



"2020, Año de Leona Vicario, Benemérita Madre de la Patria"

Productos de las LGAC 1: Procesos, tecnologías y nanomateriales para sistemas ambientales

La productividad de los investigadores en **artículos científicos** que fortalecen a la LGAC 1 "Procesos, tecnologías y nanomateriales para sistemas ambientales" del programa de Maestría se presenta en la siguiente tabla.

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José Ysmael Verde Gómez	David Macias-Ferrer, José A. Melo-Banda, Rebeca Silva-Rodrigo, Mayda Lam Maldonado, Ulises Páramo García, José Y. Verde-Gómez, Paz Del Ángel Vicente "Highly dispersed PtCo nanoparticles on micro/nano-structured pyrolytic carbon from refined sugar for methanol electro-oxidation in acid media" <i>Catalysis Today</i> (2018), in press, doi.org/10.1016/j.cattod.2018.04.064.
2020	
José Ysmael Verde Gómez Ana María Valenzuela Muñiz	Elizabeth Montiel Macias, Ana M. Valenzuela-Muñiz, Gabriel Alonso-Núñez, Mario H. Farías Sánchez, Raynald Gauvin, Ysmael Verde Gomez, Sulfur doped carbon nanohorns towards oxygen reduction reaction. <i>Diamond & Related Materials</i> 103 (2020) 107671. https://doi.org/10.1016/j.diamond.2019.107671
José Ysmael Verde Gómez Ana María Valenzuela Muñiz	Isaías Zeferino González, Ana María Valenzuela Muñiz, Raynald Gauvin, Mario Miki- Yoshida, Ysmael Verde Gómez, <i>Synthesis temperature influence on the properties of silicon doped multiwalled carbon nanotubes</i> . <i>Diamond & Related Materials</i> 104 (2020) 107743. https://doi.org/10.1016/j.diamond.2020.107743
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José Ysmael Verde Gómez	P. Pizá-Ruiz, A. Sáenz-Trevizo, Y. Verde-Gómez, P. Amézaga-Madrid, M.Miki-Yoshida "Delafossite CuFeO ₂ thin films via aerosol assisted CVD: Synthesis and characterization" <i>Ceramics International</i> , (2019) 45, 1156-1162.
Ana María Valenzuela Muñiz	Influence of ZrO ₂ nanoparticles on the microstructural development of cement mortars with limestone aggregates; <i>Applied Sciences</i> , (2019) 9, 598.
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Green Cu₂O/TiO₂ heterojunction for glycerol photoreforming

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ABSTRACT

A rapid and sustainable route for synthesizing a green photocatalyst based on nanometric Cu₂O clusters dispersed on TiO₂ (≈ 2 wt%) was developed. These nanoclusters were synthesized using reducing sugars (0.85 wt %) from aqueous onion waste (*Allium cepa*) as reducing and stabilizing agent. All this under microwave irradiation. Green photocatalysts produced hydrogen through glycerol photoreforming, ca. 4.7 mmol H₂/g_{cat}. The recyclability and reusability of these materials were demonstrated and the achieved heterojunction between Cu₂O and TiO₂ exhibited a bandgap within the visible spectrum at 2.80 eV, showing potential feasibility to solarize this process.

1. Introduction

Currently, incremental energy demands are mainly supplied by oil, coal and natural gas. Hydrogen (H₂) has proved capable for replacing fossil fuels, while alleviating the impacts to the environment. Unfortunately, industrial hydrogen production relies on steam reforming; using fossil fuels and producing carbon dioxide (CO₂) [1,2]. Therefore, it has been claimed that an efficient and sustainable hydrogen economy should rely on sunlight as main energy source inside the hydrogen production process. Among the viable options, there is solar biomass and/or derivatives reforming, under two different routes: thermochemical and photocatalytic, being the latter also known as photoreforming [3].

Contrary to water splitting, photoreforming has been seen as thermodynamically efficient, due to the addition of sacrificial organic agents [4–7]. On the other hand, the majority of the water splitting photocatalysis research employs titanium dioxide (TiO₂) as catalyst; it is stable, non-corrosive, abundant, affordable, and environmentally-friendly [4]. As a result, TiO₂ is seen as the reference catalyst for photoreforming [7,8]. Nonetheless, the photocatalytic efficiency of TiO₂ under solar irradiation is low, mainly by two factors: (1) rapid recombination of photo-generated electrons-holes; (2) and the bandgap of TiO₂ (3.2 eV), located on the ultraviolet (UV) region, which is indeed the smallest component within the solar spectrum [4].

To overcome the abovementioned issues, platinum (Pt), gold (Au),

silver (Ag), and palladium (Pd) have been proposed as cocatalysts for TiO₂ [9,10]. Pd is the cocatalyst that has shown the best synergetic effect with TiO₂ under UV radiation, producing 47.5 mmol of H₂/g-h [9]. As result of this previous research it has been found that smaller particle sizes (≈ 10 nm) are desirable. For achieving this high temperature treatments are necessary in the synthesis of metal loaded TiO₂ [10]. Moreover, high cost and low availability of these noble metals, makes necessary to develop new alternatives.

Copper(I) oxide (Cu₂O) is an affordable and non-toxic material with a broad range of applications, such as sensing, desulfurization, disinfection, organic synthesis, photodegradation, photovoltaics and photocatalysis [11–16]. It also has proven to be a suitable material to produce hydrogen, when used as cocatalyst for titanium dioxide [17–19]; There are reports of comparable levels of production to those obtained with Ag or Au as cocatalyst [20–22]. Cu₂O is a typical p-type semiconductor and TiO₂ is a popular n-type semiconductor, together they form a p–n heterojunction, which can increase charge separation efficiency, leading to higher photocatalytic activity [23–25]. Moreover, Cu₂O exhibits a band gap of 2.2 eV, allowing the Cu₂O/TiO₂ heterojunction to absorb radiation within the solar spectrum [26–28].

Other strategy to avoid recombination is by exploiting organic compounds as sacrificial agents. They can be oxidized by the holes of the valence band (VB), facilitating the reduction of water by the electrons of the conduction band (CB). Sacrificial agents can be biomass, waste organic materials or derivatives of these [2,5]. Among these,

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Highly dispersed PtCo nanoparticles on micro/nano-structured pyrolytic carbon from refined sugar for methanol electro-oxidation in acid media

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Micro/nano-structured carbon
Refined sugar

ABSTRACT

In this work, anodic electrocatalyst (20%wt of metal loading) as PtCo nanoparticles (atomic ratio of 48:52) on micro/nano-structured pyrolytic carbon (MNC) was synthesized by sequential impregnation method and chemical reduction route using citric acid and Ar-H₂ static atmosphere. MNC sample was synthesized via nanocasting process with anhydrous pyrolysis at 800 °C using SBA-15 as hard template and refined sugar as carbon source. SBA-15 was prepared via sol gel using pluronic P-123 as surfactant and tetraethoxysilane as silica precursor. The prepared materials were characterized by means of N₂ physisorption, X-ray diffraction, X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy, Raman spectroscopy, scanning electron microscopy, energy-dispersive X-ray spectroscopy and high resolution transmission electron microscopy. The performance of PtCo/MNC for methanol oxidation reaction (MOR) was measured by cyclic voltammetry, chronoamperometry. The electrochemical characterization techniques revealed that the mass activity of PtCo/MNC and the commercial electrocatalyst Pt/C (20%wt of Pt loading) at 20 cycles were 481 and 372 mA/mg_{Pt} respectively as well as the resistance to the accumulation intermediate carbonaceous species (methoxy, aldehyde, formaldehyde and carbon monoxide) denoted by the ratio I_f/I_b for these catalysts were 1.30 and 0.76 respectively. PtCo/MNC exhibit better electrocatalytic performance, electrochemical stability and best resistance to carbonaceous intermediates species in the electro-oxidation of methanol.

