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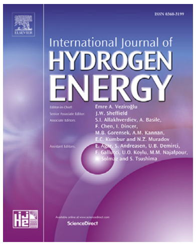

Methanol electro-oxidation reaction at the interface of (bi)-metallic (PtNi) synthesized nanoparticles supported on carbon Vulcan

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ABSTRACT

Ni-rich PtNi bi-metallic catalyst and its counterpart free of nickel supported on carbon Vulcan have been synthesized by the impregnation methodology from Na_2PtCl_6 and $Ni(C_5H_7O_2)_2$ as precursors. The obtained materials Pt/C and PtNi/C were used as electrocatalysts for the methanol oxidation reaction (MOR) in acid conditions. Electrochemical evaluations demonstrated that the addition of Ni in the Pt-Vulcan matrix promotes an important increment in the faradic current during MOR of one order of magnitude, even though the platinum load is lower in the bi-metallic catalyst. These results suggest that the incorporation of nickel promotes some structural and electronic modifications that enhance a better reaction performance at the electrode interface. Morphological characterization using scanning electron microscopy and transmission electron microscopy with energy dispersive spectroscopy (SEM-TEM-EDS) showed Pt/C and PtNi/C catalysts have a particle size of 5.7 nm and 4.4 nm, respectively. X-ray diffraction (XRD) reveals the formation of Ni_3Pt from the synthesis of PtNi catalysts. Additionally, X-ray photoelectron spectroscopy (XPS) confirmed the presence of Pt and Ni in their metallic-oxidation states on the carbon surface.

Introduction

Proton exchange membrane fuel cells (PEMFC) have attracted attention because they are electrochemical devices which convert chemical energy directly into electricity by interfacial-electrochemical reactions. There are different types of PEMFC depending on the reducing agent (fuel) used. The direct methanol fuel cell (DMFC) is a device based on proton exchange technology, because it operates at similar temperature that PEMFC using hydrogen (50–80 °C) [1]. The main characteristic of this type of cell is the methanol (CH_3OH) used in the

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anode, which is directly pumped as a source of protons. In DMFC the conversion of the chemical energy contained in liquid methanol takes place directly into electrical energy. The use of this alcohol as fuel has important advantages such as high power, operate at low temperatures (near 80 °C) and its structural system is simple, being an attractive energy source due to its easy storage that eliminates the use of hydrogen reformers. However, DMFCs has high overpotentials in the activation zone [2,3]. In this context, the electrocatalysts used in the DMFCs consist of two essential parts i) the metal (typically an expensive noble-metal) or alloys responsible of the reaction-activation (conversion and selectivity) and ii) the support material, which provides a physical surface for the dispersion of the metal particles necessary to achieve a high surface area.

One of the most employed support material in fuel cells is the carbon Vulcan XC-72R due to its low cost and unique properties, such as high surface area (250–300 m^2/g) [4,5], low density, good corrosion resistance, high electrical conductivity (2.77 S/cm) and good chemical stability. On the other hand, the most commonly used catalysts in DMFC cells are those containing noble metals, including Pt [6–9], Ru [10–12], Pd [13,14], Rh [15] and Sn [16,17]. Additionally, alloys of these metals have been proposed to improve their characteristics and reduce both CO contamination and cost of production. Each metal provides different properties, and depending on the compositions (in the alloys or composites) the dispersion and support nature, different performances in the reaction can be achieved.

Platinum is one of the most employed electro-catalyst for fuel cells presenting high capacity and specific characteristics due to its intrinsic-electronic properties [18]. However, considering the low abundance of this element and its high cost, the commercialization of PEMFC is not yet economically feasible, so the synthesis of more efficient electrocatalysts with lower content of platinum have to be considered. These challenges have led to the research of new and more efficient materials with the aim of making this technology viable on a large-scale. In this context, DMFCs is one of the most promising energy-sources with the major number of applications in mobile and portable systems. The development of new electro-catalysts has been (or should be) oriented in the study of i) materials free of platinum [19]; ii) binary or ternary systems forming some kind of link with low content of platinum [20]; and iii) materials free of noble metals [21]. In all these cases, the goal is to produce less expensive catalysts with the major efficiency versus MOR.

