INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2016) 1–14

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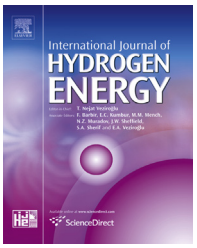

Palladium–nickel catalysts supported on different chemically-treated carbon blacks for methanol oxidation in alkaline media

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ARTICLE INFO

Article history:
Received 14 December 2015
Received in revised form
8 July 2016
Accepted 16 July 2016
Available online xxx

Keywords:
Pd–Ni catalysts
Alkaline medium
CO oxidation
Methanol oxidation
Direct methanol fuel cells

ABSTRACT

Palladium–nickel catalysts supported on carbon blacks containing similar metal contents (25 wt. %) and Pd:Ni atomic ratios (1:1 and 1:2) were synthesized. Carbon supports were chemically treated to create different oxygen and nitrogen groups on surface. X ray patterns revealed a weak alloying between Pd and Ni, whereas crystallite sizes were between 2.1 and 3.2 nm, being consistent with the values detected by transmission electron microscopy (TEM). CO strippings demonstrated a higher poisoning tolerance of the Pd–Ni catalysts than that observed for a Pd catalyst supported on Vulcan carbon black. The methanol oxidation on Pd–Ni catalysts suggested that presence of Ni increase the activity of the materials, considering that Pd/CB exhibited the lowest methanol oxidation current densities. Nevertheless, no effects associated to the presence of surface functional groups on carbon supports were observed in the performance of this reaction.

Introduction

Direct methanol fuel cells (DMFCs) are promising power sources that have raised a big interest, because they are novel, clean, low pollutant issuers and noiseless electricity sources [1]. Usually, these devices employ platinum and Pt-alloys with some transition metals such as ruthenium [2], tin [3] and nickel [4], as catalytic anodes to perform the oxidation of methanol. Nevertheless, the use of Pt results in two important problems: first, its poisoning with CO, one of the intermediates generated during the methanol electrochemical oxidation in acidic medium [5], and second, its high cost and limited abundance, which avoid the commercial implementation of DMFCs [4].

Recently, some studies suggested the use of palladium as an alternative to replace platinum, given the similarity between these metals, the lower cost and higher availability of palladium [6], and its capacity for overcoming the CO poisoning [7]. In addition, reactivity of Pd towards the oxidation of alcohols in alkaline medium is higher than that in acidic medium [8–10]. The catalytic activity of Pd could be enhanced if it is alloyed with other transition metals as Ag [11], Tb [12] and Ru [13], and also with several metal oxides

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http://dx.doi.org/10.1016/j.ijhydene.2016.07.121

such as CeO_2, Mn_3O_4, Co_3O_4 and NiO [14]. In fact, some authors have demonstrated that nickel addition to Pd supported catalysts promotes the electrochemical oxidation of alcohols in alkaline medium [5,15–20]. The improved efficiency of this material was ascribed to the formation of OH^- adsorbed ions on the Ni oxide surface, which participate in the CO oxidation [5]. In this sense, it is noteworthy the influence of the alloy composition in the electrocatalytic activity towards the oxidation of both, CO and methanol. A density functional theory study revealed that the bimetallic composition of Pd–Ni alloys affects the adsorption energy of CO and oxygen, obtaining the better results with the 1:1 Pd:Ni ratio [21]. Other authors verified this result by high-energy X ray diffraction coupled to atomic pair distribution function analysis (HE-XRD/PDF) and reverse Monte Carlo simulations, showing that synergistic union between Pd and Ni atoms affects the adsorption of both CO and oxygen, due to the structural characteristics and chemical composition of the surface [22]. Recently, Zheng et al. evaluated the CO electrochemical oxidation on Pd–M alloys (M = Pt, Co, and Ni) [23], finding electrochemical surface areas for the Pd–Ni catalysts close to 20 $m^2\ g^{-1}$ and CO oxidation onset potentials close to 0.89 V *vs* RHE. Besides these works, only a few studies related with both, the CO adsorption and its electrochemical oxidation on Pd–Ni carbon supported alloys have been reported.

