solution was heated to 90˚C. The degree of sulfonation of the polyethersulfone polymer was assessed by ATR-FTIR spectra and ion-exchange capacity determination. Nine polysulfone membranes, containing various amounts of SPES, were fabricated via phase inversion process with a continuous membrane casting machine. The membranes were also characterized using techniques such as SEM, AFM, water permeability, water content, molecular-weight-cut-off, and the negative surface charge. Effects of pH of the synthetic gray water feed (with common domestic wastewater composition, excepting microbiological components) on membrane fouling were evaluated for all nine SPES/PS membranes.

Keywords: Sulfonated polyethersulfone; Ultrafiltration membranes; Membrane fouling; Wastewater

1. Introduction

Rapid worldwide industrialization and global economic growth for past few decades have created great demands for membrane separation technology for industrial, environmental, and domestic applications [1–3]. Since Loeb and Sourirajan first introduced the phase inversion method for preparation of asymmetric membranes in the early 1960's, research and development works on membrane technology in the areas of water desalination [4], municipal [5] and industrial wastewater reuse [6], pharmaceutical production processes [7], and recovery of toxic volatile organic matter from liquid media [8] has received much attention in

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*Corresponding author.

Rev. Int. Contam. Ambie. 32 (2) 227-236, 2016
DOI: 10.20937/RICA.2016.32.02.08

PHOTOCHEMICAL DEGRADATION OF NITROBENZENE BY $S_2O_8^{-2}$ IONS AND UV RADIATION

Sergio PÉREZ-SICAIROS[1]*, Krisnar Alejandro CORRALES-LÓPEZ[1],
Óscar Martín HERNÁNDEZ-CALDERÓN[2], Moisés Israel SALAZAR-GASTÉLUM[1] and
Rosa María FÉLIX-NAVARRO[1]

[1] Instituto Tecnológico de Tijuana. Bulevar Alberto Limón Padilla y Avenida ITR de Tijuana, s/n Mesa de Otay, Tijuana, Baja California, México, C.P. 22500
[2] Facultad de Ciencias Químico Biológicas, Universidad Autónoma de Sinaloa. Bulevar Las Américas y Universitarios, Ciudad Universitaria, Culiacán, Sinaloa, México, C.P. 80010
*Autor para correspondencia: sepesi74@yahoo.com

(Received March 2015; accepted September 2015)

Key words: water remediation, homogeneous catalysis, oxidizing reagent, persulfate, advanced oxidation

ABSTRACT

In this work nitrobenzene (NB) degradation was studied through an advanced oxidation process (AOP) by using a photochemical reactor and two kinds of oxidizing reagent: potassium persulfate ($K_2S_2O_8$) and sodium persulfate ($Na_2S_2O_8$), to promote generation of $HO^•$ radicals. It was determined the effect of different parameters on nitrobenzene degradation, such as: wavelength of UV lamps, concentration of oxidizing reagent, type of oxidizing reagent and number of UV lamps in the reactor. By using UV lamps with radiation wavelength of 254 nm, NB degradation reached almost 100 % meanwhile, irradiating at 350 nm resulted in < 35 % degradation. For experiments using UV lamps of 254 nm, the reaction rate increased with the radiant energy, being higher by using four UV lamps than two UV lamps for a reaction time of 60 min. The specific energy consumption for two UV lamps showed the lowest value being of 2626.0 KW.h/Kg of NB degraded.

Palabras clave: remediación de agua, catálisis homogénea, agente oxidante, persulfato, oxidación avanzada

RESUMEN

En este trabajo se estudió la degradación de nitrobenceno (NB) mediante un proceso de oxidación avanzada empleando un reactor fotoquímico y dos agentes oxidantes: persulfato de potasio ($K_2S_2O_8$) y persulfato de sodio ($Na_2S_2O_8$), con el objetivo de generar radicales $HO^•$. Se determinó el efecto de diferentes parámetros en la degradación de nitrobenceno, tales como: longitud de onda de la lámparas UV, concentración del agente oxidante, tipo de agente oxidante y número de lámparas en el reactor. Con la lámpara de 254 nm se alcanzó una remoción de NB cercana al 100 % mientras que con la lámpara de 350 nm se obtuvo un porcentaje de degradación < 35 %. Para el caso de las lámparas de 254 nm se encontró que la tasa de degradación se incrementa con la energía radiante, es decir, aumenta al emplear cuatro lámparas respecto de utilizar dos para un tiempo de reacción de 60 min. Al considerar el consumo energético específico, con el arreglo de dos lámparas UV se tiene el menor valor, siendo de 2626.0 KW/h/kg de NB degradado.

Artículo **Revista de Tecnología e Innovación**
Junio2016 Vol.3 No.7 51-59

Automatización en la deposición de películas delgadas de nanomateriales para la posible utilización en celdas solares

REYNOSO-SOTO, Edgar*†, ALONSO-PÉREZ, Jorge, TRUJILLO-NAVARRETE, Balter y CAZAREZ-CASTRO, Nohé.

Recibido Abril 5, 2016; Aceptado Junio 2, 2016

Resumen

En este trabajo se reporta la implementación de un robot cartesiano con una arquitectura de LinuxCNC para la fabricación automatizada de películas delgadas de dióxido de titanio (TiO_2) para el desarrollo de celdas solares; dispositivos empleados para la generación de energía eléctrica a partir de fuentes alternativas de energía. Este robot cartesiano con la arquitectura LinuxCNC permite preparar películas delgadas de espesor controlado; ya que actualmente a nivel laboratorio la preparación se realiza de manera manual por métodos poco reproducibles como es el método de bisturí (doctor blade). Este tipo de dispositivos permitirán un avance significativo en las tecnologías de fuentes alternas de energía y su investigación debido a que da acceso a maquinarias que actualmente en el mercado son muy costosas.

En el presente trabajo, se muestra que las películas delgadas de TiO_2 obtenidas por spray coating a partir de una solución de etilcelulosa-TiO_2disuelta en etanol, se depositan con éxito en sustratos de vidrio, con un espesor entre 0.8 y 1.2 µ m.

LinuxCNC, robot cartesiano, películas delgadas, nanomateriales

Abstract

This paper describes the implementation of a cartesian robot with LinuxCNC architecture for the automatization of titanium dioxide (TiO_2) thin films development for solar cells fabrication; this types of devices are employed in the generation of electricity from alternative energy sources. The Cartesian robot with LinuxCNC arquitecture allows prepare thin finlms with controlled thickness; since currently at laboratory level thin film preparation is done manually with low reproducibility method such doctor blade method. Cartesian robot significant thecnological advance in alternative source energy investigation. In this work is reported the fabrication of TiO_2 thin film obtained by spray coating employing ethylcellulose-TiO_2 ethanolic solution, this was coating succefully on glass, with a thickes of 0.8 to 1.2 µm.

LinuxCNC, Cartesian robot, thin films, nanomaterials

Citación: REYNOSO-SOTO, Edgar, ALONSO-PÉREZ, Jorge, TRUJILLO-NAVARRETE, Balter y CAZAREZ-CASTRO, Nohé. Automatización en la deposición de películas delgadas de nanomateriales para la posible utilización en celdas solares. Revista de Tecnología e Innovación 2016, 3-7: 51-59

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*Correspondencia al Autor (Correo electrónico: edgar.alonso@tectijuana.mx)

†Investigador contribuyendo como primer autor.

Journal of The Electrochemical Society, **161** (12) H845-H853 (2014)
0013-4651/2014/161(12)/H845/9/$31.00 © The Electrochemical Society

Development of a Pt-Ir Bimetallic Nanoparticulated Electrocatalyst Deposited on MWCNT for an Electro-Fenton Process

Rosa María Félix-Navarro,[a,z] Moisés Israel Salazar-Gastélum,[a] Mara Beltrán-Gastélum,[a] Edgar Reynoso-Soto,[a] Shui Wai Lin,[a] Sergio Pérez-Sicairos,[a] Francisco Paraguay-Delgado,[b] and Gabriel Alonso-Núñez[c]

[a] *Centro de Graduados e Investigación en Química, Instituto Tecnológico de Tijuana, Tijuana, Baja California 22500, Mexico*
[b] *Centro de Investigación en Materiales Avanzados, Chihuahua, Chihuahua, Mexico*
[c] *Centro de Nanociencias y Nanotecnología, Km, Ensenada, Baja California, Mexico*

Synthesis of a novel cathode of bimetallic Pt-Ir nanoparticles deposited on multiwall carbon nanotubes (MWCNT) by a microemulsion method is reported in this paper; the composite material was dispersed with Nafion to deposit a film onto Reticulated Vitreous Carbon (RVC), the modified electrode was used as catalyst in an electrochemical reactor for H_2O_2 generation. The bimetallic catalyst showed higher activity toward O_2 reduction compared to Ir/MWCNT, Pt/MWCNT and MWCNT. The O_2 reduction pathway was determined. Only the bimetallic catalyst was found to lead to the reduction of O_2 to produce H_2O_2. A high H_2O_2 rate was produced with the bimetallic catalyst. This approach was employed to carry out the Fenton process. Experimental evidence for the generation of hydroxyl radicals ($^{\bullet}OH$) was provided by using coumarin and the fluorescence detection of its hydroxylated product (7-hydroxycoumarin). The Pt-Ir/MWCNT cathode showed very stable behavior and could be reused without decrease of the catalytic activity. This suggests its potential use in wastewater treatment application.