1. Introduction

The high reactivity of platinum with methanol and the excellent catalytic activity towards the electro-oxidation of methanol, particularly at low temperature (below 80 °C) makes this metal is indispensable in DMFC anode electrocatalyst [1]. However, it is well known that there is a series of technical problems in DMFC that limit their marketing [2]. The Pt particles quickly poisoned due to the intermediate species formed during oxidation of methanol, mainly CO, since molecules of CO can adsorb chemically on the surface of Pt, blocking the active sites and producing a poor kinetics in the process methanol oxidation [3–6]. At present, the most effective fuel cell catalysts, both in cathode and anode, are highly dispersed Pt-based nanoparticles [7]. These Pt nanoparticles are normally supported on carbon materials such as carbon black (Vulcan XC-72R, Shawinigan, Black Pearl 2000, Ketjen Black and Denka Black), carbon nanostructures like mesoporous carbon, carbon nanotubes (CNTs), nanodiamonds, carbon nanofibers

(CNF), ordered mesoporous carbon (OMC) and reduced graphene oxide (rGO) and others, in order to increase the active surface area of Pt and improve the catalyst utilization. It is important the carbon support structure, because help in dispersing the metal catalyst and facilitate electron transport, as well as in promoting mass transfer kinetics at the electrode surface [8,9]. Although electrocatalysts based on Pt and Pt-Ru alloy (Ru as second metal) have shown a good catalytic activity for electro-oxidation of methanol, another of the limitations in the development of DMFC for commercial applications is the high cost of both noble metals [10,11]. Therefore, many efforts have focused on the development of new electrocatalysts replacing the Ru, to achieve enhancing the electrocatalytic activity by inhibiting the CO poisoning effect according the bifunctional mechanism and reducing cost of the electrocatalysts [12]. Several researchers have developed Pt-based nanoparticle-alloy catalysts as well as catalyst with core-shell morphology to increase the electrocatalytic activity towards electro-oxidation of methanol. Various metals (e.g. Bi, Ti, Pb, In, Ir, Os, Cu, Au, Pd, V, Fe,

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Sulfur doped carbon nanohorns towards oxygen reduction reaction

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Sulfur doped
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ABSTRACT

Platinum has been proved to be the most effective electrocatalyst for oxygen reduction reaction (ORR) in proton-exchange membrane (PEM) fuel cells; however, it presents some disadvantages such as its scarcity and, consequently, high cost. Recently, the development of electrocatalysts has been directed towards designing low Pt or Pt free materials. Carbon nanomaterials have shown good performance when used as Pt catalyst supports. Moreover, by modifying the properties, carbonaceous materials can be used also as catalysts. An alternative to change the carbon nanomaterial properties is their modification with heteroatoms. In the present work sulfur-doped carbon nanohorns (SCNHs) were synthesized by a modified chemical vapor deposition method (mCVD). Toluene and thiophene were used as respective carbon and carbon-sulfur sources and ferrocene as catalytic agent. Iron amount was evaluated to determine the optimal synthesis conditions and influence in its properties. Physical and chemical characterization were performed by means of X-ray diffraction, scanning electron microscopy, Raman spectroscopy and high resolution scanning and transmission electron microscopy, energy dispersive spectroscopy and X-ray photoelectron spectroscopy. Additionally, the behavior of the obtained materials towards the ORR was studied by linear sweep voltammetry. Tubular structures with conical and horn-like shapes were obtained where sulfur and carbon formed thiophene type bonds. According to iron amount variation results, reducing Fe concentration improves morphological properties and maintains structural characteristics. Electrochemical results show acceptable activity for ORR, hence SCNHs can be considered as non-Pt electrocatalyst for fuel cell electrodes.

Prime novelty statement: The originality reported in the manuscript is the synthesis of novel sulfur-doped carbon nanohorns with appropriate physical and chemical properties towards electrochemical energy devices applications.

1. Introduction

The oxygen reduction reaction (ORR) is the principal reaction at the cathode side in low-temperature fuel cells (e.g., polymer electrolyte fuel cells (PEFCs) [1–7], direct methanol fuel cells (DMFCs) [8–12], alkaline fuel cells (AFC) [1,2,13], and metal-air batteries [14–17]). Due to slow kinetics in the ORR and stability issues of the catalyst in the electrochemical environment, expensive precious metals are often utilized in these devices to promote the ORR [8,9,18]. However, due to the scarcity and high cost of Pt, alternative materials to replace or reduce the amount of metal need to be investigated.

It has been found that by doping carbon materials with heteroatoms (i.e., N, S, B, P) during the synthesis, some of their properties are

affected, such as electrical conductivity, basicity, oxidation stability, electrocatalytic activity, among others [19]. Recently, some research works have been addressed towards doping carbons using nitrogen [20–24], boron [25,26] and phosphorus [27,28]. Modifying the intrinsic activity of carbon to create charged sites is a key factor to enhance the ORR activity, especially when they are doped with N, B or P atoms. Recently, S-doped carbon materials have also attracted attention as dopant candidates in carbon materials [29–34].

The catalytic activity towards the ORR in carbonaceous materials modified with heteroatoms could be attributed to electroneutrality breakage on the graphitic materials, creating favorable charged sites for O₂ adsorption. Sulfur has close electronegativity (2.58) to carbon (2.55) compared to N (3.04), B (2.04) or P (2.19). In the case of S, spin density

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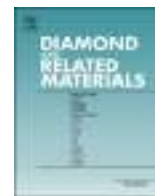
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Influence of the synthesis temperature and silicon concentration on the properties of Si doped MWCNT



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Triphenylsilane
CNT growth mechanism

ABSTRACT

Silicon doped multiwalled carbon nanotubes (Si-CNT) were synthesized by a modified chemical vapor deposition method, using toluene as carbon source, ferrocene as metal catalyst and triphenylsilane to provide the dopant atoms. The effect of synthesis temperature and concentration of Si-containing precursor on the microstructural properties were studied by high-resolution scanning electron microscopy (HR-SEM), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS), Raman spectroscopy and Thermogravimetric analysis. The microscopy results showed that the Si-CNT were structurally modified with various forms of roughness, distortions and defects not only in the inner walls but also on outer walls. The elevated synthesis temperature had the most significant effect in the graphitic carbon network. XPS elemental surface composition analysis showed that the maximum silicon content was 1.3 ± 0.2 at.%. It was found that the increment in the silicon content, inhibited the growth of Si-CNT. According to Raman results, the Si-CNT presented greater structural disorder due to the integration of silicon atoms in the carbon, which increased the disorder in the hexagonal network due to the higher ionic radius of Si. TGA confirmed that silicon was introduced into the Si-CNT and that they are also thermally stable. Based on the results, the nanotube growth mechanism was proposed, which showed that silicon has high mobility and diffusion on the carbon network as the temperature rises. *Prime novelty statement:* The originality reported in the manuscript is the novel and facile method to obtain carbon nanotubes doped with silicon and the effect of synthesis temperature on the physical-chemical properties. Also the growth mechanism of the Si-CNT is proposed.

1. Introduction

One of the most remarkable properties of carbon is its atoms' ability to combine allowing a great diversity of nanostructures, e.g., carbon nanotubes (CNT). Although, because of the on growing applications of doped materials, an interesting research area that is getting attention, is the structural modification of CNT through doping with other heteroatoms such as N, S, B, F, Si among others. It has been established that the inclusion of heteroatoms on the CNT structure, changes its physical and chemical properties. Moreover, the addition of silicon atoms allow the use of the CNT in various energy production or storage applications such as electrocatalysts for the oxygen reduction reaction in a fuel cell, anodic materials in Li-ion batteries, solar cells for photovoltaic devices, gas sensors etc. [1–4].

However, one of the main limitations for the substitution doping

using this heteroatom, is that the silicon atomic radius (1.34 \AA) is larger than carbon atomic radius (0.86 \AA) [1]. Nevertheless, studies have revealed that the difference in the electronegativities of carbon and silicon [2,5,6] facilitates the covalent bonding of silicon in the structure of the CNT. In specific, theoretical studies have shown that small silicon concentrations can greatly affect the electronic structure and the nature of the carbon nanotube band gap [7]. Studies have proposed that Si substitutional doping in the CNT can introduce an empty level in the gap, changing the electronic arrangement tending to the sp^3 configuration. The atomic interaction increase the Si reactivity, which could offer a preferential path towards the adsorption of different atoms and molecules [8,9]. In addition, when silicon is incorporated into the CNT, this atom can function as a donor, since electrons are transferred from the silicon to carbon atom [10,11].

So far, theoretical studies show that CNT have fascinating properties

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Delafossite CuFeO_2 thin films via aerosol assisted CVD: Synthesis and characterization



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ABSTRACT

The optimal synthesis conditions for the growth of delafossite CuFeO_2 thin films via aerosol assisted CVD were studied. An iterative synthesis process was followed until the average atomic ratio of Cu/Fe in the synthesized thin films was close to 1. TiO_2 coated borosilicate was initially used as substrate. Complete characterization of selected samples revealed the formation of polycrystalline CuFeO_2 in a rhombohedral phase. Small amounts of tenorite (CuO) were also observed. Further investigation of the growth of CuFeO_2 was achieved using ZnO coated borosilicate substrates. The synthesized thin films were in all cases homogeneous and had an average thickness of 45 ± 3 nm and 41 ± 3 nm when grown onto TiO_2 or ZnO, respectively. Outcomes indicated an almost negligible influence of the buffer layer on the microstructure and optical properties of CuFeO_2 . Therefore, the direct synthesis via AACVD technique of this bimetal and visible light absorbing oxide was verified.

