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Preparation, characterization and electrochemical evaluation of Ni–Pd and Ni–Pd–Pt nanoparticles for the oxygen reduction reaction

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ARTICLE INFO

Article history:

Received 16 April 2016

Received in revised form

21 July 2016

Accepted 21 July 2016

Available online 12 August 2016

Keywords:

Ni–Pd–Pt catalyst

Trimetallic catalyst

Oxygen reduction reaction

Catalytic activity

PEM fuel cells

ABSTRACT

The aim of this work is the development of a bimetallic nanocatalyst based on Ni–Pd and a trimetallic nanocatalyst with low Platinum content (Ni–Pd–Pt). Both materials were electrochemical evaluated to study their catalytic activity towards the oxygen reduction reaction (ORR). The Ni₈₀Pd₂₀/C catalysts were produced by two consecutive steps: 1) reduction of the Nickel precursor followed by, 2) galvanic displacement for Pd deposition and by the addition of small amounts of Pt (20 wt.% with respect to Ni–Pd), to obtain carbon supported (Ni₈₀Pd₂₀)Pt₂₀/C nanocatalyst. The synthesized powders were characterized by X-ray Diffraction (XRD) and Scanning Transmission Electron Microscopy (STEM). Results indicate that the synthesis led to formation of a new phase in the bimetallic catalyst associated to the incorporation of Pt with an average particle size of 4.35 ± 1.0 nm. The electrochemical characterization shows that the addition of a second non-noble metal (Ni) to Pd slightly increases the catalytic activity towards the oxygen reduction reaction; however, when a small amount of Pt is incorporated to the Ni–Pd nanocatalyst to form a trimetallic catalyst the specific and the mass activity were increased by a factor of 2.5 and 3, respectively.

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Introduction

Nowadays Polymeric Exchange Membrane Fuel Cells (PEMFC's) are considered a promising source for electrochemical energy conversion, which represents an attractive alternative to mitigate the effects of global warming. They offer benefits in portable, stationary and transport applications due to their ability to convert energy in a single step with

high efficiency, greater than that obtained with internal combustion engines [1]. In a PEMFC the oxygen reduction reaction (ORR) represents the prevalent challenge because of its sluggish kinetics limiting the overall PEMFC performance [2,3]. Catalysts based on platinum nanoparticles are being currently used to accelerate the kinetics on the cathode electrode obtaining the maximum catalytic activity towards the ORR; however, these materials are expensive preventing the successful introduction of PEMFC technology to industrial scale.

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<http://dx.doi.org/10.1016/j.ijhydene.2016.07.178>

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This is the reason behind numerous investigations providing insights regarding electrocatalyst formulations tailoring with great catalytic activity and low cost, taking special interest in optimizing their surface area, adequate stability, selectivity and durability [2,4,5]. Due to problems associated to Pt scarcity, there are basically two alternatives: the first one is the development of novel materials that completely replace Pt as catalytic material and the second one consists in the reduction of Pt amount by alloying or forming intermetallic compounds. Replacing Pt by using cheaper or non-precious metals has been widely explored [6,7], however the fuel cell performance is still limited regarding the targets established by the U.S. Department of Energy (DOE) [8]. The second (and the most explored) alternative is by alloying Pt or Pd with a more abundant and cheaper non-noble metal such as Mo, Fe, Co, Ni, Cu, W and Ru, which have resulted in great improvements towards the catalytic activity [9–12]. In bimetallic catalysts, the addition of a second metal as alloying element with Pt significantly improves the catalytic activity due to electronic and geometrical effects in the structure and distribution of active sites, which modify the reactivity of the nanoparticle surface [13]. In other words, platinum atoms decrease their interatomic distances when attempting to adopt the structural lattice of the second alloying metal, named as compression effects of the crystal lattices. While on the alloying metal the expansion of its lattice parameters is attained in the attempt to adopt the structure of the Pt atoms which are larger in size [14–16]. Recently, catalysts based on Pd have been proposed as an alternative to replace platinum due to its high catalytic activity for the ORR and its approximately 3–4 times lower cost.

Moreover, by a similar effect in the electronic and geometrical structure, as occurs for Pt, palladium alloys have shown an improvement in the ORR activity compared to pure palladium [17–22]. At the same time, electronic structures with vacancies in the 5d orbital are formed, which promote in the case of a reduction process, electron donation from the catalyst surface to the π antibonding orbitals of the oxygen molecule. This is believed to facilitate the formation of M–OH_{ads} species on the surface of the alloy particles, followed by the subsequent dissociation of the O–O bond and desorption of the formed products [14].