Manuscript submitted July 17, 2014; revised manuscript received August 5, 2014. Published September 16, 2014.

Toxic organic compounds are the main pollutants in industrial effluents. Conventional wastewater treatment processes remove the bulk of the material, and leave behind trace amounts of organic compounds. These organic compounds in water can lead to serious health issues, even at trace level, and is a concern to many water authorities. Advanced oxidation processes (AOPs) have emerged as an additional method to destroy these trace amounts of organic compounds in wastewater. AOP is an oxidation process that involves hydroxyl radical ($^{\bullet}OH$), which is a powerful oxidizing agent with short lifetime. When $^{\bullet}OH$ radicals are produced in sufficient quantities, they can oxidize the organic material into non-toxic species. Among the various AOP methods available, the electro-Fenton oxidation has attracted much attention in recent years. The method has the ability to destroy many types of organic compounds and is environmental friendly.[1] In the electro-Fenton oxidation, $^{\bullet}OH$ radicals are produced in the solution by the reaction between Fe^{2+} and hydrogen peroxide (H_2O_2) (Eq. 1).

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \qquad [1]$$

In electro-Fenton process, $^{\bullet}OH$ radicals are generated following either of two approaches, producing Fe^{2+} ions by the oxidation of a Fe anode (anodic Fenton process) or generating H_2O_2 according to Eq. 2 (cathodic Fenton process). For environmental purpose and low cost production, the cathodic Fenton process approach was studied in this work.

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad [2]$$

Alternatively, the hydroxyl radical ($^{\bullet}OH$) can also be produced electrochemically from the oxidation of water at high oxygen overpotentials with anodes, such PbO_2,[2,3] SnO_2-Sb_2O_5[4] and boron doped diamond[5–7] ((Eq. 3):

$$H_2O \rightarrow {}^{\bullet}OH + H^+ + e^- \qquad [3]$$

The high oxidizing power of $^{\bullet}OH$ radicals allow them to oxidize most organic compounds and many inorganic pollutants in the bulk solution.[8–11]

The electrochemical generation of hydrogen peroxide (H_2O_2) by the reduction of oxygen has been reported, using cathodes fabricated from various materials such as carbon felt,[8–10] activated carbon fiber,[11] graphite[12,13] and reticulated vitreous carbon.[14] Nanomaterials have been also used for this purpose, to name few, multiwalled carbon nanotube,[15] composite of Cu_2O nanocubes and carbon nanotubes,[16] Fe_3O_4@Fe_2O_3/activated carbon aerogel[17] and Fe@Fe_2O_3/active carbon fiber.[18,19] As reported in our previous work, bimetallic catalyst Pt-Pd/MWCNT was used for H_2O_2 generation at the best applied potential of 0.5 V vs Ag/AgCl, 72 μM of H_2O_2 in aqueous solution was obtained, this scheme was also used for nitrobenzene degradation.[20]

Due to its high reactivity and short life-time (usually 10^{-9} s); the direct detection of $^{\bullet}OH$ radicals is a very difficult task. Convincing evidence for $^{\bullet}OH$ radicals formation were obtained by photochemical and radiation chemical studies using various spin traps combined with transient absorption measurements in the UV-Vis range and electron spin resonance (ESR) detection.[21–23] Other methods such as steady-state UV-Vis absorption,[21,24] High Performance Liquid Chromatography,[25] electrochemical detection[26,27] and fluorescence[28–34] were also used to measure the quantity of scavenged $^{\bullet}OH$ radicals. Czilli et al.[33] demonstrated that a fluorescence technique can be used for the detection of $^{\bullet}OH$ radicals over TiO_2 particles by using coumarin as fluorescence probe. Also, Fujishima et al.[34] described the detection of $^{\bullet}OH$ radicals generated on an anodically polarized diamond electrode, by using coumarin as a scavenger, and fluorescence for the detection of coumarin's hydroxylated product.

In this work, bimetallic Pt-Ir nanoparticles were deposited by the microemulsion method on MWCNT to yield Pt-Ir/MWCNT. This bimetallic Pt-Ir nanomaterial was used as electrocatalyst for the electrosynthesis of hydrogen peroxide. The hydrogen peroxide generated allows the cathodic Fenton process. We provide evidence for the $^{\bullet}OH$ radical generation in an Electro-Fenton System by using coumarin and the fluorescence detection of its hydroxylated product (7-hydroxycoumarin).

Experimental

Chemicals.— Potassium hexachloroplatinate (IV) ($K_2PtCl_6{\bullet}xH_2O$, 98%), iridium chloride hydrate ($IrCl_3{\bullet}xH_2O$, 98%), sodium citrate tribasic hydrate ($C_6H_5Na_3O_7{\bullet}xH_2O$, 99%), Brij30, Nafion-117 solution (5%), ferrous sulfate heptahydrated ($FeSO_4{\bullet}7H_2O$) and coumarin ($C_9H_6O_2$, 99.9%) were purchased from Sigma Aldrich. Ascorbic acid ($C_6H_7O_5OH$, 99.6%), sulfuric acid (H_2SO_4, 97%), hexane (C_6H_{14}, 95%), isopropanol (C_3H_8O, 99%) and methanol (CH_3OH, 99.9%) were supplied by Fermont. All the chemicals were used as received. All aqueous solutions were prepared with Milli-Q water (18 MΩ, Millipore). The MWCNT used in this work were obtained by the spray pyrolysis technique and

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[z] E-mail: rmfelix2003@yahoo.com.mx

Available online at www.sciencedirect.com

Journal of Energy Chemistry 23(2014)483–490

JOURNAL OF ENERGY CHEMISTRY
www.elsevier.com/journals/
journal-of-energy-chemistry/2095-4956
www.elsevier.com/locate/jngc

Synthesis of Pt and Pt-Fe nanoparticles supported on MWCNTs used as electrocatalysts in the methanol oxidation reaction

J. R. Rodriguez[a*], R. M. Félix[b], E. A. Reynoso[b], Y. Gochi-Ponce[c],
Y. Verde Gómez[d], S. Fuentes Moyado[a], G. Alonso-Núñez[a]

a. Universidad Nacional Autónoma de México, Centro de Nanociencias y Nanotecnología, Ensenada, B. C., C. P. 22860, Mexico;
b. Instituto Tecnológico de Tijuana, Centro de Graduados e Investigación, Tijuana, B. C., C. P. 22000, Mexico;
c. Instituto Tecnológico de Oaxaca, Departamento de Ingeniería Química y Bioquímica, Oaxaca, Oax., C. P. 68030, Mexico;
d. Instituto Tecnológico de Cancún, Av. Kabah Km. 3, Cancún, Q. R., C. P. 77500, Mexico

[Manuscript received October 24, 2013; revised January 13, 2014]

Abstract
This work reports a feasible synthesis of highly-dispersed Pt and Pt-Fe nanoparticles supported on multiwall carbon nanotubes (MWCNTs) without Fe and multiwall carbon nanotubes with iron (MWCNTs-Fe) which applied as electrocatalysts for methanol electrooxidation. A Pt coordination complex salt was synthesized in an aqueous solution and it was used as precursor to prepare Pt/MWCNTs, Pt/MWCNTs-Fe, and Pt-Fe/MWCNTs using $FeCl_2\cdot4H_2O$ as iron source which were named S1, S2 and S3, respectively. The coordination complex of platinum $(TOA)_2PtCl_6$ was obtained by the chemical reaction between $(NH_4)_2PtCl_6$ with tetraoctylammonium bromide (TOAB) and it was characterized by FT-IR and TGA. The materials were characterized by Raman spectroscopy, SEM, EDS, XRD, TEM and TGA. The electrocatalytic activity of Pt-based supported on MWCNTs in the methanol oxidation was investigated by cyclic voltammetry (CV) and chronoamperometry (CA). Pt-Fe/MWCNTs electrocatalysts showed the highest electrocatalytic activity and stability among the tested electrocatalysts due to that the addition of ”Fe” promotes the OH species adsorption on the electrocatalyst surface at low potentials, thus, enhancing the activity toward the methanol oxidation reaction (MOR).