About the methanol oxidation on Ni and Pd–Ni alloys, recent studies have determined some kinetic parameters for this reaction when these materials are supported on carbon blacks [5,20]. A study from Shen and collaborators showed that addition of Pd and Pt to NiO/C reduces the methanol oxidation onset potential and yields current densities close to 50 mA cm^{-2} [15], suggesting that nickel oxide plays a similar role to that observed for ruthenium oxides in the Pt–Ru catalysts. High activities of Pd–Ni/C catalysts have been attributed to the formation of adsorbed OH^- on the catalyst surface promoted by both, the presence of Ni and changes in the electronic properties of Pd [19]. Qi demonstrated that presence of nickel would increase the currents associated to the adsorption/desorption process of hydrogen and the tolerance towards the accumulation of carbonaceous intermediates during the methanol and ethanol oxidation [24], reaching geometric area-normalized current densities close to 60 mA cm^{-2}. The authors suggested that nickel contributes to enhance the poisoning tolerance of palladium, making this alloy very efficient for methanol oxidation. Moreover, the use of different types of alloys has also been reported, e.g. Pd–Ni nanowire arrays [25], exhibited maximum current density values of 4 mA cm^{-2}. Pd–Ni–P metallic glass nanoparticles supported on Vulcan XC-72 also were tested in the methanol oxidation, obtaining a highest current density close to 0.5 mA cm^{-2} [26] and Pd–Ni hierarchical structure catalysts made by electro-deposition with a highest methanol oxidation current density close to 0.6 mA cm^{-2} [27]. Regarding the oxidation of other organic compounds on this alloy, some reports displayed its uses in the electrochemical oxidation of ethanol [28], ethylene glycol [16,23,29,30], formic acid [6] and allyl alcohol [17].

Another important factor is the role of the support and its functionalization in the catalytic activity of these materials. Thus, the purpose of chemical treatments for carbon blacks is to generate surface groups with different nature, bearing in mind their importance in the catalytic activity of the materials. In the case of the oxygen surface groups, they play a key role in the impregnation of metal precursors on the carbon support during the synthesis procedures, depending on the basic or acid nature of the oxygen group [31] and in the electron transfer from the metal particles to the carbon material, acting as a mediator during the redox reactions [32]. Regarding to the nitrogen surface groups, some authors reported the obtaining of small size nanoparticles with low sintering degree in presence of these groups [33], thus favoring the stability of the materials during different operation times. Moreover, the increase of the catalytic activity of nanoparticles supported on some nitrogen-doped or functionalized carbon materials towards both, the oxygen reduction reaction [34–36] and the methanol oxidation has been reported [37–39].

In this study, as alternatives for the replacement of platinum in anodes for alkaline direct methanol fuel cells, Pd–Ni catalysts supported on different chemically treated carbon blacks with similar metal contents (close to 25 wt. %) and Pd:Ni atomic ratios (near to 1:1 and 1:2) have been synthesized, in order to evaluate their catalytic activity towards the methanol electrochemical oxidation. Textural properties of carbon materials, composition, physicochemical properties, size and dispersion of the nanoparticles on carbon supports and surface composition of catalysts were determined by energy dispersive X-ray (EDX), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). Catalytic activity of synthesized materials at 20 °C, towards the electro-oxidation of CO and methanol was investigated, using cyclic voltammetry and comparing the obtained results with those observed for a Pd catalyst supported on Vulcan carbon black.

Experimental

Carbon supports

Vulcan XC72-R (Cabot®) carbon black (here named as CB) was used as the base for producing different modified carbon materials. In order to obtain the oxygen-functionalized carbon black (named as CBO), Vulcan XC72-R was submitted to a chemical treatment with concentrated nitric acid, following the procedure reported by Calvillo et al. [40]. Briefly, 25 mL of HNO_3 65 wt. % were added to 25 g of the carbon support and the mixture was refluxed at 110 °C during 2 h. Then, it was filtered, washed with distilled water to achieve pH 7.0 and dried for 24 h. To generate nitrogen surface groups (carbon material named as CBN), CBO was mixed with ethylenediamine, in a 10:6 ratio, at room temperature for 24 h. Then, the CBN material was washed to pH 7.0 and dried at 85 °C for 24 h.

Synthesis of catalysts

Carbon supports were dispersed in ultra-pure water, first by sonication and then by magnetic stirring for 12 h. Next, an appropriate concentration of the precursor salts (Na_2PdCl_4, 98 wt. %, $NiCl_2$, 99.999 wt. %, Aldrich) was slowly added to the

Please cite this article in press as: Calderón JC, et al., Palladium–nickel catalysts supported on different chemically-treated carbon blacks for methanol oxidation in alkaline media, International Journal of Hydrogen Energy (2016), http://dx.doi.org/10.1016/j.ijhydene.2016.07.121