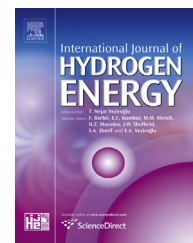




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Palladium–nickel materials as cathode electrocatalysts for alkaline fuel cells

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ABSTRACT

In this work, Pd–Ni catalysts supported on carbon nanofibers were synthesized, with metal contents and Pd:Ni atomic ratios close to 25 wt.% and 1:2, respectively. Previously, the carbon nanofibers were chemically treated, in order to create surface oxygen and/or nitrogen groups. The synthesized catalysts displayed low crystallinity degree and high dispersion on carbon supports, especially in those with surface functional groups. Oxygen reduction reaction (ORR) was studied by rotating ring-disk electrode (RRDE) techniques. When the kinetic current is normalized by the mass of Pd present in the electrode, higher activities were obtained for the synthesized materials in comparison with the activity observed for a commercial Pd/C E-TEK catalyst. Some differences are reported for the different materials under study, mainly dependent on the presence of oxygen surface groups on the carbon support. In light of the results, we can propose the synthesized catalysts as possible candidates for cathodes in alkaline direct methanol fuel cells.

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1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) have been postulated as possible alternatives in the production of electricity for portable and stationary applications, due to their advantageous characteristics such as low working temperature, high energy conversion efficiency, high power density, low or zero pollution emissions, quick start-up and long lifetime [1]. Several works in the literature predicted that PEMFCs could develop similar efficiencies to batteries, internal combustion engines and/or power grids [2]. However, the implementation of this technology still must confront challenges related

to technical details such as the low kinetics in the oxygen reduction reaction (ORR) at the cathode side [3].

The main progresses in the cathodic side have been devoted to the development and improvement of activity and stability of non-platinum materials, such as heat-treated macrocyclic compounds of transition metals [4–6], ruthenium based chalcogenides [7–9] and palladium alloys catalysts [10–12]. The last being the most promising alternatives, due to lower price and higher Pd mining sources in comparison with platinum. Besides Pd being cheaper (\$654.1 per oz.) than Pt (\$1796.9 per oz.) [13], the addition of other metals can increase its activity towards the ORR, in a similar way to the Pt–M catalysts. This increase is caused by the modification of the Pd electronic structure [14], an

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effect related to the oxygen dissociative adsorption energy. This effect has been reported for 1 nm M@Pd core-shells, which have shown that surface strain and charge distribution can change the Pd shell *d*-band energy [15].

Into the research of Pd alloys, some authors focused their attention in the Pd:Ni alloy. Li et al. prepared palladium–nickel alloys supported on carbon, observing lower onset potentials and higher ORR activities than those of a Pd/C catalyst in alkaline media [16]. Ramos-Sánchez et al. focused their research into the catalysts metal loading, preparing bimetallic PdNi nanoparticles supported on carbon by borohydride reduction in a THF solution. These electrocatalysts were also tested as cathode in a PEM fuel cell, finding power densities near 122 mW cm^{-2} for a 45% metal loading [17]. Previously, the same authors reported higher activity on Pd–Ni catalysts compared to Pd materials, showing a shift in the onset potential for ORR close to 110 mV towards more positive values [18]. Unsupported Pd–Ni catalysts have also been prepared and tested towards ORR. Xu et al. [19] de-alloyed a PdNiAl composite, forming a Pd–Ni alloy with uniform and interconnected structure, which displayed both high activity towards the oxygen reduction reaction and higher tolerance to methanol crossover than a Pt/C catalyst in acidic media. Wang et al. [20] reported the synthesis of Pd–Ni hollow nanoparticles by galvanic replacement, employing Ni nanoparticles as sacrificial electrodes. These materials exhibited better performances towards the oxygen reduction reaction compared to Pt and Pd carbon supported catalysts in alkaline media.

If Pd–Ni nanoparticles are supported on carbon materials, the role of the support and the content and nature of surface functional groups must be considered, when the catalytic activity is assessed. Surface oxygen groups assist the impregnation of metal precursors on the carbon support during the synthesis process [21] and promote the electron transfer between metal particles and the carbon material [22]. In the case of surface nitrogen groups, formation of small size nanoparticles with low sintering degree in presence of these groups has been reported, resulting in more stable catalysts [23].