Key words
coordination complex salt; MWCNTs; nanoparticles; catalysts; electrooxidation

1. Introduction

Nowadays the direct methanol fuel cells (DMFCs) have attracted considerable attention as a power source for zero emission electric vehicles and portable electronic devices due to their high efficiencies and environmental friendliness [1,2]. Unfortunately, the sluggish anodic methanol oxidation reaction (MOR) catalyzed in the anode by Pt electrocatalysts and the high cost of the noble metal, are some problems which should be overcome [3]. Therefore it is imperative for the development of new electrocatalytic materials with high efficiencies and low costs [4]. Currently, the strategies adopted to improve the catalysts performance and cost-efficiency include the synthesis of new low loading Pt-based electrocatalysts [5], the development of better catalyst supports [6], and the searching of new alternatives of Pt-free active metals [7,8]. Although the use of the non-Pt electrocatalysts is attractive, its application for the oxidation of small organic molecules in fuel cell is still far yet to occur [9]. In recent years the electrocatalysts of Pt nanoparticles coupled with transition metals such as Ru, Au, and Fe have been tested to improve the electrocatalytic activity in MOR [10−12]. Besides, in the last years, the multiwall carbon nanotubes (MWCNTs) have been applied as an alternative support for metal catalysts [13]. It has been found that MWCNTs can provide better electrochemical performances as catalyst supports on the fuel cells in comparison with traditional carbon supports (carbon black) [14,15]. Its excellent stability in acid media and its high electrical conductivity can be the main factors responsible for such findings [16]. On the other hand, Alonso-Nuñez et al. [17] and J. R. Rodriguez et al. [18] reported the synthesis of coordination complexes salts with different noble metals used as precursors of nanostructures supported on MWCNTs. In this direction, the present work also describes the synthesis of a Pt coordination

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[*] Corresponding author. Tel: +52-646-1744602; E-mail: jrodrig@cnyn.unam.mx
This work was supported by CONACyT (Project 155388 and 174689).

doi: 10.1016/S2095-4956(14)60175-3

This article was downloaded by: [Dalhousie University]
On: 01 January 2015, At: 07:32
Publisher: Taylor & Francis
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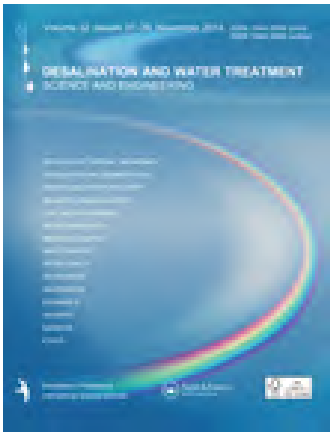

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Desalination and Water Treatment
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/tdwt20

Wastewater treatment via electrochemically generated ferrate and commercial ferrate

Sergio Perez-Sicairos[a], Alma J. Carrillo-Mandujano[b], Juan R. Lopez-Lopez[b] & Shui Wai Lin-Ho[a]

[a] Centro de Graduados e Investigación del Instituto Tecnológico de Tijuana, Blvd. Industrial s/n, Mesa de Otay, C.P. 24500, Tijuana, B.C., Mexico, Tel. +52 664 6233772

[b] Facultad de Ciencias Químico Biológicas de la Universidad Autónoma de Sinaloa, Blvd. Las Américas y Av. Universitarios, C.P. 80010, Ciudad Universitaria, Culiacán, Sinaloa, Mexico.

Published online: 08 Aug 2013.

To cite this article: Sergio Perez-Sicairos, Alma J. Carrillo-Mandujano, Juan R. Lopez-Lopez & Shui Wai Lin-Ho (2014) Wastewater treatment via electrochemically generated ferrate and commercial ferrate, Desalination and Water Treatment, 52:37-39, 6904-6913, DOI: 10.1080/19443994.2013.827823

To link to this article: http://dx.doi.org/10.1080/19443994.2013.827823

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Preparación y caracterización de membranas compuestas elaboradas a partir de 2,4,6 Trimetil *m*-Fenilendiamina y Cloruro de Trimesoílo

Jesús Álvarez-Sánchez[1], Evelia Encinas-Meneses[1], Sergio Pérez-Sicairos[2], Nidia J. Ríos-Vazquez[1], Germán E. Dévora-Isiordia[1], Rodrigo González-Enríquez[1]
Ciencias del Agua y Medio Ambiente[1], Centro de Graduados e Investigación[2]
Instituto Tecnológico de Sonora[1], Instituto Tecnológico de Tijuana[2]
Cd. Obregón, Son.[1], Tijuana, B.C.[2]; México
[jesus.alvarez, german.devora, nidia.rios, rodrigo.gonzalez]@itson.edu.mx, hiromy_evelia@hotmail.com, sperez@tectijuana.mx

Abstract— In this article is reported the preparation of a nanofiltration membrane chlorine-resistant, via interfacial polymerization between an aqueous solution of 2,4,6 trimethyl-m-phenylenediamine and an organic solution of trimesoyl chloride, on a porous substrate of polysulfone. Polysulfone membrane was characterized by photonic microscopy (PM) and water contact angle (CA), and the polyamide film was characterized by infrared spectroscopy (IR-ATR) and atomic force microscopy (AFM). PM analysis revealed the average pore diameters from 8.11 microns to 8.9 microns, so PS membrane is a microfiltration membrane and CA suggests a moderate hydrophobicity due to the presence of benzene rings and methyl groups. Infrared analysis showed the presence of group C=O and CONH at 1653.62 cm-1 and 1530.2 cm-1 respectively, corresponding to the aramid polymer. Atomic force microscopy technique suggested that the roughness on membrane surface is inversely proportional to the concentration in weight of trimesoyl chloride. The chemical structure of the aramid layer improves its resistance to chlorine, because their methyl substituents provide by to the steric effect protection to the aromatic ring and the nitrogen of the N-C bond.

Keyword— Interfacial Polymerization, Phase Inversion, Composite membranes, Reverse Osmosis, Membranes Characterization, Atomic Force Microscopy (AFM).

Resumen— En este artículo se reporta la preparación de una membrana de nanofiltración resistente al cloro, vía polimerización en interfase, entre una solución acuosa de 2,4,6 Trimetil-m-Fenilendiamina y una solución orgánica Cloruro de Trimesoílo, sobre un sustrato poroso de polisulfona. La membrana de polisulfona se caracterizó mediante Microscopía Fotónica (PM) y Ángulo de Contacto (CA), y la película de poliamida formada se caracterizó mediante espectroscopía de infrarrojo (IR-ATR) y Microscopía de Fuerza Atómica (AFM). La PM reveló diámetros de poro promedio desde 8.11 µm a 8.9 µm, por lo que la membrana de PS es de microfiltración y el CA sugiere una hidrofobicidad moderada debido a la presencia de anillos bencénicos y grupos metilos. El análisis de IR demostró la presencia del grupo C=O y CONH, en 1653.62 cm^{-1} y 1530.2 cm^{-1}, respectivamente, correspondientes al polímero de aramida. El análisis de AFM sugiere que la rugosidad en la superficie es inversamente proporcional a la concentración en peso del Cloruro de Trimesoílo. La estructura química de la capa de aramida la hace resistente al cloro, porque sus sustituyentes metilos dan protección por medio del efecto estérico al anillo aromático y al nitrógeno del enlace N-C.

Palabras claves— Polimerización en Interfase, Inversión de Fase, Membranas Compuestas, Ósmosis Inversa, Caracterización de Membranas, Microscopia de Fuerza Atómica (AFM).

I. INTRODUCCIÓN

Medina [1] publicó que en el planeta tierra sólo el 0.3% de agua es apta para consumo humano. Este porcentaje se localiza en ríos, lagos, arroyos, acuíferos, embalses, etc. La escasez de agua potable y para riego es un problema a nivel mundial [2]. Una de las alternativas para minimizar este problema es usar un proceso viable como lo es la ósmosis inversa [2-4]. La osmosis inversa (OI) se basa en el uso de membranas poliméricas con carácter semipermeable para eliminar el soluto de una solución o para

PREPARACIÓN Y APLICACIÓN DE MEMBRANAS COMPUESTAS A PARTIR DE 2, 6 METIL M-FENILENDIAMINA Y CLORURO DE TRIMESOÍLO

Carrasco A. E. E. ;(1)* Álvarez S. J. ;(1)* Faz R. B. A.;(1) Ríos V. N. J. ;(1) Devora I. G. E. ;(1)
González E. R. ;(1) y Pérez S. S. (2)

(1) Programa Educativo de Ingeniería Química, Departamento de Ciencias del Agua y medio Ambiente, Instituto Tecnológico de Sonora, 5 de Febrero 818 Sur Cd. Obregón Sonora 85000, México. E mail: elix_emilio16@hotmail.com y jesus.alvarez@itson.edu.mx

(2) Centro de Graduados e Investigación. Instituto Tecnológico de Tijuana. Apdo. Postal 1166. Tijuana, B. C. 22000, México. E mail: sepesi74@yahoo.com