1. Introduction

The rise in energy demand along with environmental problems, are global concerns. In consequence, much attention has been redirected to the study and application of cost effective and efficient materials to reduce water, soil and air pollution as well as to develop new processes for energy generation. It is precisely in the field of energy that the development of clean and sustainable energy sources is urgent. Photoassisted water splitting is currently considered as a promising alternative to directly convert solar energy into chemical fuels [1–4]. Water splitting processes offer a clean, sustainable and environmentally friendly way to produce H_2 [1–5]. From studied candidates, oxide-based materials have shown the most beneficial and promising results [1,4,6]. However, low efficiencies associated to the limited absorption of the solar spectrum restrict their utilization [4,5,7]. Delafossite materials, with a general formula ABO_2 , consist of A cations linearly coordinated with two oxygen ions and, B cations situated in edge-sharing BO_6 octahedra [8]. These class of materials have attracted interest not only for its electrical and optical properties but also, because of its oxidation corrosion resistance [4,8,9]. Among the family members of the delafossite class, CuFeO_2 exhibits p-type conductivity and it has a proper position of the conduction band edge, making it suitable for the generation of H_2 [7,8,10]. In addition, CuFeO_2 is formed of atoms that

are abundant in earth's crust [2]. Because of its outstanding properties, pure or doped CuFeO_2 has been incorporated in plenty applications, including transparent conductive oxides (TCO) [9,10,12–14], light emitting diodes (LEDs), dye sensitized solar cells [14] and photo or electro catalysts for water splitting [4,5,7,11,13].

A diverse number of techniques have been adopted for the synthesis of CuFeO_2 , including sol-gel [2,14], electrodeposition [4,6], dip-coating [8], spray pyrolysis [9], spin-coating [10], solid state reaction [11,16,17], glycine nitrate process [12,15] and, hydrothermal method [13,18]. Nevertheless, the control of the crystalline structure, composition and morphology, as well as its immobilization onto low cost and inert substrates, remain as challenging tasks.

In search for alternative routes to obtain CuFeO_2 thin films in a single step, this paper outlines the utilization of the aerosol assisted CVD method (AACVD) to prepare such bimetal material. The investigation of the optimal synthesis conditions was based on the modification of the molar concentration of the Cu and Fe precursors in solution, to obtain an average atomic ratio of both elements of about 1. The later as an initial approximation that could match with the stoichiometric proportion of Cu and Fe in the delafossite phase (CuFeO_2). The characterization of selected samples using energy dispersive x-ray spectroscopy, scanning and transmission electron microscopy, grazing incidence x-ray diffraction, atomic force microscopy, Raman

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Article

Influence of ZrO₂ Nanoparticles on the Microstructural Development of Cement Mortars with Limestone Aggregates

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Abstract: In this research, the effect of the addition of zirconium oxide-synthesized nanoparticles on the microstructural development and the physical–mechanical properties of cement mortars with limestone aggregates was studied. Zirconia nanoparticles were synthesized using the co-precipitation method. According to XRD analysis, a mixture of tetragonal (t) and monoclinic (m) zirconia phases was obtained, with average crystallite sizes around 15.18 and 17.79 nm, respectively. Based on the ASTM standards, a mixture design was obtained for a coating mortar with a final sand/cement ratio of 1:2.78 and a water/cement ratio of 0.58. Control mortars and mortars with ZrO₂ additions were analyzed for two stages of curing of the mortar—7 and 28 days. According to SEM analysis, mortars with ZrO₂ revealed a microstructure with a high compaction degree and an increase in compressive strength of 9% on the control mortars. Due to the aggregates' characteristics, adherence with the cement paste in the interface zone was increased. It is suggested that the reinforcing effect of ZrO₂ on the mortars was caused by the effect of nucleation sites in the main phase C–S–H and the inhibition of the growth of large CH crystals, and the filler effect generated by the nanometric size of the particles. This produced a greater compaction volume, suggesting that faults are probably originated in the aggregates.

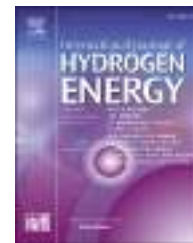
Keywords: zirconium oxide nanoparticles; microstructure; limestone aggregates; cementitious composites

1. Introduction

Mortars and concretes are cementitious composites whose physical and mechanical properties are affected by each material in their constitution, such as the cementing agent, the fine and/or coarse aggregates, and the water. In the construction industry, mortar is the mixture of the raw materials, the binder component such as cement or lime, water, and sand, which form a paste that hardens during the process and hydration kinetics. It is essential to know the components and the characteristics of each element, such as the type and content of sand or fine aggregates, since these physical or chemical characteristics modify, in a different way, the structure of the mixture from workability to performance in the use phase [1]. The sand, or fine aggregate, used for the manufacture of mortars, can come from different sources, such as natural deposits (called natural sand or siliceous sand) or as crushed rock products (like limestone aggregates), each of them having distinctive physical characteristics that influence mortars and concretes differently [2,3]. When it comes to concrete, the mixture volume

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Solvent effect in the synthesis of nanostructured Pt–Sn/CNT as electrocatalysts for the electrooxidation of ethanol

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ABSTRACT

Pt and Pt–Sn nanoparticles were synthesized and supported onto carbon nanotubes (CNT), the electrocatalytic activity towards the ethanol oxidation reaction was analyzed. The effect of the solvent employed for the synthesis was evaluated. Metal nanoparticles synthesis was made using water (Pt–Sn/CNT-W) or ethanol (Pt–Sn/CNT-E) as a solvent. Pt–Sn/CNT-W material presented only Pt–Sn alloy nanoparticles homogeneously distributed on the carbon nanotubes support. Pt–Sn/CNT-E sample showed non well-dispersed nanoparticles forming agglomerates along the CNTs surface with predominantly Sn⁴⁺ superficial species (SnO₂) as show the XPS, FTIR and electrochemical results. These surface arrangements had important effects on the electrocatalytic properties. Pt–Sn/CNT-W shows higher ethanol electrooxidation activity than the Pt–Sn/CNT-E, which is attributed to: a) the double catalytic effect and the intrinsic electronic mechanism favored by the presence of Sn; b) the good particle dispersion of the bimetallic active phase on the CNT and; c) the absence of SnO₂ species.

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Introduction

The growing energy demand leads to depletion in the reserves of the fossil fuels. The difficulties to reach these resources and the growing interest for the environment have turned the efforts towards the search of new renewable and more eco-friendly energy sources. Direct alcohol fuel cells are being positioned as an excellent option of clean energy source due to

its high energy density, low emission of pollutants, low operating temperature and ease of handling liquid fuel [1–4].

However, there are still critical obstacles that prevent the development of these devices for wide applications. One of the main challenges is the development of materials with high electrocatalytic activity in the oxidation reactions of alcohols that can be used as anodes [1]. From all the catalysts reported in the actuality, platinum nanoparticles supported onto carbon

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Artificial neural network-based surrogate modeling of multi-component dynamic adsorption of heavy metals with a biochar



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ABSTRACT

This paper reports the application of four neural network surrogate models for the correlation and prediction of asymmetric breakthrough curves obtained from the multi-component adsorption of cadmium, nickel, zinc and copper ions on a biochar. Artificial neural networks namely: Feed forward back propagation neural network, Feed forward back propagation neural network with distributed time delay, Cascade forward neural network and Elman neural network have been assessed and compared where their limitations and capabilities have been discussed. The impact of the architecture of these surrogated models, including the activation functions and training algorithms, has been analyzed using error and residuals analyses in different zones of the adsorption breakthrough curves obtained from single, ternary and quaternary solutions of tested heavy metals. Overall, the bed adsorption capacities for these metals ranged from 2.01 to 5.40, 0.16 to 4.46 and 0.03 to 2.15 mmol/g in single, ternary and quaternary feeds, respectively, at tested operation conditions. Highest adsorption capacities were obtained for copper in single and multi-metallic solutions and they ranged from 2.15 to 5.4 mmol/g. Results of this paper showed that Cascade forward neural network was the best model for multi-metallic adsorption breakthrough curve modeling. This neural network showed the lowest modeling errors for the multi-component adsorption breakthrough curves. This paper introduces new results on the application of ANNs surrogate models for the simulation of multi-component adsorption process involved in water treatment and purification.