In this work Pd–Ni catalysts supported on different chemically treated carbon nanofibers have been synthesized, obtaining similar metal contents (close to 25 wt.%) and Pd:Ni atomic ratios close to 1:2, in order to evaluate their catalytic activity towards the oxygen reduction reaction, as an alternative to platinum electrocatalysts for oxygen reduction reaction. The synthesized catalysts were analyzed by EDX, XRD and TEM for determining their physical and morphological properties (composition, size and dispersion of the nanoparticles on carbon supports) whereas an electrochemical study with RRDE techniques was performed in order to evaluate the catalytic activity of synthesized materials at 20 °C towards the oxygen reduction reaction.

2. Experimental

2.1. Carbon nanofibers

Carbon nanofibers (CNFs) were prepared by catalytic thermal decomposition of methane [24] on a Ni:Cu:Al catalyst (atomic ratio = 78:6:16) at 700 °C for 10 h [25]. Then, CNFs were treated

in HNO₃ 65% (v/v) for 2 h at 110 °C, in order to create surface oxygen groups (carbon support here named as CNFO) and remove the metals used in the synthesis (Ni, Al and Cu) [26]. Nitrogen surface groups on carbon nanofibers were generated mixing CNFO with ethylenediamine, 10:6 molar ratio, at room temperature for 24 h. Then, the new carbon material (here named as CNFN) was washed to pH 7.0 and dried at 85 °C for 24 h.

2.2. Preparation of Pd–Ni catalysts

The modified carbon materials were well-dispersed in ultra-pure water by sonication and magnetic stirring. Next, a solution of the precursor salts (Na₂PdCl₄, 98 wt.%, NiCl₂, 99.999 wt.%, Aldrich) was slowly added to the dispersion and then, pH was adjusted to 5.0 with a concentrated NaOH solution (98%, Panreac). After 12 h, a 26.4 mM sodium borohydride solution (99%, Aldrich) was added drop by drop under sonication. Reaction mixture was kept under magnetic stirring for 12 h, before the filtering, washing and drying at 60 °C. Nomenclature of the synthesized catalysts depends on the carbon support and the Pd:Ni atomic ratio, labeling them as Pd–Ni/CNF 1:2, Pd–Ni/CNFO 1:2, Pd–Ni/CNFN 1:2 and Pd–Ni/CB 1:2.

Additionally, carbon black (Cabot®) was employed for preparing a Pd:Ni 1:2 catalyst, which was used as a comparison. A commercial Pd/C from E-TEK was also used as a standard.

2.3. Physical characterization

Metal content and Pd–Ni atomic ratios for the synthesized materials were determined by energy dispersive X ray analysis (EDX) using a scanning electron microscope Hitachi S-3400 N coupled to a Röntec XFlash analyser, operating at 15 keV, with a Si(Li) detector and a Be window.

A Bruker AXS D8 Advance diffractometer was employed for obtain the X-ray diffraction (XRD) patterns. This equipment works with a θ - θ configuration and a Cu-K α radiation at 40 kV and 40 mA. Scans were collected at 1° min^{-1} for 2θ values between 10 and 100°.

Analyses of the dispersion and particles size distribution were performed by transmission electron microscopy analysis (TEM). A transmission electron microscope 200 kV JEOL-2000 FXII was employed. Images were obtained by means of a MultiScan CCD (Gatan 694) camera, and they were treated with the Fourier Transform software Digital Micrograph (3.7.0, Gatan) for obtaining the particle size distribution histograms.

2.4. Electrochemical characterization

An AUTOLAB NS 85630 modular equipment connected to a three electrodes cell was used for carry out the potentiostatic measurements. Working electrode was a glassy carbon disk modified with the Pd–Ni catalysts. It was prepared from an ink containing 2.0 mg of catalyst, 15 μL of Nafion® (5 wt.%, Aldrich) and 500 μL of ultra-pure water; then, a 60 μL aliquot was deposited and dried on the glassy carbon disk. As counter electrode, a glassy carbon bar was used, whereas a reversible hydrogen electrode (RHE) placed inside a Luggin capillary was

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