RESUMEN

El trabajo de investigación consistió en preparar membranas de polisulfona mediante el método de inversión de fase y membranas compuestas a partir de los monómeros 2,6-Dimetil M Fenilendiamina (2-MMPD)y Cloruro de Trimesoilo (TMC) por polimerización interfacial. Las membranas fueron caracterizadas por espectroscopia de infrarrojo. La señales a 1653.62 y 1530 cm^{-1} *de amida I y II respectivamente indican que se efectuó la polimerización interfacial. Las membranas compuestas se aplicaron en la eliminación de sales de* $NaCl$ *y* Na_2SO_4*. La membrana de* $2\text{-}MMPD_{0.5\%}\text{-}TMC_{0.5\%}$ *fue la que presentó mejores resultados en cuanto a rechazo de NaCl 70 % y flujo de permeado 4.0 L/día. También rechazó 70 % de* Na_2SO_4 *con un flujo de permeado de 13.3 L/día. La mejor membrana compuesta fue* $2\text{-}MMPD_{0.5\%}\text{-}TMC_{0.5\%}$*. La finalidad de esta investigación es la de preparar una membrana compuesta capaz de eliminar el 99 % de las sales del agua marina.*

Palabras clave: Polimerización interfacial, inversión de fase, membrana compuesta, ósmosis inversa, desalación.

I. INTRODUCCIÓN

Prieto[1] menciona que la abundancia del agua y su buen uso señalan el nivel de vida y desarrollo de un pueblo, por ello se hace necesario estudiar y resolver el problema del manejo y preservación del agua ante el gasto que viene en aumento, pues el agua dulce en este siglo XXI va a ser el problema ambiental y político más decisivo que enfrentará la humanidad.

La UNESCO[2] en 2013 mencionó que el agua dulce es el recurso más importante para la humanidad, transversal para todas las actividades sociales, económicas y

Journal of Environmental Protection, **2013, 4, 270-279**
doi:10.4236/jep.2013.43032 Published Online March 2013 (http://www.scirp.org/journal/jep)

Evaluation of the Physicochemical Behavior of Waste Water Treatment Polyelectrolytes with Metal Ions

Eduardo A. López Maldonado[1], Mercedes T. Oropeza Guzmán[1,2], Georgina Pina-Luis[1], Adrián Ochoa-Terán[1*]

[1]Graduate and Research Center of the Technical Institute of Tijuana, Tijuana, México; [2]Centre for Research and Technological Development in Electrochemistry, Tijuana, México.
Email: *ochoa@tectijuana.mx

Received November 25th, 2012; revised January 3rd, 2013; accepted February 2nd, 2013

ABSTRACT

In this paper is describing the physicochemical behavior of polyelectrolytes (PEs) used in waste water treatment with mono-, di- and trivalent metal ions as K^+, Mg^{2+}, Zn^{2+}, Fe^{3+}, Sn^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+}, Ni^{2+}, Al^{3+} and Cr^{3+}. A coagulant polyelectrolyte Poly(vinyl sulfate) potassium salt (PVSK), and a commercial available Flocculant Trident 2756, were used as models for the study. The colloidal titration UV-Vis spectroscopy technique was successfully implemented in order to evaluate the complexation of PEs with Toluidine Blue O (OTB) and the ability of different metal ions to displace the OTB from the PE-OTB complex and form the PE-metal ion complex. From the experiments was concluded that PVSK has a high affinity for Al^{3+} and Mg^{2+} while the Flocculant has the highest affinity for Sn^{2+} followed by Zn^{2+} and Mg^{2+}. The absorbance profiles of polyelectrolyte-OTB complex (Absorbance vs. Metal/PE) were used to calculate association constants. On the other hand, the mass balance of OTB and its absorbance profiles were used to calculate the association constants of polyelectrolyte-metal ion complexes. Thus metal ions with the highest affinities have the highest association constant. Metal ions with the highest affinities present the highest values of association constant.

Keywords: Polyelectrolytes; Metal Ions; Colloidal Titration; UV-Vis Spectroscopy; O-Toluidine; Wastewater Treatment

1. Introduction

Polyelectrolyte chains have atoms or groups of atoms which have the ability to chelate or exchange sities with metal ions [1]. The most common coordinating atoms present in a polymer chain, either central or side chain, are nitrogen, oxygen, phosphorus and sulfur [2]. For those polymers in which the polymer-metal ion interaction involves an ion exchange process, the most common are the quaternary ammonium with chloride, sulphate and hydroxyl counterions [3]. Polyelectrolyte-metal ion interaction could be electrostatic or may include the formation of coordinated bonds. The type of interaction depends on the chemical nature (ionization potential and electronic affinity) of the functional groups. The variables that affect the PE-metal ion interaction are classified into two groups: intrinsic and extrinsic to the polymer [4]. The former group includes the polymer structure in terms of composition and geometry, which affects the flexibility of the chains in solution: branches of the chain, chemical nature of the functional groups, and their distribution at the polymer chain, etc. The second group includes the charge and type of the metal ion, pH, ionic strength, temperature and dielectric constant of the medium [5,6]. The knowledge of association phenomena of metal ions with charged macromolecules is essential for understanding of their physicochemical behavior in environmental, biological systems and in waste water treatment by coagulation-flocculation [7-9].

Polyelectrolytes are used in coagulation-flocculation processes mainly to remove suspended particles, turbidity and color. However, due to their chemical nature, polyelectrolytes also interact with oppositely charged species as metal ions that are present in the wastewater. For example, the treatment of waste water from semiconductor fabrication industry with high suspended solids content of heavy metals, where the objective is to remove suspended solids as well as heavy metals content. Therefore, it is important to study the physicochemical behavior of polyelectrolytes with different metal ions present in the waste water, with the aim of determining the affinity and capacity of removal of each metal with polyelectrolytes, in order to determinated the optimal

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*Corresponding author.

J Nanopart Res (2013) 15:1802
DOI 10.1007/s11051-013-1802-3

RESEARCH PAPER

Pt–Pd bimetallic nanoparticles on MWCNTs: catalyst for hydrogen peroxide electrosynthesis

R. M. Félix-Navarro · M. Beltrán-Gastélum · M. I. Salazar-Gastélum · C. Silva-Carrillo · E. A. Reynoso-Soto · S. Pérez-Sicairos · S. W. Lin · F. Paraguay-Delgado · G. Alonso-Núñez

Received: 4 February 2013 / Accepted: 15 June 2013 / Published online: 10 July 2013

Abstract Bimetallic nanoparticles of Pt–Pd were deposited by the microemulsion method on a multiwall carbon nanotube (MWCNTs) to obtain a Pt–Pd/MWCNTs for electrocatalytic reduction of O_2 to H_2O_2. The activity and selectivity of the catalyst was determined qualitatively by the rotating disk electrode method in acidic medium. The catalyst was spray-coated onto a reticulated vitreous carbon substrate and quantitatively was tested in bulk electrolysis for 20 min under potentiostatic conditions (0.5 V vs Ag/AgCl) in a 0.5 M H_2SO_4 electrolyte using dissolved O_2. The bulk electrolysis experiments show that the Pt–Pd/MWCNTs catalyst is more efficient for H_2O_2 electrogeneration than a MWCNTs catalyst. Nitrobenzene degradation by electrogenerated H_2O_2 alone and Electro-Fenton process were also tested. Our results show that both processes decompose nitrobenzene, but the Electro-Fenton process does it more efficiently. The prepared nanoparticulated catalyst shows a great potential in environmental applications.

Keywords Bimetallic electrocatalyst · MWCNTs · O_2 electro-reduction · H_2O_2 generation · Electro-Fenton

Introduction

In recent years, electrosynthesis of hydrogen peroxide has gained increased attention, because this powerful oxidizing agent finds applications in a wide variety of organic and inorganic synthesis reactions; in advanced oxidation processes (AOPs) for wastewater treatment, in the pulp and paper industry and in textile bleaching. This is mainly due to the exceptional pollution control ability of this compound, which is transformed into non-contaminating products such as water and oxygen. Clean water is also a critical feedstock in a variety of key industries including electronics, pharmaceuticals, and food (Savage and Diallo 2005). Hydrogen peroxide is considered a green chemical in the treatment of waste water as a replacement for chlorine.