The aim of the present study is the development of an active carbon supported Ni–Pd and Ni–Pd decorated with Pt nanocatalysts to evaluate their catalytic activity for the ORR in acid media. The Pd₂₀/C, Ni₈₀Pd₂₀/C and (Ni₈₀Pd₂₀)Pt₂₀/C catalysts were synthesized using a methodology previously developed by our research group [15,16] and Pt (20 wt.%) /C Etek catalyst was used as a reference. Physical characterization was performed by X-ray diffraction (XRD) and Scanning Transmission Electron Microscopy (STEM) and results are discussed.

Experimental

Chemicals and materials

Nickel (II) acetylacetonate (Ni(acac)₂, 99.9%), Potassium hexachloropalladate (IV) (K₂PdCl₆, 99.9%) and Potassium hexachloroplatinate (IV) (K₂PtCl₆, 99.9%) were used as metallic

precursors. Sodium Borohydride (NaBH₄, >99%) was used as reducing agent. Tetrabutylammonium bromide (TBAB, 98%) and Polyvinylpyrrolidone (PVP, average mol wt 40,000) were used as surfactants and size controlling agents. Ethanol (C₂H₆O, 98%) was used as solvent for the bimetallic synthesis; while ethylene glycol (C₂H₆O₂, 98%) was used as solvent for the trimetallic synthesis together with deionized water. All chemicals were obtained from Sigma–Aldrich and used without further purification. Vulcan Carbon XC-72R (Cabot) was employed as nanoparticles support, previously functionalized with monoethanolamine (C₂H₆O, 98%) as explained in the following section.

Carbon functionalization

1.5 g of Vulcan carbon XC-72R were thermally treated in a tube furnace at 500 °C under hydrogen atmosphere for 2 h in order to remove volatile impurities. Subsequently, 600 mg of thermally treated carbon were dispersed in 100 mL of a 20% v/v HNO₃ solution under ultrasonic bath for 1 h. Then the dispersion was refluxed for 1 h at 90 °C. The carbon was recovered by centrifugation and washed with abundant deionized water (18.2 MΩ) until the filtered water reached neutrality. Then the material was dried under N₂ flow at 100 °C for 1 h. The functionalization process consisted in the dispersion of 260 mg of the treated carbon in 50 mL of deionized water and 6 mL of monoethanolamine under reflux for 2 h at 190 °C. The carbon was recovered by centrifugation, washed several times with deionized water and finally dried under N₂ flow at 100 °C for 1 h.

Synthesis of catalysts

The Ni₈₀Pd₂₀/C nanocatalyst was synthesized by a chemical reduction route through a two steps-procedure following our previously published methodology [15,16]. Briefly: i) 0.215 mmol of Ni(acac)₂, 0.215 mmol of TBAB and 60 mg of functionalized Vulcan Carbon XC-72R (80 wt.% with respect to metallic Ni) were dispersed in 70 mL of ethanol under ultrasonic bath for 15 min. Then, the mixture was maintained under reflux conditions at 80 °C during 1 h with constant magnetic stirring while adding a NaBH₄ solution dropwise (0.542 mmol in 20 mL of ethanol) to reduce the precursors salts into metallic state. ii) In the second stage a K₂PdCl₆ solution (0.035 mmol, 20 wt.% with respect to metallic Ni in 5 mL of 0.5 M HCl solution) was dropwise added maintaining magnetic stirring for another 4 h. Finally, a black powder was recuperated by centrifugation and washed several times with deionized water and ethanol. The solid powder was completely dried at 120 °C during 2 h under N₂ atmosphere.

To obtain the decorated (Ni_{0.8}Pd_{0.2})Pt_{0.2}/C nanocatalyst: 35 mg of the Ni₈₀Pd₂₀/C nanocatalyst previously synthesized and 0.045 mmol of PVP were dispersed in 30 mL of Ethylene glycol under ultrasonic bath for 15 min. Then a solution of K₂PtCl₆ (0.023 mmol, 20 wt.% with respect to metallic Ni–Pd dissolved in 15 mL of deionized water) was dropwise added to the mix increasing gradually the temperature until 90 °C under magnetic stirring for 4 h to carry out the galvanic replacement reaction. Finally, the powder was recuperated by centrifugation and washed several times with deionized

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