Then, the use of Pt-M alloys (M = Pd, Ru, Au, Pb, Mo, Sn, Ni, Re, Rh, Os) not only help to decreases the amount of Pt used, but also could increase the activity in the MOR. Different bimetallic systems have been studied, showing higher catalytic activity with respect to the monometallic catalysts [22]. However, the alloys with the highest activity for the methanol oxidation reaction are based on Pt–Ru systems [23]. In contrast, previous studies have shown that PtNi and PtRuNi catalysts, present higher activity than the catalysts of Pt and PtRu during methanol oxidation in acid conditions [22–24].

In this context, nickel is a less expensive metal in comparison with Ru [25]. In fact, as nickel is a transition metal with its incomplete-electrons *d*-orbital, presents interesting catalytic properties as a component with Pt-based electrocatalysts. Theoretical and experimental results suggest that the incorporation of nickel could displaces the center of the *d* Pt-band far from the Fermi level, and/or shifts the electron-binding energy of the platinum-nucleus to lower values [26]. Therefore, the improvement of the catalytic activity in the presence of nickel is attributed to an electronic effect at platinum-core causing a weakness of the CO-adsorption process at the surface of the bi-metallic (PtNi) and inhibiting the formation of nickel-oxide species, as demonstrated by a shift in the Pt binding-energy at PtNi catalyst by using XPS technique [22,24,27]. The mixed nickel-oxides (nickel oxides, nickel hydroxides and nickel oxy-hydroxides), which are formed through the reversible redox reaction at catalysts containing Ni, provide a good proton and electronic conductivity that facilitates the transfer of charge during the oxidation process, thus catalyzing the methanol oxidation, due to its high corrosion resistance and high stability [22]. Additionally, the chemisorption of methanol is more efficient when at least three neighboring Pt-atoms are in the correct crystallographic arrangement at the surface; as a consequence, there is a contribution in the catalytic response by each metal of the bimetallic system [25,26].

Yuan Q. et al. showed that the catalytic activity of nanostructured nickel-core wrapped with Pt crystalline thin film is three times higher than that obtained from the commercial 40 wt% Pt/C E-TEK catalysts [28]. Whereas the prepared bimetallic Pt–Ni nanospheres showed high activity and stability in the methanol electro-oxidation compared with the Pt/C catalyst from commercial source [29]. Also, the bi-metallic system $Ni_1@Pt_{0.067}/C$ nanoparticles showed significantly improvement in the catalytic activity towards ORR and MOR [30].

On the other hand, Mathiyarasu et al. found that 8%wt Ni in NiPt smooth films as catalyst showed high catalytic activity towards MOR [26,31]. According to this, it has been reported in several investigations that the use of Pt and Ni alloys increases the catalytic activity towards the MOR due to Ni stability in the Pt lattice [32]. Ultrafine PtNi nanoparticles (2.5–5.4 nm) supported on reduced graphene oxides demonstrates that Ni modification (Pt:Ni atomic ratio 2:1–5:1) can promote the electrocatalytic activity of Pt catalysts on the oxidation of methanol which is 2.65 times higher than the Pt catalysts without Ni modification [33]. Also, PtNi alloy particles with an atomic ratio of 1:1 were uniformly deposited on the surface graphitized nanodiamond (GND) through co-reduction process using the microwave heating EG method. The PtNi/GND exhibited better electrocatalytic activities than the Pt/GND either for MOR and ORR [34]. PVP-stabilized PtNi nanocrystals (~8 nm) supported on hollow carbon spheres with metal precursor ratio (Pt/Ni = 1:1) were synthesized via one-step solvothermal process showing 9 times higher catalytic activity and stability for methanol oxidation than commercial Pt/C [27]. Also, the synthesis method, crystal structure, chemical composition and the support used in these catalysts strongly influence its activity [26].

The performance of bi-metallic Pt catalysts with non-noble metals used in PMFC has been previously reported. Among these PtCo/C catalysts synthesized by microwave-heating with particle size from 2 to 5 nm is obtained [35]. PtNi

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