AOPs characterized by the in situ generation of the hydroxyl radical ($^{\bullet}OH$) in the degradation of organic contaminants had become the focus of increasing

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R. M. Félix-Navarro (✉) · M. Beltrán-Gastélum ·
M. I. Salazar-Gastélum · C. Silva-Carrillo ·
E. A. Reynoso-Soto · S. Pérez-Sicairos · S. W. Lin
Centro de Graduados e Investigación, Instituto
Tecnológico de Tijuana, Apdo. Postal 1166,
22000 Tijuana, BC, Mexico
e-mail: moi6salazar@hotmail.com;
rmfelix2003@yahoo.com.mx

F. Paraguay-Delgado
Centro de Investigación en Materiales Avanzados, Apdo.
Postal 31109, Miguel de Cervantes 120, Chihuahua,
CHIH, Mexico

G. Alonso-Núñez
Centro de Nanociencias y Nanotecnología, Apdo. Postal
356, Km. 107 Carretera Tijuana-Ensenada,
22800 Ensenada, BC, Mexico

Inorganica Chimica Acta 406 (2013) 138–145

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Coordination complex synthesis of noble metals in the preparation of nanoparticles supported on MWCNTs used as electrocatalysts

J.R. Rodriguez [a,]*, R.M. Félix [b], E.A. Reynoso [b], S. Fuentes Moyado [a], G. Alonso-Núñez [a]

[a] *Universidad Nacional Autónoma de México, Centro de Nanociencias y Nanotecnología, Ensenada, B.C. C.P. 22860, Mexico*
[b] *Instituto Tecnológico de Tijuana, Centro de Graduados e Investigación, Tijuana, B.C. C.P. 22000, Mexico*

ARTICLE INFO

Article history:
Received 20 April 2013
Received in revised form 21 June 2013
Accepted 24 June 2013
Available online 9 July 2013

Keywords:
Coordination complex salts
Nanoparticles
MWCNTs
Electrocatalysts

ABSTRACT

Coordination complex salts were synthesized in an aqueous solution and used as precursors to prepare metallic and bimetallic nanoparticles supported on multiwalled carbon nanotubes (MWCNTs) to be applied as electrocatalysts on methanol electrooxidation. The precursors were obtained by the reaction between $(NH_4)_2PtCl_6$, $(NH_4)_2PdCl_6$, $(NH_4)_3RuCl_6$ and $HAuCl_4$ with tetraoctylammonium bromide (TOAB). These were obtained as $(TOA)_nMCl_y$ salts (where "M" = Pt, Pd, Ru or Au) and were characterized by FT-IR and TGA analysis. The precursors were used to prepare metallic and bimetallic nanoparticles of Pt, Pt–Pd, Pt–Ru, as well as Pt–Au coated on MWCNT (Pt–M/MWCNTs, where M = Pd, Ru or Au). Materials were characterized by TEM, XRD and TGA. The electrocatalytic properties of the Pt–M/MWCNTs electrodes for the methanol oxidation were determined by cyclic voltammetry (CV) and chronoamperometry (CA). The bimetallic nanoparticles presented a higher electrocatalytic activity and stability than the Pt/MWCNTs electrocatalyst, attributed to the addition of "M" which not only led to a smaller average particle size and higher dispersion of Pt of the metallic nanoparticles on MWCNTs but also promoted an elevated electronic transfer between bimetallic nanoparticles.

1. Introduction

The synthesis of nanostructure materials with controlled size and composition is very important for numerous applications, because of their novel and attractive physical and chemical properties [1], which differ from those properties that exhibited for bulk [2,3]. For example, the transition metal nanoparticles of Pt, Pd, Ru and Au have been studied as catalysts in organic reactions [4–6], as electrocatalysts in fuel cells [7], or as materials with novel electronic [8], chemical sensor [9] and magnetic properties [10]. The catalytic and electronic properties are strongly influenced by the size of the particles, especially in the range 1–10 nm, evidencing the need for size-selective synthesis techniques. The synthesis of metallic and bimetallic nanoparticles is mainly achieved by the chemical reduction of coordination complex salts using different reduction agents such as hydrogen, borohydrides, hydrazine or aldehyde [11–14]. The nanoparticles synthesized by reduction of the coordination complex salts using sodium borohydride as a reducing agent, generally allows the obtaining a very small and uniform particle size because sodium borohydride enables a rapid reduction to afford very small nuclei whose growth and agglomeration is hindered [15].

The use of a capping agent improves the control of the size and shape of the nanoparticles, according to the Brust–Schiffrin method [16,17], where the TOAB is used as a capping agent, which permits the preparation of the nanoparticle of 2–3 nm, also this precursor allow to control the morphology of the nanoparticles, which can be spherical or cubic [18–20].

We are interested in the preparation of Pt nanoparticles following the Brust–Schiffrin method, with the aim of controlling their size and surface properties [21–23]. Beside catalysis, the synthesis of coordination complex salts as agent precursors for the preparation of nanoparticles has allowed to acquire nanostructured materials with attractive catalytic properties [24]. In particular, Pt–M nanoparticles have been investigated for their high electrocatalytic activity for methanol oxidation and CO tolerance oxidation related to fuel cell application [25,26].

The present report describes a new promising approach based on the synthesis of new organometallic salts which were characterized by FT-IR and TGA analysis. These salts precursors were used for the preparation of nanoparticles of noble metals to be deposited on MWCNTs and used as electrocatalysts. The materials were characterized by TEM, XRD and TGA. Moreover the Pt–M nanoparticles deposited on MWCNTs (Pt–M/MWCNTs) were studied as electrocatalysts, by cyclic voltammetry (CV) and choronoamperommetry (CA) in the methanol oxidation reaction (MOR).

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* Corresponding author. Tel.: +52 646 1744602.
E-mail address: jrodrig@cnyn.unam.mx (J.R. Rodriguez).

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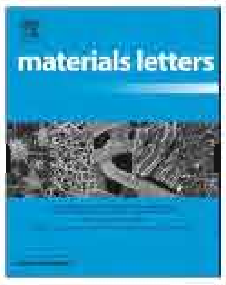
http://dx.doi.org/10.1016/j.ica.2013.06.042

Materials Letters 109 (2013) 163–166

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet



Novel catalyst based on Co-complex to prepare MWCNT

G. Alonso-Núñez [a,*], C. Belman [a], I. Gradilla [a], B. Arango [b], Y. Gochi-Ponce [b], R.M. Félix [c], E. Reynoso [c], J. Lara-Romero [d]

[a] *Universidad Nacional Autónoma de México, Centro de Nanociencias y Nanotecnología, Ensenada, B.C. C.P. 22860, Mexico*
[b] *Instituto Tecnológico de Oaxaca, División de Estudios de Posgrado e Investigación, Oaxaca, Oax C.P. 68030, Mexico*
[c] *Instituto Tecnológico de Tijuana, Centro de Graduados e Investigación, Tijuana, B.C., Mexico*
[d] *Facultad de Ingeniería Química, Universidad Michoacana de San Nicolás de Hidalgo, Morelia, Michoacan C.P. 58010, Mexico*

ARTICLE INFO

Article history:
Received 6 December 2012
Accepted 20 July 2013
Available online 26 July 2013

Keywords:
Carbon nanotubes
Spray pyrolysis
New Co-complex
Nanostructures

ABSTRACT

A new Co-complex as catalytic agent {[(Pentyl)$_4$N]$_3$CoBr$_3$}Cl$_2$ to prepare Multiwalled Carbon Nanotubes (MWCNTs) has been synthesized through the reaction of tetrapentylammonium bromide (Pentyl)$_4$NBr and cobalt chloride (CoCl$_2$) in aqueous solutions. MWCNT were obtained by spray pyrolysis of toluene as carbon source using this new Co-complex as catalyst. The synthesized catalytic agent was characterized by Ultraviolet–visible Spectroscopy, Fourier Transform Infrared Spectroscopy, and Thermal Analysis techniques. Spectroscopic results indicated that the new Co-complex has suitable characteristics to grow MWCNTs by spray pyrolysis. The MWCNTs were analyzed by Scanning Electron Microscopy, Transmission Electron Microscopy and X-ray Diffraction techniques. The MWCNTs grow vertically aligned with respect to the glass tube surface and are several microns long with diameters ranging from 20 to 50 nm. XRD patterns exhibit the 2-H graphite characteristics peaks of MWCNT as well as fcc-cobalt nanoparticles.

1. Introduction

Carbon nanotubes and nanofibers are graphitic filaments/whiskers with diameters ranging from 0.4 to 500 nm and lengths in the range of several micrometers to millimeters. They are grown by the diffusion of carbon via catalytic decomposition of carbon containing gases or vaporized carbon from arc discharge or laser ablation through a metal catalyst and its subsequent precipitation as graphitic filaments [1–4]. Three distinct structural types of filaments have been identified based on the angle of the graphene layers with respect to the filament axis [4,5], namely *stacked*, *herringbone* [6], and *nanotubular* [7].

MWCNTs have attractive chemical, electrical and mechanical properties for electronic, catalytic and electrochemical applications [8]. The techniques widely used to produce high-quality MWCNTs are laser ablation [9], electric arc discharge [10], and chemical vapor deposition which provides the appropriate conditions for MWCNTs synthesis [11,12].