1. Introduction

Packed-bed column is the common process configuration used for the adsorption of pollutants from industrial streams, groundwater and wastewaters in large-scale applications [1,2]. The determination of several operating parameters of adsorption columns implies the analysis of breakthrough curves [1–5]. In particular, the modeling of packed-bed adsorption of water pollutants is challenging due to the nonlinear behavior of the adsorption process that depends on the number of adsorbates, pH, temperature, feed flow and column characteristics [1,3,4]. For example, the axial dispersion and mass transfer phenomena influence the shape of concentration profile of adsorption columns causing asymmetric breakthrough curves. The presence of several pollutants in the column feed also increases the complexity of breakthrough modeling [6]. The correlation and prediction of multi-

component breakthrough curves are difficult due to non-interaction, antagonistic and synergistic adsorption effects caused by the pollutants present in the fluid to be treated.

The study of the adsorption process in packed-bed columns generally involves the application of mechanistic and phenomenological models such as mass transfer equations [1,3,7]. These models are developed considering certain assumptions and may show some limitations for the simulation of adsorption breakthrough curves in multi-component solutions. Mass transfer equations also require different parameters that are usually obtained from empirical correlations. As an alternative, these adjustable parameters can be generated from the data fitting of experimental data but the inaccuracies involved in this task could significantly affect the modeling results [3].

The application of surrogate models is an option for the breakthrough analysis especially in multi-component adsorption. These

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Synthesis of Micro/nanostructured Carbon from Refined Sugar and its Electrochemical Performance

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Micro/nano-structured carbon (MNC) was synthesized using nanocasting method and anhydrous pyrolysis process at 1000 °C using refined sugar as carbon precursor and SBA-15 as structure directing agent. SBA-15 was prepared through sol gel using the copolymer triblock non ionic pluronic P-123 as surfactant and tetraethyl orthosilicate as Si precursor. The prepared materials were characterized by means of N₂ physisorption, Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), high resolution transmission electron microscopy (HRTEM) and cyclic voltammetry (CV). The applied characterization techniques revealed that MNC has a mesoporous and turbostratic structure with rope like morphology composed by a set of carbon nanofibers and carbon nanopipes wrapped by thin graphene layers with large specific surface area (1292 m²/g) and large pore volume (1.2 cc/g), so MNC is a promising material for applications in adsorption, energy storage and solar cells, supercapacitor electrodes and electrocatalytic supports.

Keywords: SBA-15, nanocasting, carbon nanopipes, carbon nanofibers, turbostratic carbon

1. INTRODUCTION

According with the International Union of Pure and Applied Chemistry (IUPAC), porous materials are divided into three classes: microporous (< 2 nm), mesoporous (2–50 nm) macroporous (> 50 nm) [1-2]. Porous carbon materials have generated tremendous interest in many areas of science and technology because of their excellent chemical, thermal and mechanical stability, electrochemical



Influence of the Synthesis Parameters in Carbon Nanotubes Doped with Nitrogen for Oxygen Electroreduction

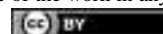
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Nitrogen doped carbon nanotubes (N-CNTs) were synthesized by modified chemical vapor deposition method using a novel two steps thermal technique. Pyridine was used as carbon and nitrogen source and ferrocene as catalyst for nanotubes growth. The effects of reactor temperature and carrier gas flow were investigated using scanning electron microscopy, transmission electron microscopy, Raman spectroscopy, X-ray photoelectron spectroscopy and linear scan voltammetry. Results show that the synthesis temperature and gas flow rate have influence on the physical, chemical and electrochemical properties of the nanostructures. Microscopy studies exhibit that synthesis temperature modify the length, yield and diameter of the N-CNTs. Transmission microscopy electron images show multiwalled carbon nanotubes with the typical bamboo like structures. High temperature and low flow rate generate more defects, as revealed by Raman analyses. N-CNTs synthesized at the highest temperature and flow rate show better electrocatalytic activity toward oxygen reduction reaction with promising lower onset potential and current densities up to 80% when compared to traditional Pt/C. The favorable performance is attributed to the higher nitrogen content and the type of nitrogen species, mainly pyrrolic and pyridinic incorporated in the carbon lattice.

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For the last decades, platinum (pure and Pt alloys) has been the best and well known electrocatalyst for the oxidation and reduction reactions in fuel cells. However, scarcity, high price and degradation of platinum as catalyst in fuel cell represent a challenge for commercial proposes.^{1,2} In recent years, there have been efforts to reduce the platinum loading, or even to eliminate it from the electrodes. It is therefore necessary to develop non-Pt catalytic materials available, cheap and electroactive to replace the precious metal. Carbon nanotubes doped with nitrogen (N-CNTs) have reached the point to become an alternative catalyst for oxygen reduction reaction (ORR) in fuel cells cathode.³ There have been many studies concerning the synthesis of carbon nanotubes doped with nitrogen atoms using different carbon-nitrogen precursors using chemical vapor deposition (CVD) method and having a good electrocatalytic activity for oxygen reduction. Alexeyeva⁴ synthesized N-CNTs using acetonitrile as carbon and nitrogen sources. They studied the electrocatalytic reduction of oxygen with and without doped nanotubes in 0.5M H₂SO₄ solution where the N-CNTs show significantly more activity for ORR than the free-doping nanotubes. Wong² obtained N-CNTs through CVD technique using three different chemical precursors as nitrogen sources: aniline (A), diethylamine (DEA) and ethylenediamine. The analysis revealed that the N-CNTs obtained from EDA with 6.5 at. % N was more active for ORR in acidic medium than nanotubes from A and DEA with 5.9 at. % N and 4.3 at. % N, respectively. Other studies^{1,5-8} have also showed the important role of nitrogen precursors on the N-CNTs structure. Nevertheless, few studies have been made on the different synthesis conditions of N-CNTs and the impact to improve the electrocatalytic properties for ORR. This work presents the production of N-CNTs by Modified Chemical Vapor Deposition (M-CVD) using pyridine as nitrogen and carbon source and the electrochemical study of the effects of two parameters, such as the synthesis temperature and carrier gas flow. The materials were evaluated toward the ORR by linear sweep voltammetry measurements using a catalyst-coated rotating disk electrode at different rotation rates in acid media.

Experimental

N-CNTs synthesis.—The synthesis of N-CNTs was carried out by the M-CVD method and it is shown in Figure 1. A solution with Pyridine (99.5%, Merck, carbon and nitrogen source) and Ferrocene (98%, Aldrich, metal catalyst) were mixed. Two step synthesis processes were used; first the solution was pre-heated in a home-made vaporizer connected to a tubular furnace where the synthesis takes place. Argon is used as carrier gas and Vycor tube as substrate. After synthesis, the furnace was cooled down and the final products were removed from the inside of the Vycor tube. Before the electrochemical characterization, N-CNTs were treated with concentrated nitric acid in a reflux system for 12 h. The carrier gas flow rate and the synthesis temperature were the two variables considered for the parametric study, with two levels each one (low and high). Table I shows the labelling used to name the samples. A total of 4 experiments were carried out in order to know the effects of the two different factors on the electrocatalytic performance of N-CNTs.

Physical and chemical characterization.—Scanning electron microscopy (SEM) was carried out to determine the morphology of N-CNTs using a Vega 3 system from Tescan. Different random areas were selected to have a statistical approach. Energy-dispersive X-ray spectrometer (EDS) attached to the SEM was used to determine chemical composition of each sample. Several random measurements were

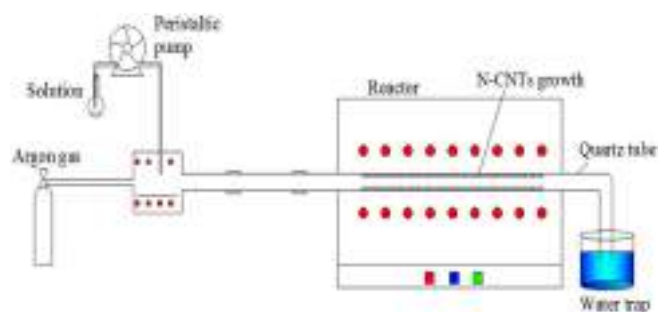
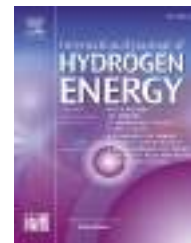


Figure 1. Scheme of the modified chemical vapor deposition system.