In general, carbon nanotubes and nanofibers are grown using metallic nanoparticles catalyst (usually Fe, Co, or Ni); a carbon feedstock (e.g., hydrocarbon or CO) and a thermal treatment. The peculiar ability of these transition metals to form graphitic carbon is thought to be related to a combination of factors that include their catalytic activity for the decomposition of volatile carbon compounds, the formation of metastable carbides, and the diffusion of carbon through the metal particles [13].

A recent development in the field of organometallic chemistry has been the use of organometallic complexes for the high yield catalytic synthesis of carbon nanotubes (CNTs) [14]. Some reports describe the exploration in the design of new ligands based on ferrocene. As an example, we have previously reported the synthesis of Fe-Complex ([(Hexyl)$_4$N]$_3$FeCl$_3$Br$_3$) catalyst. This catalytic precursor was a good nucleation agent in the synthesis of multi-walled carbon nanotubes using toluene as the main carbon source. The MWCNTs obtained from this catalyst had a diameter of 50 nm and length of several micrometers. These dimensions are comparable with MWCNTs synthesized from ferrocene [15]. Others authors have reported the synthesis of CNTs employing inorganic catalyst by a combustion method [16]. Maneerung et al. reported the synthesis of MWCNTs using a LaNiO$_3$ perovskite as catalyst for rapid decomposition of methane [17]. While Kuras et al. [18] used LaNiO$_3$ as precursor for catalytic carbon nanotubes growth. Recently Ma et al. [19] reported the in-situ fabrication of CNT/TiO$_2$ interpenetrating network film on nickel substrate by chemical vapor deposition. In this work we successfully synthesized and characterized a new Co-complex ([(Pentyl)$_4$N]$_3$-CoBr$_3$, which was used as a catalytic agent to produce MWCNTs by the spray pyrolysis method.

2. Experimental section

Preparation and characterization of the Co-complex catalyst: In order to obtain the catalytic agent, the required stoichiometric amount

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[*] Corresponding author. Tel.: +52 646 1744602.
E-mail address: galonso@cnyn.unam.mx (G. Alonso-Núñez).

0167-577X/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.matlet.2013.07.077

Article

J. Mex. Chem. Soc. **2013**, *57(2),* 127-132

ISSN 1870-249X

1,4-Dioxane Degradation Using Persulfate Ion and Ag(I) Ion

Rosa María Felix-Navarro,[1]* Shui Wai Lin,[1] Arturo Zizumbo-López,[1] Sergio Pérez-Sicairos,[1] Edgar Alonso Reynoso-Soto,[1] and José Heriberto Espinoza-Gómez[2]

[1] Centro de Graduados e Investigación, Instituto Tecnológico de Tijuana A.P. 1166, C.P. 22000, Tijuana, B. C. México. rmfelix2003@yahoo.com.mx

[2] Facultad de Ciencias Químicas e Ingeniería, Universidad Autónoma de Baja California, Calzada Universidad 14418, Parque Industrial Internacional, CP. 22390, Tijuana, B.C.

Received September 24, 2012; accepted April 22, 2013

Abstract. The kinetics of oxidation of 1,4-dioxane by persulfate ion with Ag^+ in aqueous solutions at various temperatures and concentrations of $S_2O_8^{2-}$, Ag^+ and H_2SO_4, were investigated. Experimental results indicate that 1,4-dioxane degradation follows a pseudo-first-order decay model and that reaction rate significantly accelerate by increasing temperature and concentration of oxidant, sulfuric acid and Ag^+ ions up to 0.46 mM; for the range from 0.46-0.70 mM of Ag^+ ions the reaction rate remains constant and at higher concentrations the reaction rate decreases. It was possible to degrade approximately 100% of 1,4-dioxane in less than one hour with the following conditions: $[Ag^+] = 0.46$ mM, $[H_2SO_4] = 0.30$ M and from a concentration of 25 mM Na_2SO_4.

Keywords: 1,4-dioxane, degradation, kinetics, persulfate ion, advanced oxidation.

Resumen. En este trabajo se investigó la cinética de oxidación de 1,4-dioxano mediante iones persulfato con iones Ag^+, en soluciones acuosas a diferentes temperaturas y concentraciones de $S_2O_8^{2-}$, Ag^+ y H_2SO_4. La degradación de 1,4-dioxano presenta un decaimiento de pseudo-primer orden y la velocidad de reacción aumenta al incrementar la temperatura y concentración del oxidante, del H_2SO_4 y de Ag^+ hasta 0.46 mM; en el intervalo de 0.46 a 0.70 mM de Ag^+, la velocidad de reacción se mantiene constante y a concentraciones mayores, la velocidad de reacción disminuye. Fue posible degradar aproximadamente el 100% de 1,4-dioxano en menos de una hora con las siguientes condiciones: $[Ag^+] = 0.46$ mM, $[H_2SO_4] = 0.30$ M y a partir de una concentración de Na_2SO_4 de 25 mM.

Palabras clave: 1,4-dioxano, degradación, cinética, ion persulfato, oxidación avanzada.

Introduction

The 1,4-dioxane is a cyclic ether and a problematic water pollutant that has major impacts on the human health and the environment. It is used widely in industry as a solvent for many organic and inorganic compounds. It is also produced as byproducts in many industrial processes such as ethylene glycol, ethylene oxide, and polyethylene terephthalate manufacturing. Moreover, 1,4-dioxane is a known carcinogen to animals and a suspected carcinogen to human, and hence, is classified as a hazardous compound and a priority pollutant [1]. If it is not removed from industrial wastewater effluent, 1,4-dioxane appears as a xenobiotic constituent of groundwater and drinking water [2].

Conventional water and wastewater treatment processes [3] may include chemical treatment, air stripping, carbon adsorption, and biological treatment; however these treatment processes are generally ineffective for eliminating 1,4-dioxane because of its high aqueous solubility and resistance to biodegradation. There is currently very little data on the removal of 1,4-dioxane by conventional biological wastewater treatment plants. However, the available information on biodegradation, sorption and air stripping suggest that removal efficiencies for 1,4-dioxane are very low by these methods. The advanced oxidation processes (AOP), which use the hydroxyl radical as the oxidant, can achieve substantial reductions in 1,4-dioxane. Choi *et al.* [4] used boron-doped diamond electrodes for the anodic oxidation of 1,4-dioxane, in their study the removal of 1,4-dioxane was monitored by chemical oxygen demand (COD), they reported that the anodic oxidation of 1,4-dioxane by boron-doped diamond electrodes were both an economical and an efficient process. Yanagida *et al.* [5], prepared stainless mesh with TiO_2 coating using electrophoretic deposition (EPD), and used this stainless coated mesh as electrode to examine the synergy effect on photocatalysis of both 1,4-dioxane and ethylene glycol diformate (EGDF), a main intermediate of the photocatalysis of 1,4-dioxane. They reported that the photocatalytic decomposition rate of 1,4-dioxane depends on applying voltage and that the voltage swing provides high-efficiency photocatalysis of 1,4-dioxane while suppressed the EGDF formation.

Maurino *et al.* [6] found that sodium persulfate combined with UV light was more effective in degrading 1,4-dioxane than UV light with H_2O_2. The effect of pH on TiO_2 photocatalysis reactor systems used to degrade the 1,4-dioxane were investigated by Vescovi *et al.* [7], their experimental results indicate that at neutral pH the degradation of 1,4-dioxane was found to be most effective. Kinetic study on the degradation of 1,4-dioxane by zero-valent iron (Fe^0)/UV light system was studied by Son *et al.* [8]; they determined that the increase supply of $HO^\bullet$ radicals induced by the photolysis of Fe^0 and H_2O was responsible for the greatly increase of the degradation rate of 1,4-dioxane. Coleman *et al.* [9] studied the photocatalytic degradation of 1,4-dioxane using TiO_2 and the H_2O_2/UV process. For the photocatalytic process, this group used magnetic photocatalyst as TiO_2 particles (P25) as well as suspended and fixed arrangement. They concluded that mineralization of 1,4-dioxane, by the photocatalysis (with TiO_2 and magnetic photocatalyst) was complete.