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Parametric study on the influence of synthesis variables in the properties of nitrogen-doped carbon nanotubes

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ABSTRACT

Nitrogen doped carbon nanotubes (N-CNT) were synthesized by a Modified Chemical Vapor Deposition method, using pyridine as carbon and nitrogen source, and ferrocene as catalytic agent for the nanotubes growth. The influence of synthesis parameters as the temperature, carrier gas flow rate, concentration of the reactants and preheating temperature over the morphology and physical properties of the N-CNT, were investigated by high-resolution scanning electron microscopy, transmission electron microscopy and X ray diffraction. The statistical analysis for the length of the N-CNT forest revealed that the synthesis temperature and carrier gas flow rate have significantly influenced on the physical properties of the material. The synthesis temperature not only affected the length of N-CNT forest, but also influenced the mass production, as well as, in diameter and the nitrogen content in the nanotubes. This is an important step towards the high yield production of N-CNT for applications in hydrogen storage, electrocatalysts for fuel cells and other electrochemical devices.

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Introduction

The exceptional properties of carbon nanotubes, such as good electrical conductivity, chemical and mechanical stability, high thermal conductivity, light weight, and physicochemical compatibility make them an ideal material to be utilized in electrochemical devices [1]. However, in certain applications,

it is necessary to modify the nanotubes characteristics to improve their electrochemical properties. One way to enhance such properties is by adding different heteroatoms to their structure (i.e. N, S, B, and Si). Nitrogen atoms have been used as dopant in the carbon structure [2], the so-called nitrogen doped carbon nanotubes (N-CNT) have different potential applications in various areas, such as hydrogen storage [3–5], field emission devices [6,7] and catalysis [8,9]. One of the

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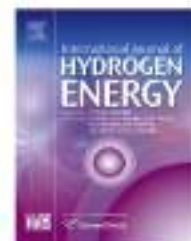
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Catalytic activity of Pt-Ni nanoparticles supported on multi-walled carbon nanotubes for the oxygen reduction reaction

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ABSTRACT

The synthesis and characterization of Pt–Ni nanoparticles with different Ni:Pt atomic ratios and supported on multi-walled carbon nanotubes (MWCNTs) for oxygen reduction reaction (ORR) is investigated. The crystal structure and the elemental analysis of Pt–Ni/MWCNTs nanocatalysts are characterized by X-ray diffraction (XRD) and energy dispersive X-ray spectroscopy (EDS), respectively. The morphology of these nanocatalysts is observed by transmission electron microscopy (TEM). The results reveal that Pt–Ni nanocatalysts with a nanoparticle size ranging from 6 to 7 nm are immobilized on the surface of MWCNTs. The kinetics and mechanism of the ORR were analyzed in a 0.5 M H₂SO₄ solution. The cyclic voltammetry response indicates that Pt–Ni/MWCNTs catalyst displays a higher performance than Pt/MWCNT, which may be due to the alloy of Ni species in Pt–Ni systems, demonstrating that they are promising materials for using in fuel cells.

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Introduction

Due to the overuse of non-renewable energy sources such as fossil fuels, as well as the environmentally damaging consequences of their use, research into alternative energy sources has emerged actively during the past decades. The transportation sector is one of the most dependent on fossil fuels, generating 23% of the global CO₂ emissions since 2009 [1] and producing large quantities of greenhouse gases (GHGs). Polymer electrolyte membrane (PEM) fuel cells have emerged as a

highly efficient and high-performance energy source [2]. In PEM fuel cells the most used electrocatalyst is Pt due to its activity in acid media, but this, like all precious metals, is expensive and, in a few years, it will be scarce. In the case of ORR, the Pt strongly binds oxygen, so high overpotentials are required to perform the process, affecting the fuel cell efficiency [3]. Therefore, considerable research has focused on reducing the amount of Pt needed in electrocatalysts and improve the ORR kinetics by using doped carbon catalysts [4] or alloy nanoparticle configurations [5,6].

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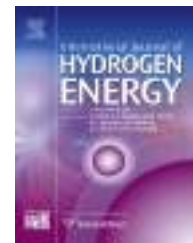
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Short Communication

Sustainable application of pecan nutshell waste: Greener synthesis of Pd-based nanocatalysts for electro-oxidation of methanol

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Alkaline methanol fuel cells

ABSTRACT

Palladium-based electrocatalysts are widely used in alkaline direct alcohol fuel cells. The synthesis and characterization of carbon-supported bimetallic nanoparticles (NP) of AuPd and AgPd is described using pecan nutshell extract (*Carya illinoensis*) which serves as both, reducing and the stabilizing agent. This environmentally friendly route generates bimetallic NP for a wide range of applications, including electrocatalysis; since particularly AuPd NP proved to be a potentially suitable electrode material for alkaline direct methanol fuel cells. The electrocatalytic activity of these nanomaterials was comparable to commercially available Pd/C 1% in the electro-oxidation of methanol in alkaline media.

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Synthesis, characterization and sensitivity tests of perovskite-type LaFeO₃ nanoparticles in CO and propane atmospheres



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ABSTRACT

Nanoparticles of perovskite-type LaFeO₃ were synthesized by a simple process using stoichiometric lanthanum and iron nitrates, ethylenediamine, and distilled water as a solvent. Microwave radiation, with a power of ~350 W, was applied for solvent evaporation. The obtained precursor powders were calcined at 200, 400, 500, 600 and 700 °C in static air, and analyzed by X-ray diffraction and cyclic voltammetry. The samples showed catalytic activity and high physical and chemical stability. The calcined powders at 700 °C were analyzed through scanning and transmission electron microscopy; agglomerated nanoparticles, forming a porous structure, were observed with an average size of 28 nm. Their magnetic properties correspond to magnetization up to 0.83 emu/g and coercivity of 182 Oe. Pellets from these powders were prepared to measure the sensitivity to CO and propane gases, obtaining high performance at different gas concentrations and operation temperatures.

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1. Introduction

Advances in the preparation of new transition metal oxides have allowed the development of complex materials such as the perovskite-type oxides. These compounds are grouped among the advanced materials due to their special physical and chemical properties [1–10]. Materials with a perovskite-type structure take the general form of ABO₃ [11,12], where A stands generally for a lanthanide or an alkaline earth element, such as La, Pr, Nd, Gd, Sm and Sr; B represents a transition metal, mainly Co, Fe and Ni [13]. Several combinations that can be accomplished through A and B yield a great variety of compounds with highly relevant chemical and physical properties for technological applications [14], e.g. gas sensors, electrodes for solid oxide fuel cells (SOFC), catalysts, magnetic devices, among others [15–20]. Since past decades, several investigation groups have used different synthesis methods to obtain perovskite-type materials, being the ceramic method the

most commonly employed [14]. Nevertheless, other chemical routes have been explored [21], such as the synthesis of Sm_{1-x}Ba_xCoO₃ through an aqueous solution method [22], LaFeO₃ through sol-gel route [23], BaTiO₃ by means of a sol-precipitation process [24] and LaCoO₃ through a glycine nitrate (G/N) plus EDTA route [25]. These synthesis routes allowed obtaining nanomaterials with high porosity and specific morphologies of a great relevance due to its potential applications.

Recently, the research on perovskite-type oxides as possible gas sensors has been extensive, due to the high thermal stability, catalytic activity and semiconductor behavior of the oxides [26,27]. For example, Ca_xPb_{1-x}TiO₃ has been studied as a possible humidity sensor [28], SmFeO₃ is considered for the detection of NO₂ and CO [29], and SrFeO₃ is a strong candidate as an ethanol vapors sensor [17]. The lanthanum ferrite, LaFeO₃, is being nowadays heavily investigated because it shows an excellent electric response in different gases. Different authors [30–33] report the successful use of this perovskite-type oxide, with different morphologies (ranging from thin films to hollow fibers) for detecting triethylamine, CO, NO and NO₂. A pending issue is, notwithstanding the foregoing, to determine the best microstructure

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Enhanced performance of direct ethanol fuel cell using Pt/MWCNTs as anodic electrocatalyst