Journal of Environmental Protection, **2013, 4, 136-143**
doi:10.4236/jep.2013.41016 Published Online January 2013 (http://www.scirp.org/journal/jep)

Electrochemical and Photoelectrochemical Decoloration of Amaranth Dye Azo Using Composited Dimensional Stable Anodes

Moisés I. Salazar-Gastélum, Edgar A. Reynoso-Soto, Shui W. Lin, Sergio Perez-Sicairos, Rosa M. Félix-Navarro[*]

Ingeniería en Nanotecnología, Centro de Graduados e Investigación en Química del Instituto Tecnológico de Tijuana, Tijuana, México
Email: [*]rmfelix2003@yahoo.com.mx

Received November 13th, 2012; revised December 15th, 2012; accepted January 7th, 2013

ABSTRACT

In this paper we report the results of our experimental work conducted to decoloration of a well-known highly toxic Amaranth dye by electrochemical and photoelectrochemical methods. Throughout this investigation were used two different Dimensional Stable Anode (DSA) electrodes, namely, IrO_2-Ru_2O-SnO_2-TiO_2/Ti and Ru_2O-SnO_2-TiO_2/Ti. The experimental results show that IrO_2-Ru_2O-SnO_2-TiO_2/Ti electrode has higher performance on amaranth decoloration than Ru_2O-SnO_2-TiO_2/Ti electrode, but with the disadvantage of higher energy consumption. For higher degradation of Amaranth dye with both DSA electrodes, the process was carried out via photoelectrochemical method. Our experimental results clearly shown the decrease in absorbance of all UV-Vis peaks due to the mineralization of the azo dye; also, it was noteworthy photoelectrochemical process consumes less energy under the same experimental conditions than electrochemical process. The IrO_2-Ru_2O-SnO_2-TiO_2/Ti electrode reaches a higher degradation degree of Amaranth solutions than Ru_2O-SnO_2-TiO_2/Ti electrode using a photoelectrochemical technique.

Keywords: Photoelectrochemical; Decoloration; DSA, Azo; Amaranth Dye

1. Introduction

Textile dyeing industry consumes large quantity of water and the wastewater volumes produced from different steps in dyeing is equally large to the finishing processes. The discharge of none or poorly treated textile dye wastewater into aquatic habitats is detrimental to the environment. Even though treatment methods of dye wastewater had been developed throughout the years, however the classical methods of disposal are not adequate due to the fact that partial oxidation or reduction of the chemical dyes would produce highly toxic byproducts. At the present time conventional practice of wastewater decontamination can be classified as biological [1], physical [2], chemical [3] and advanced oxidation process [4] methods. Beside these categories of treatment methods, the electrochemical methods have been proved to be very effective specifically to wastewater containing water soluble toxic inorganic and organic compounds [5, 6]; these methods are mainly characterized by being inexpensive to operate and the systems are stable during the treatment operation. For example, one of the most common electrochemical methods employed for degradation of dissolved organic compounds in water is the indirect oxidation, wherein the degradation of the organic compound is performed by generation of oxidizing species from an anode coated with electro-catalytic material. Many materials are being employed for generation of oxidizing species, one of them is the Dimensional Stable Anodes or DSA electrodes, these electrodes are composed by a mixture of metal oxides deposited on a metallic substrate such as titanium. These kinds of DSA electrodes had been used in the degradation of some toxic organic compounds like cyanide [7], herbicides [8] and for the decoloration of different dyes [9]. DSA electrodes, composed by mixtures of Ti, Ir, Ru, Sn and/or Sb oxides, have high surface area, excellent mechanical and chemical resistance even at high current density and in strongly acid media. However, these active anodes show limited oxidation power to destroy the dyestuffs due to their low ability to generate the hydroxyl free radical (•OH).

Amaranth, also known as acid red 27, is a well-known azo dye which is widely used for coloring textile materials, paper, wood, leather, etc. For long time it was also used as coloring agent for foodstuffs like jams, jellies,

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[*]Corresponding author.

Article

J. Mex. Chem. Soc. **2013**, *57(4)*, 298-305

ISSN 1870-249X

Photocatalytic Degradation of Nitrobenzene Using Nanocrystalline TiO_2 Photocatalyst Doped with Zn Ions

Edgar Alonso Reynoso-Soto,[a,*] Sergio Pérez-Sicairos,[a] Ana Patricia Reyes-Cruzaley,[a] Christian Leonardo Castro-Riquelme,[a] Rosa María Félix-Navarro,[a] Francisco Paraguay-Delgado,[b] Gabriel Alonso-Núñez,[c] Shui Wai Lin-Ho[a]

[a] Centro de Graduados e Investigación. Instituto Tecnológico de Tijuana. Apdo. Postal 1166. Tijuana, B. C. 22000, México.
[b] Centro de Investigación en Materiales Avanzados. Miguel de Cervantes 120 Apdo. Postal 31109, Chihuahua, México.
[c] Centro de Nanociencias y Nanotecnología. Universidad Nacional Autónoma de México. Km. 107 Carretera Tijuana-Ensenada. Apdo. Postal 356 Ensenada, B. C. 22800, México.

Received February 13, 2013; Accepted May 31, 2013.

Abstract. Photocatalysis is a method widely used in the degradation of organic pollutants of the environment. The development of new materials is very important to improve the photocatalytic properties and to find new applications for TiO_2 as a photocatalyst. In this article we reported the synthesis of a photocatalyst based on TiO_2 doped with Zn^{2+} ions highly efficient in the degradation of nitrobenzene. The results of photocatalytic activity experiments showed that the Zn^{2+} doped TiO_2 is more active than un-doped TiO_2 catalyst with an efficiency of 99% for the nitrobenzene degradation at 120 min with an apparent rate constant of 35×10^{-3} min^{-1}.

Keywords: Doped titanium dioxide, nanostructure, photocatalysis and nitrobenzene.

Resumen. La fotocatálisis es un método ampliamente utilizado en la degradación de contaminantes orgánicos del medio ambiente. El desarrollo de nuevos materiales es muy importante para proporcionar mejoras respecto a las propiedades fotocatalíticas y encontrar nuevas aplicaciones para TiO_2 como fotocatalizador. En este artículo se reporta la síntesis de un fotocatalizador a base de TiO_2 dopado con iones Zn^{2+} altamente eficiente para la degradación fotocatalítica de nitrobenceno. Los resultados de las pruebas de actividad fotocatalítica mostraron que TiO_2 dopado es más activo que TiO_2 con una eficiencia del 99% para la degradación de nitrobenceno en 120 min y una constante de velocidad aparente de 35×10^{-3} min^{-1}.

Palabras clave: Dióxido de titanio dopado, nanoestructura, fotocatalizador, nitrobenceno.

Introduction

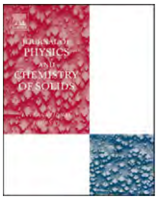
Nitrobenzene (NB) is a carcinogenic pollutant widely used in the production of different products such as dyes, explosives and pesticides [1]. It is frequently released in the effluent from explosives manufacturing industry as well as in the manufacturing of organic chemicals and plastics [2]. Even at low concentrations NB can involve high risks to ecological and human health [3]. Continuous exposure of humans and animals to NB can result in methemoglobinemia and liver and kidney damage [4] The US Environmental Protection Agency (US EPA) stipulates that wastewater with NB concentrations exceeding 2 mg L^{-1} is proclaimed as hazardous waste [5]. Owing to the strong electron affinity of the nitro group of NB, it is resistant to chemical or biological oxidation [6]. Meanwhile, a variety of possible treatment technologies, such as adsorption [7], photochemical reduction [8], oxidation by O_3/UV processes [9] and ozonation [10] have been adopted to remove NB from aqueous media. Another set of techniques relatively newer, more powerful and very promising are called Advanced Oxidation Processes (AOPs) which are been developed and employed to the treatment of contaminated wastewater effluents [11]. Photocatalytic degradation has proven to be a promising technology for removal of organic compounds [12]. This technique is more effective as compared to other AOPs because semiconductors are inexpensive and can easily mineralize various organic compounds [13, 14]. The basics steps for heterogeneous photocatalysis consist initially in transferring of the reactants in the liquid phase onto the catalyst surface followed by adsorption of the reactant on the catalyst surface, reaction in the adsorbed phase, desorption of the final product and finally the removal of the final products in the liquid phase [15]. The development of photocatalysis has been the focus of considerable attention in recent years with photocatalysis being used in a variety of products across a broad range of research areas, including especially environmental and energy-related fields [16]. From several semiconductors used in photocatalysis, titanium dioxide (TiO_2) is one of the most important photocatalyst for the degradation of pollutants in water. This is because of its high photocatalytic activity, non-toxicity, chemical stability under different conditions and it is relatively inexpensive [17]. The photocatalytic properties of TiO_2 are derived from the formation of photogenerated charge carriers (hole and electron), which occurs due to the absorption of ultraviolet (UV) light corresponding to the band gap [16]. The photogenerated holes in the valence band diffuse to the surface of TiO_2 and react with adsorbed water molecules, forming hydroxyl radicals (•OH) [18]. The photogenerated holes and the hydroxyl radicals oxidize nearby organic molecules on the surface of TiO_2. Meanwhile, electrons in the conduction band typically participate in reduction processes, and react with molecular oxygen to produce superoxide radical anions (O_2•-) [19]. However, because of its large band gap (3.2 eV), it cannot absorb sunlight successfully. To reduce the band gap and increase the photoactivity of TiO_2 various ways have been tested, including the doping with different metal ions and oxides [20]. ZnO is a main semiconductor for