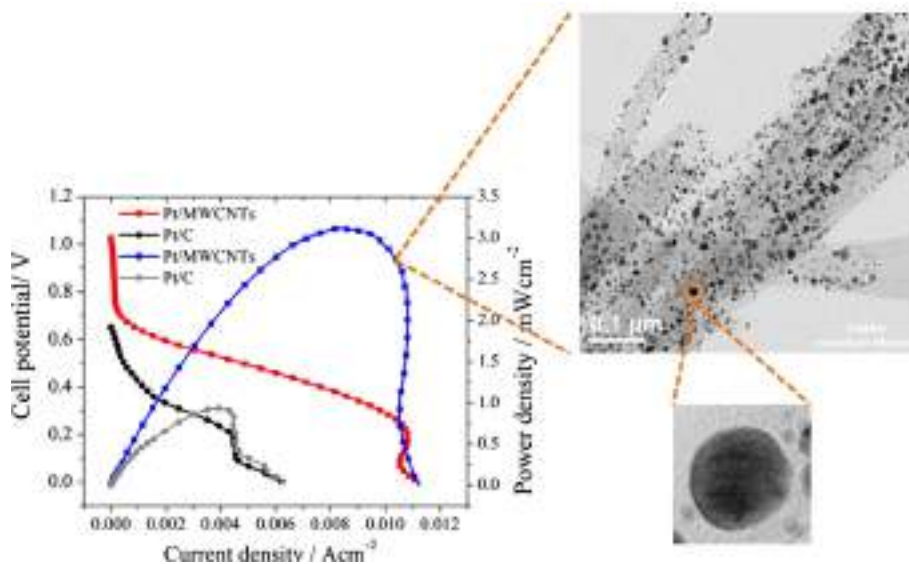
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Abstract Platinum nanoparticles with a size distribution ranging from 3 to 6 nm were synthesized at room temperature by chemical reduction of platinum chloride, using NaBH₄ as the reduction reagent and poly(*N*-vinylpyrrolidone) as the stabilizer. The Pt colloidal nanoparticles obtained were deposited onto multi-walled carbon nanotubes (MWCNTs) synthesized by the chemical vapor

deposition method. Pt/MWCNTs prepared with a metal content of 20 wt% was evaluated as the anode electrocatalyst in a 9 cm² direct ethanol fuel cell using PtRu/C as the cathode material. Both electrodes had a metal loading of 1 mgPt cm⁻². Polarization curves showed higher electroactivity for Pt/MWCNTs than commercial material (Pt/C).

Graphical Abstract



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Keywords MWCNTs · Pt/MWCNTs · Ethanol electro-oxidation · Direct ethanol fuel cell

1 Introduction

Direct ethanol fuel cells (DEFC) based on a polymer electrolyte membrane (PEM) are attractive alternative devices for transport and portable applications because of their high thermodynamic efficiency and the ease of

High Resolution Transmission Electron Microscopy Study of Multi-Walled Carbon Nanotubes Growth on Manganese Oxide Thin Film

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ABSTRACT

Many efforts have been done to get multiwalled carbon nanotubes (MWCNT) using nickelocene as catalytic agent. However, characteristics such as an aligned growth and high yield have not been achieved yet. This work presents an alternative method to improve the growth efficiency, using nickelocene and manganese oxide covered tubing as catalyst and substrate respectively. The manganese oxide (MnOx) thin film was deposited using an improved aerosol assisted chemical vapor deposition system. Subsequently, MWCNT were grown by spray pyrolysis, inside the MnOx covered tubing. Different temperatures were tested from 800 to 900 °C. The higher yield was achieved at 800 °C, obtaining MWCNT of around 30 μm and 50 nm of length and diameter, respectively. Surface morphology and chemical composition of the film and MWCNT were studied by scanning electron microscopy and X-ray energy dispersive spectroscopy (EDS). The crystalline structure was analyzed by X-ray diffraction. High resolution transmission electron microscopy studies of the MWCNT and cross section of the interface film-MWCNT evinced the interaction of the MnOx and Ni catalyst in the root of well aligned carbon nanotubes. Diffusion of Ni into the MnOx film was found by EDS. Nanobeam diffraction of the cross section was consistent with X-ray diffraction results.

KEYWORDS:

1. INTRODUCTION

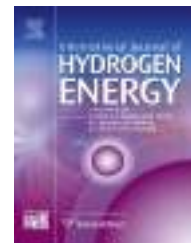
Interesting properties of multi-walled carbon nanotubes (MWCNT), such as thermal stability¹ and electron conduction² allow them suitable for applications in different areas such as electronic and optoelectronic devices,³ gas sensors,⁴ super-capacitors⁵ and electro-catalysts.^{6,7} In the last decade several methods for carbon nanotubes (CNT) synthesis have had an important development and progress. The most commonly used are Laser Ablation,⁸ Arc Discharge,⁹ Catalytic Chemical Vapor Deposition (CCVD)¹⁰ and Spray Pyrolysis.^{11–13} Furthermore, different catalytic agents have been used, principally organometallic materials such as ferrocene, nickelocene and cobaltocene.¹⁴ Ferrocene has been proved to produce high quality MWCNT.^{12,15} However iron precursors

usually left impurities as secondary reactions products. Remained Fe based particles in the MWCNT surface are not appropriate for some catalyst applications; therefore a cleaning process needs to be done before the final application. On the other hand nickelocene has been proved as a good catalyst to growth MWCNT by spray pyrolysis;^{16,17} nevertheless it has a low yield to produce MWCNT directly over a glass substrate.¹⁸ Combinations of ferrocene and nickelocene also have been used as a catalytic agent in the spray pyrolysis method¹⁹ but cleaning process is still necessary. The main goal of this work is to obtain well aligned MWCNT using nickelocene as catalytic agent. It is expected that the residual nickel particles on the CNT surface will improve the electrochemical activity,²⁰ mainly in direct methanol fuel cells,^{21,22} opening the opportunity of use this materials in posterior applications as support of fuel cell electrocatalyst. In a previous work²³ it was evidenced the problematic growth of well aligned MWCNT over glass substrates using a Ni catalytic agent. Several studies have shown that the use of a coating can improve

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Nitrogen self-doped electrocatalysts synthesized by pyrolysis of commercial polymer fibers for oxygen reduction reaction

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ABSTRACT

In this study, metal-free electrocatalysts were obtained from the pyrolysis of commercial Kevlar™ and Twaron™ carbon fibers (pKf and pTf, respectively). An easy and low cost synthesis method was developed. The obtained electrocatalysts have a significantly lower cost than conventional platinum based electrocatalysts. Synthesis of the electrocatalyst was made by pyrolysis treatment of the carbon fibers, under nitrogen atmosphere, followed by an activation treatment under carbon dioxide atmosphere. Properties and electrochemical performance of pyrolyzed (pKf, pTf) and activated (aKf and aTf) samples were compared. The electrocatalysts obtained have surface areas of up to 1000 m²/g after the activation treatment. Morphology and structural characteristics were studied by Scanning Electron Microscopy (SEM), X-ray diffraction (XRD), Raman Spectroscopy and X-ray photoelectron spectroscopy (XPS). The electroactivity of these electrocatalysts was evaluated by the oxygen reduction reaction (ORR) in acid media by rotating disk electrode technique. Carbon fibers showed an improvement in the ORR after receiving the activation treatment.

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Introduction

The development of fuel cells is a very promising alternative to solve the problem of clean energy generation with high efficiency [1,2]. However, one of the main challenges to achieve a large-scale production of fuel cells is to reduce

production costs due to the high cost of platinum. Several alternatives have been proposed, mainly focused on reducing the platinum amount without affecting the performance of the fuel cell, e.g. enhanced support and platinum dispersion [3], to reduce particle size in order to increase the active area of platinum and using bimetallic systems as co-dopants that protect platinum from poisoning [4]. However, these methods

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Sonochemical synthesis and characterization of Pt/CNT, Pt/TiO₂, and Pt/CNT/TiO₂ electrocatalysts for methanol electro-oxidation



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ABSTRACT

Pt electrocatalyst supported on composite formed of multi-walled carbon nanotubes and titanium oxide (CNT/TiO₂) was successfully synthesized by a sonochemical method without heat treatments, surfactants or additives. This electrocatalyst could be used for direct methanol fuel cells (DMFC) applications. For comparison, Pt/CNT and Pt/TiO₂ electrocatalysts were prepared as reference samples. Structural properties and morphology of the synthesized materials were examined by X-ray diffraction, transmission electron microscopy, Raman spectroscopy, X-ray photoelectron spectroscopy and their specific surface areas were determined by the Brunauer-Emmett-Teller method. The Pt and acid-treated CNT contents were analyzed by inductively coupled plasma atomic emission spectroscopy and thermogravimetric analysis, respectively. The electrochemical properties of the synthesized electrocatalysts were evaluated by cyclic voltammetry (CV) and chronoamperometry in a three-electrode cell at room temperature. The evaluation performed using electrochemical techniques suggests that TiO₂ promotes the CO-tolerance due to TiO₂-Pt interaction. The CV tests demonstrated that 6 wt.% of acid-treated CNT increases significantly the current density when Pt selectively interacts with TiO₂.