Journal of Physics and Chemistry of Solids 73 (2012) 338–342

Contents lists available at SciVerse ScienceDirect

Journal of Physics and Chemistry of Solids

journal homepage: www.elsevier.com/locate/jpcs



N-methylpyrrolidine-based precursors for chemical vapor deposition of GaN_x particles

Gregorio Guadalupe Carbajal Arízaga [a],*, Edgar A. Reynoso-Soto [b], Oscar Edel Contreras López [c]

[a] *Departamento de Química, Universidad de Guadalajara, Marcelino García Barragán 1421, CP 44430, Guadalajara, Jalisco, México*
[b] *Centro de Graduados e Investigación, Ingeniería en Nanotecnología, Instituto Tecnológico de Tijuana, Apdo. Postal 1166, Tijuana, B.C. 22000, México*
[c] *Centro de Nanociencias y Nanotecnología, Universidad Nacional Autónoma de México, Km. 107 Carretera Tijuana-Ensenada, Apdo. Postal 14, CP 22800, Ensenada, Baja California, México*

ARTICLE INFO

Article history:
Received 13 July 2011
Received in revised form
5 October 2011
Accepted 13 October 2011
Available online 21 October 2011

Keywords:
A. Nanostructures
A. Organometallic compounds
A. Thin films
B. Vapor deposition

ABSTRACT

An attempt to prepare a metalorganic precursor of gallium with reactivity at low temperature in chemical vapor deposition (CVD) systems was done by reacting N-methylpyrrolidine with metal gallium or gallium nitrate under mild conditions. The precursors were bubbled into a CVD assemblage and then reacted with ammonia at temperatures between 400 and 700 °C. The depositions onto silicon substrates were pyramidal particles of 100 nm width at the base and up to 55 nm in height. The rise in growth temperature increased particle density from 0.9 to 27.1 particles per square micron, but reduced the height from 50 to 10 or 2 nm. XPS spectra showed the presence of gallium and nitrogen. The intensity of the gallium spectrum decreased as the process temperature increased indicating that GaN_x particles were deposited rather than the stoichiometric gallium nitride (GaN). An additional N1s band of impurities appeared whose intensity increases with the reaction temperature. The lower impurity content corresponded to the sample prepared with $Ga(NO_3)_3$ at 400 °C.

1. Introduction

The electronic properties of GaN have attracted much attention because of their numerous applications in the design of light-emitting devices or light detectors in the blue region of the visible spectrum or in the UV region. Several techniques have been reported to synthesize GaN, ranging from physical techniques such as molecular beam epitaxy, laser ablation or physical vapor deposition to chemical techniques like chemical vapor deposition (CVD) and atomic layer deposition or hot-wire CVD [1].

One of the challenges to overcome regarding GaN deposition by CVD is the growth temperature, which ranges from 750 to 1100 °C [2]. High temperature is a disadvantage because (i) GaN nitride can decompose above 850 °C depending on the vacuum applied [2], and because (ii) it increases the lattices' mismatches between substrates and GaN structures owing to the difference in dilatation constants.

This temperature is usually reached with the growth techniques currently used, for example, the literature indicates that laser ablation produces temperatures of around 900 °C and the CVD processes are conducted at around 800 °C.

Regarding the CVD processes, some strategies to decrease the temperature of GaN synthesis have been attempted, e.g. the dispersion of metal gallium in CaF_2, which increases the surface area of gallium and then the rate of vaporization, making it possible to grow GaN at 650 °C [2]. The use of metalorganics (MO) is another way to reduce reaction temperature. Key features of MO reagents used in chemical vapor depositions (MOCVD) are low reagent boiling point and high vapor pressure to facilitate transportation into the reactor, in addition to high reactivity with the nitrogen reagent, which is normally NH_3. One reagent with such properties is trimethylgallium (TMGa), with vapor pressure of 64 mm Hg and boiling point at 92.5 °C [3]; nevertheless, it is pyrophoric and expensive.

On the other hand, amines seem to be a good option to prepare MO gallium reagents because of the available electron pair in the amino group, which could be accepted by metal cations [4]. Adduct formation between such Lewis bases and metals is a suitable approach to improve reactivity of CVD precursors [5]. The adducts formed by gallium halides and disubstituted amines undergo three possible reactions as depicted in Fig. 1, which is adapted from the model proposed by Litvinenko et al. [4]; thus if a three-substituted amine would be employed, the dimerization and the dehydrogenation depicted in Fig. 1 would be avoided.

The aim of this work was to test N-methyl pyrrolidine (NMP) as an electron donor ligand for gallium and examine the resulting organometallic compound as a precursor of GaN synthesized by CVD. NMP is a trisubstituted amine, which was selected because of its low boiling point (76–80 °C) [3] and because the methyl group in this compound seemed to offer a moderate steric

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* Corresponding author. Tel.: +52 33 1378 59 00x27529.
E-mail address: gregoriocarbajal@yahoo.com.mx (G.G.C. Arízaga).

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doi:10.1016/j.jpcs.2011.10.013

Journal of Environmental Protection, 2012, 3, 1559-1570
http://dx.doi.org/10.4236/jep.2012.311172 Published Online November 2012 (http://www.SciRP.org/journal/jep)

A Multiparameter Colloidal Titrations for the Determination of Cationic Polyelectrolytes

Eduardo A. López Maldonado[1], Adrián Ochoa-Terán[1], Mercedes T. Oropeza Guzmán[1,2]

[1]Centro de Graduados e Investigación del Instituto Tecnológico de Tijuana, Blvd. Industrial s/n Mesa de Otay, Tijuana, México; [2]Centro de Investigación y Desarrollo Tecnológico en Electroquímica-Unidad Tijuana, Carretera Tijuana-Tecate, Parque Industrial El Florido, Tijuana, México.
Email: oropeza1@yahoo.com, moropeza@cideteq.mx

Received August 10th, 2012; revised September 9th, 2012; accepted October 6th, 2012

ABSTRACT

In water treatment processes and conditioning drinking water, PEs are widely used; however, their environmental impact is still doubtful, since residual concentrations increase organic matter content and represents a potential health hazard. This paper demonstrates a multiparametric study of two colloidal titration methods: spectrophotometric and zeta potential end point detection. The first one was optimized to guarantee the accuracy of cationic commercial PE quantification. It includes the indicator dose optimization using analytical criteria for competing equilibria, a calibration curve for two ranges of CPE concentration (1 - 5 ppm and 5 - 100 ppm) and the interference study of flocculant and Sn in the CPE quantification. The second method provides a physicochemical validation of the electric surface phenomena occurring during the colloidal titration and the end point detection. As an additional contribution the zeta potential titration was discussed and proposed as an alternative method for quantifying CPE when the sample is metal free.

Keywords: Polyelectrolyte Quantification; Colloidal Titration; Zeta Potential; Polydadmac; O-Toluidine Blue Indicator; Wastewater Treatment

1. Introduction

A polyelectrolyte, PE, is a polymer that dissociates in solution. Usually, PEs are identified as macroions, *i.e.* charged macromolecules or dissociable groups covalently linked to the polymeric structure and balanced by simple counterions. Natural and synthetic PEs are used in different industrial areas by their ability to modify the stability of dispersed solid particles in water. In the environmental area, for example, PEs are mainly employed in sludge conditioning, removal of heavy metals [1], coagulants and flocculants in the wastewater treatment and drinking water conditioning. In those cases, PEs play the role of neutralizing agents that adsorb strongly into the solid particles, usually found in after-process raw water. When suspended or colloidal particles in waste water do not precipitate or they take long time to sediment two popular cationic polyelectrolytes are used: Polydadmac and EPI-DMA [1]. Frequently, the dose of PEs is exceeded looking for a faster sedimentation; however, this phenomenon depends on the particle size and particle density. For this reason PEs are recommended to promote solids separation by gravity [2]. Although cationic and anionic PEs are effective in the water treatment processes, in recent years they have claimed attention due to the environmental impact of residual concentration. Another environmental risk is that PEs may contain considerable amounts of toxic raw materials commonly used in their production chains. Moreover, there are reports [3] that show the adverse effect caused by PEs linked with toxic substances after a water treatment process. Consequently, operators of waste water treatment plants need to control the residual concentration of PEs, in the early stages of the treatment process, and improve the quality of treated water.

Therefore, sensitive and rapid analytical methods for measuring the concentration of PEs in different systems (biochemical, biomedical and environmental) are necessary, as well as in those cases where an overdose (processes out of control) or accidental spills occur. The desired limit of detection for polymers is 1 mg/L suggested by Michael Fielding AWWA [3] which is 10% of the maximum allowable dose (10 mg/L) for Polydadmac. This paper demonstrates how to optimize and guarantee the accuracy of cationic commercial PE quantification performing a multiparametric study of two colloidal titration methods: spectrophotometric and zeta potential end point detection. For the spectrophotometric end point detection the indicator dose optimization, two differente