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1. Introduction

Direct methanol fuel cells (DMFC) are being widely studied to satisfy the increasing demand of the power systems of portable electronic devices [1,2]. However, the main obstacles for the DMFC commercialization are the high cost of Pt-based electrocatalysts, as well as the sluggish kinetics of methanol electro-oxidation due to the Pt poisoning surface, caused by CO-like intermediates produced during methanol reaction. To solve this issue, Pt alloys have been extensively investigated to enhance the catalytic activity or to avoid the poisoning problems [3–5]. It has been established that the presence of Ru in the catalyst promotes the oxidation of CO by a bi-functional mechanism [6,7]. Nevertheless, the limited supply and the high cost of Ru prevent its use on a commercial

scale. On the other hand, the general requirements of the supporting materials for Pt-based electrocatalysts are: high surface area to allow a good dispersion of metal loading, good electrical conductivity to facilitate electron transport during the electrochemical reaction, a mesoporous structure in order to maximize the triple-phase boundary and a high corrosion resistance. Typically, multi-walled carbon nanotubes (CNT) have been used as promising supporting materials for DMFC electrocatalysts due to their good electrical conductivity [8,9]. However, the corrosion of carbon support under the harsh reaction conditions would lead to a rapid catalytic activity loss, and hence the reduction of the fuel cell life [10,11]. Recent researchers have reported the use of metal oxides as supports for DMFC electrocatalysts [12–18]. These studies have demonstrated that the incorporation of oxide nanoparticles can enhance their durability, catalytic activity, and CO-tolerance. Metal oxides as titanium oxide have attracted the attention as supports of catalysts due to their stability at fuel cell operation conditions, low cost, nontoxicity, and commercial availability.

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A novel stand-alone mobile photovoltaic/wind turbine/ultracapacitor/battery bank hybrid power system

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This paper presents a new mobile hybrid system using a photovoltaic array, a wind turbine, an ultracapacitor, and a battery bank for grid-independent applications in the city of Cancun, Mexico. A main controller is proposed to manage these different power sources. This controller permits autonomous operation and control over power generation and loading. This proposal used high power and high energy density storage devices, including short- and long-term storage strategies for energy management. An independent load management subsystem was added, given that the mobile application requires the management of critical loads. This subsystem included an ON/OFF pattern for the connection and disconnection of DC and AC power outlets installed inside and outside the mobile unit. In order to verify system performance, each component of the system was modeled and simulated under realistic operating scenarios with a practical load using MATLAB, Simulink, and SimPowerSystems. The results obtained for this simulation showed that, by means of power balancing, this management scheme coordinated the power flow among the different sources and the load. The manager behavior shows that the difference between the power generated and the power demand was 2.08 kW h/day and 4.01 kW h/day in winter and summer, respectively. © 2015 AIP Publishing LLC.

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I. INTRODUCTION

Growing energy demand, rising fossil fuel prices combined with concerns over greenhouse gas emissions, and the difficulty of covering demand in remote regions make renewable energy sources an attractive solution because they are environmentally friendly and low cost compared to electrical grid expansion in these areas.¹⁻³

However, renewable energy sources can present certain deficiencies when used individually, such as intermittency due to weather conditions. To overcome this problem, these power sources may be integrated with other alternative power generation or storage systems using hybrid topologies.^{4,5}

The requirements for the design and operation of hybrid systems depend on the type of components, management strategy, control system, size, availability of primary sources, and load demand.^{6,7}

Operation of a hybrid system should include control strategies for energy management of the entire system that coordinate the power flows among the different energy sources to ensure constant power load, with special attention given to problems of power quality or variations that may affect it.

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Síntesis de nanopartículas Pt-Ni soportadas sobre nanotubos de carbono multicapa para la electro-oxidación del metanol

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Palabras clave: nanopartículas, nanotubos de carbono, celdas de combustible, reacción de oxidación de metanol

Resumen

El uso del Pt en celdas de combustible de metanol directo (DMFC) es afectado por el envenenamiento de intermediarios producidos durante la oxidación del metanol. Para esto se pueden utilizar nanopartículas de Pt con metales baratos tales como el Ni, Co y Fe en configuración núcleo-coraza o aleación, ya que la estructura electrónica del Pt es modificada de tal modo que la energía de enlace con los intermediarios disminuye evitando su contaminación. En este trabajo se sintetizaron nanopartículas Pt-Ni en aleación sobre nanotubos de carbono (NTC) a una relación atómica Ni:Pt=1:1 con el objetivo de estudiar su comportamiento electrocatalítico para la electro-oxidación del metanol. El material obtenido fue caracterizado física y químicamente por Microscopía Electrónica de Barrido (SEM) y Transmisión (TEM), Difracción de Rayos X (XRD) y Espectroscopía de Energía Dispersiva (EDS). Para el estudio de la oxidación del metanol se utilizó una celda con un electrodo de trabajo de carbón vítreo, un electrodo de Ag/AgCl (KCl sat) como referencia y un alambre de Pt como contraelectrodo. Se usó un electrolito de 0.5 M CH₃OH + 0.5 M H₂SO₄. Las voltamperometrías cíclicas fueron realizadas a una velocidad de barrido de 20 mV/s de -0.2 a 1 V vs Ag/AgCl (KCl sat). El material Pt-Ni/NTC se comparó con nanopartículas de Pt sobre NTC y el catalizador comercial Pt/Vulcan 10% E-tek. De acuerdo con estos resultados, la aleación estudiada podría ser útil en electrodos para celdas de combustible de metanol.

Palabras clave: nanopartículas, nanotubos de carbono, celdas de combustible, reacción de oxidación de metanol

1.- Introducción

Las celdas de combustible tipo PEM de metanol directo (Direct Methanol Fuel Cells, DMFC por sus siglas en inglés), han recibido mucha atención por su simplicidad, fácil manejo, baja temperatura de operación, alta densidad de energía y su potencial aplicación como una fuente de energía portátil y verde [1]. El desempeño de las DMFC ha sido limitado por la lenta cinética de la reacción de oxidación del metanol (ROM) en medio ácido. El Pt es aún el electrocatalizador más ampliamente utilizado para la ROM [2], pero su fácil envenenamiento por intermediarios de reacción reduce la eficiencia de este tipo de celdas de combustible. Actualmente se trabaja en la síntesis de electrocatalizadores bimetalicos Pt-M (M=metal) en configuración núcleo-coraza y aleación que reduzcan el envenenamiento de estos materiales y aumente la actividad electrocatalítica [3]. Con respecto a la utilización de catalizadores basados en Ni, estos han sido de especial interés debido a su bajo costo, alto desempeño catalítico y buena tolerancia al CO₂ y estabilidad en medios alcalinos [4]. Cabe mencionar, que el material utilizado como soporte para las nanopartículas catalíticas juega un importante rol en los electrocatalizadores para celdas de combustible. Es conocido que los negros de humo se oxidan en ambientes ácidos como el de una celda de combustible, provocando la aglomeración de nanopartículas de Pt, y una disminución en la actividad electrocatalítica. Una opción factible como material de soporte son los nanotubos de carbono (NTC) debido a sus propiedades excepcionales como su tamaño nanométrico, alta área superficial, resistencia a la corrosión, buena conductividad eléctrica, y alta estabilidad en comparación con los negros de humo tradicionales [5]. El presente trabajo se enfoca en la síntesis de nanopartículas Pt-Ni soportadas sobre nanotubos de carbono para utilizarse como electrocatalizadores para la oxidación de metanol en DMFCs.

2.- Metodología experimental

2.1- Síntesis de nanopartículas Pt-Ni sobre nanotubos de carbono (NTC)

Síntesis de NTC por deposición de vapor químico (DVQ)

Los nanotubos de carbono (NTC) fueron sintetizados mediante el método de deposición de vapor químico (DVQ), usando ferroceno como catalizador y tolueno como fuente de carbono. Se preparó una solución de ferroceno/tolueno la cual fue inyectada mediante una bomba peristáltica y un flujo de argón hacia un sustrato de cuarzo. Este último se encontraba colocado dentro de un horno tubular a 900 °C. El material obtenido de la síntesis de los NTC fue sometido a un tratamiento con peróxido de hidrógeno (H₂O₂) y ácido nítrico (HNO₃) durante 2 y 12 horas respectivamente, para su limpieza y funcionalización.

Síntesis de la aleación PtNi/NTC

Se empleó un método coloidal mediante reducción química para obtener las nanopartículas utilizando los siguientes reactivos: polivinilpirrolidona (PVP, Sigma-Aldrich) como surfactante, metanol (J.T. Baker) como solvente, PtCl₄ (Sigma-Aldrich) precursor de Pt, NiCl₂·6H₂O (Sigma-Aldrich) como precursor de Ni, y NaBH₄ (Fermont) como agente reductor.

La muestra Pt-Ni fue sintetizada considerando que tuviera una relación atómica Pt:Ni= 1:1 y un porcentaje total de metal de 10% en peso. La síntesis de las nanopartículas se realizó mediante el siguiente procedimiento. Primera parte, a cierta cantidad de NiCl₂·6H₂O se le añadió metanol en una relación de 1ml de solvente



Influence of nickel on the electrochemical activity of PtRu/multiwalled carbon nanotubes electrocatalysts for direct methanol fuel cells

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Abstract This paper presents the effect of Ni in PtRu electrocatalysts over multiwalled carbon nanotubes (MWCNT) utilized for the electro-oxidation of methanol with the purpose of increasing reaction activity and tolerance to carbon monoxide. Two kinds of MWCNT were prepared using the same technique but different catalytic agents, ferrocene, and nickelocene. MWCNT obtained from ferrocene were treated after the synthesis to eliminate amorphous carbon and Fe excess, while MWCNT from nickelocene were used as synthesized to leave the nickel nanoparticles formed during the synthesis. PtRu particles were deposited over the surface of both types of MWCNT in order to study the effect of the Ni presence. The structure of the electrocatalysts was analyzed by transmission electron microscopy (TEM) and X-ray diffraction (XRD). Chemical elemental microanalysis was carried out by X-ray energy dispersive spectroscopy (EDS). The synthesized MWCNT had an average diameter in the order of 60 nm and an average length of about 30 microns. Metallic

nanoparticles deposited had a particle size in the order of 10 nm each. The electrochemical surface area (ESA) was measured using CO stripping curves and the activity toward the methanol oxidation reaction was evaluated. The ESA was improved with the presence of Ni, achieving an activity and onset potential similar to a commercial electrocatalyst (20 wt% PtRu/C, ETEK) with a lower PtRu loading (10 wt% PtRu).

Keywords Carbon nanotubes · PtRuNi nanoparticles · Methanol fuel cells · Methanol electro-oxidation

1 Introduction

Direct methanol fuel cell (DMFC) is a technology in the process of development. It is of great interest due to the wide range of mobile applications. The use of DMFCs could potentially solve different problems in the fuel cell area, such as hydrogen storage and transportation.

In DMFCs, the oxidation of methanol takes place at the anode of the cell according to



takes place at the anode of the cell. Pt electrodes are active for the oxidation of methanol; however, CO groups strongly adsorb on the Pt sites causing the poisoning of the catalyst [1], hence it is necessary for the addition of a second metal. Typically, Pt Ru catalysts are used in DMFCs, demonstrating by far to be the best ones for reaction (Eq. 1). Lima et al. [2] established that Ru provides oxygenated species creating additional active sites for the adsorbed CO oxidation. However, efforts are required in this area in order to decrease the metal loading and in consequence the production costs of the DMFCs.

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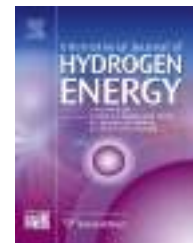
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Sizing of a solar/hydrogen system for high altitude long endurance aircrafts

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ABSTRACT

High altitude long endurance (HALE) aircrafts are aerial platforms operating in the stratosphere, providing relay services for wireless communication networks. These platforms are an alternative to increase the effectiveness of future communication. Nevertheless, the power system is a key part that determines the implementation and feasibility of these platforms. One effective and renewable option to power an HALE aircraft is a photovoltaic system (PVS) with hydrogen storage. In this paper, the simulation of the solar/hydrogen closed loop system is carried out for a parametric combination of the subsystems power. Power consumption of the propeller was determined as a function of the aircraft weight in steady flight and in still air. In order to obtain the optimal nominal powers the efficiencies are calculated at hourly intervals over the course of the year by means of an analytical energy balance. The proposed method was implemented in an algorithm, which allows fast estimation of the actual time of flight and the system efficiency. Finally, the energy system of three HALE aircrafts was analyzed in relation of their wing area and total and empty mass.

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Introduction

At present, the fast progress of technology is without doubt one of the key progress indicators for every country. Furthermore, communications play an important role due to the direct impact on the economic and social development. Technology and communication provide unlimited opportunities in social as they play a vital role in human existence. Moreover, energy also plays an important role; in a globalized world a lack of energy makes impossible the proper functioning of the production system to deliver the goods and services that people

and societies need. In this way, it is clear that the current communication systems are closely bound up to energy. In recent years, the terrestrial optical fiber communications system has grown enormously. In the same way, satellite communication systems have shown a remarkable development. The latter dominated basically by three reasons: 1) there are places that terrestrial systems cannot cover, 2) the need of satellite communications in natural disasters, wars, etc. and 3) the demand cannot be covered only with the use of optical fiber [1]. Satellites are also attractive for interconnection of geographically distributed high speed networks [2].

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Short Communication

Enhanced Catalytic Activity for the Ethanol Oxidation Reaction (EOR) using Novel Pt-Fe₃O₄/MWCNT Bimetallic Electrocatalyst

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Abstract: In this work, 20% Pt-Fe₃O₄/MWCNT (Pt:Fe₃O₄ weight ratio of 80:20) and 20% Pt/MWCNT nanoparticles were synthesized and characterized as anode electrocatalysts in H₂SO₄ media. First, the electrocatalyst were submitted to accelerated catalyst degradation test (ACDT) by performing 500 cycles between 0.6 and 1.2 V (vs. SHE). Then, their performance for the EOR was evaluated. The magnetite-containing nanoparticles demonstrated to be highly electrochemically stable, with negligible surface area losses (less than 7%) in the hydrogen adsorption/desorption region. Moreover, Pt-Fe₃O₄/MWCNT showed a significantly enhanced catalytic activity for the EOR when compared to Pt/MWCNT, with almost 46% increase in current density when using Fe₃O₄ as co-catalysts.

Keywords: MWCNTs; magnetite as co-catalyst; Pt-Fe₃O₄ electrocatalysts; ethanol oxidation reaction; Direct Alcohol Fuel Cells

1. INTRODUCTION

Direct Alcohol Fuel Cells (DAFCs) are having a growing attention of research groups worldwide because of their energetic advantages over other power conversion devices. Pt is the most widely used catalyst for fuel cell applications [1]. However, due to the formation of reaction intermediates, such as CO, acetaldehyde and acetic acid, the efficient electrooxidation of ethanol in DAFCs requires the use of metallic alloys or composite nanocatalysts at which the bifunctional mechanism takes place. Under these conditions, the kinetic of the EOR is faster and occurs at lower potentials when compared to Pt-alone materials.

It has been demonstrated that nanosized Pt-Sn/C is one of the most active alloys for the EOR [2-3]. Also, some Pt-metal oxides have shown an enhanced performance for the EOR. For example, Pt-CeO₂/C can promote the oxidation of ethanol and other organic

molecules at more anodic potentials related to Pt-alone anodes [4]. Also, it has been shown that the use of a Pt-Ni-TiO₂NT/C anode can oxidize ethanol at lower potentials than Pt/C and Pt-Ni/C due to the interaction of the alloy with the TiO₂ nanotubes [5].

Recently, some authors have reported the use of iron oxides as relatively cheap and active co-catalyst. Fe₃O₄ and Fe₂O₃ have been studied in composite materials along with noble metals, for the oxidation of organic molecules and the Oxygen Reduction Reaction (ORR) [6-9]. The results are promissory, indicating that iron oxides in combination with Pt can promote the activation of the DAFCs anode and cathode reactions at lower overpotentials than Pt-alone in acid media [6-9]. For example, the work by Sun et al. shows that dumbbell-like Pt-Fe₃O₄ nanoparticles have a high catalytic activity for the ORR [6]. Moreover, the electrochemical characterization of Fe₃O₄@Pt core-shell nanostructures has revealed that their catalytic activity for the EOR is higher than that of Pt-alone nanoparticles [8]. Along with magnetite, the use of Fe₂O₃ as co-catalyst with Pt has demonstrated to be advantageous for the

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

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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 $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ as iron source which were named S1, S2 and S3, respectively. The coordination complex of platinum $(\text{TOA})_2\text{PtCl}_6$ was obtained by the chemical reaction between $(\text{NH}_4)_2\text{PtCl}_6$ 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 elec-

trocatalysts 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-Núñez et al. [17] and J. R. Rodríguez 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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