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PtCu catalyst for the electro-oxidation of ethanol in an alkaline direct alcohol fuel cell

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ABSTRACT

A PtCu electrocatalyst was synthesized using a galvanic displacement route obtaining nanoparticles with a semi-spherical morphology and an average size of 4 nm, supported on carbon black (Vulcan). The crystallographic characterization by X-ray diffraction showed a certain degree of Pt–Cu alloying. The electrocatalytic activity of the prepared electrocatalyst for the electro-oxidation of ethanol in alkaline media was investigated. A 2-fold increase of the peak current density and a negative shift of the potential were recorded in half-cell experiments for the bimetallic catalyst compared to a commercial Pt/C. The presence of Cu promotes ethanol oxidation in alkaline electrolyte by hindering the Pt–H adsorption at low overpotentials. Additionally, the PtCu electrocatalyst was used as anode in an anion-exchange-membrane direct ethanol fuel cell (AEM-DEFC) exhibiting about 2-fold higher power density than the benchmark Pt/C.

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Introduction

Direct Ethanol Fuel Cells (DEFCs) have received great attention in recent years due to the growing need of renewable energy sources with low environmental impact. This technology has the potential to be applied in portable electronic devices,

biosensors, transport sector and stationary electricity sources [1,2]. However, its widespread commercialization has not been reached, essentially due to the high cost of the electrode catalysts and low durability [3,4]. Consequently, the production of highly electro-active and durable catalysts for the ethanol oxidation reaction (EOR) and the oxygen reduction reaction (ORR) is still a challenge.

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One common strategy to decrease the cost while improving the activity and stability of the catalysts is alloying noble metals, like Pt or Pd, with other low cost materials [5–7]. In acidic media, Pt-based electro-catalysts are widely used for the EOR due to the high activity of platinum in the dehydrogenation of small organic molecules at low temperatures, which is the first step of the electro-oxidation process [8,9]. Some of Pt-based formulations with high performance in acidic media are PtRu, PtSn and PtRuSn [10–17]. The role of the less noble metal is to supply OH^- species at lower potentials, promoting the activity for the alcohol electro-oxidation. Furthermore, the alloy formation alters the electronic structure of the platinum-based electrocatalysts [18].

Traditionally, polymer electrolyte fuel cells incorporate an acidic polymeric membrane, such as Nafion[®], for the transport of protons from the anode to the cathode. In the last years, there is a growing interest on the use of alkaline anion-exchange polymeric membranes, in which the transport of anions (OH^-) takes place from the cathode to the anode. Good prospects for the application of such membranes are envisaged mainly due to the facile kinetics at the electrodes at high pH, even with cheaper non-noble metal catalysts [19–21]. Anion-exchange membranes (AEM) exhibit also reduced methanol, ethanol and ethylene glycol permeabilities when compared to Nafion[®] proton-exchange membrane (PEM) [22,23], and that behaviour contributes to reducing the crossover of the fuel molecules from the anode to the cathode, which directly impacts in an enhancement of the open circuit voltage and in the performance of the direct alcohol fuel cell (DAFC); this leads to the possibility of using thinner alkaline polymer electrolytes with lower ionic resistances [21]. Nevertheless, there are important challenges in AEM development for DAFCs because of some limitations, such as the unwanted precipitation of salts (such as carbonates), or the production of acids during alcohol oxidation [24], which could limit the performance and life time of the DAFC in alkaline media.

Some authors showed that the ethanol electro-oxidation in alkaline media occurs faster on Pd-based catalysts than on Pt-based ones. Pd is a cheaper and more abundant metal than Pt in nature. For these reasons, the research on Pt-based systems in acid media diminished with the concomitant increase in research on Pd-based catalysts in alkaline solutions in recent years [25]. For instance, Pd–Ni catalysts exhibited a good performance for the EOR [26], showing an improvement when compared with the commercial Pd/C electro-catalyst in alkaline solutions. In recent years, some authors found that Pt is intrinsically more active than Pd for ethanol electro-oxidation in alkaline media [27]. Furthermore, Gong et al. found that Cu can improve the stability and activity of Pt for the EOR in alkaline solutions. These benefits have been attributed to the synergistic effects between Pt and Cu and to the bi-functional mechanism that ease the desorption of carbonaceous-species that poison the catalyst [28]. The lattice parameter and the electronic properties of Pt at the surface can be modified by the second metal, leading to catalytic sites with high activity and long stability [29]. In addition, the partial substitution of Pt with other cheap metals, like Cu, could be an efficient way to significantly decrease the catalysts cost. Nevertheless, from the mentioned results, it is evident that the most active noble

metal (Pt or Pd) for the oxidation of ethanol in alkaline media is still an open discussion.

In the present work, the synthesis of PtCu catalyst by a galvanic displacement route supported on carbon Vulcan is reported. The electrochemical behaviour of the catalyst was evaluated in half cell experiments by cyclic voltammetry with and without ethanol in alkaline media. The characterization of the PtCu/C catalyst as anode in AEM-DEFC is also reported and compared with a commercial Pt/C electrocatalyst.

Experimental

Synthesis of PtCu/C electrocatalyst

The synthesis procedure is based on a method that was previously used to obtain well-defined PdCu nanoparticles [30]. In brief, 0.1 g of polyvinylpyrrolidone (PVP, wt. 40,000 Sigma-Aldrich) and 0.662 g of ascorbic acid (99.0%, Sigma-Aldrich) were placed in a round-bottomed flask containing 10 mL of ethylene glycol (J.T. Baker 99.92%) and heated to 80 °C. Copper salt (0.06 g CuSO_4 , reagent grade Sigma-Aldrich) was added to this solution and stirred for 30 min to form Cu nanoparticles. Subsequently, 0.25 g of sodium bromide (NaBr, 99.0% J. T. Baker) was added to the mixture, followed by 0.035 g of potassium tetrachloroplatinate (II) (K_2PtCl_4 , 99%, Aldrich). The mixture was then stirred for 90 min. Vulcan carbon (XC72, Cabot[®]) was then added to the solution as a support of the nanoparticles, followed by stirring for another 60 min. Finally, the catalyst was washed several times with deionized water and dried overnight. The metal concentration on the carbon support was 20 wt% (Fig. S1).

Physicochemical characterization

The resulting powders were characterized by X-ray diffraction using a Bruker D8 Advance diffractometer operated at 30 kV and 30 mA, using Cu $K\alpha$ radiation, with θ - θ configuration, at 0.05° step with 3 s acquisition time. Transmission electron microscopy (TEM) micrographs were acquired using a high-resolution field emission transmission electron microscope (HR-FE-TEM, JEOL JEM-2200FS) coupled with an energy-dispersive X-ray (EDX) analyzer. X-ray photoelectron spectroscopy (XPS) measurements were performed by using a Physical Electronics (PHI) 5800-01 spectrometer. A monochromatic Al $K\alpha$ X-ray source was used at a power of 350 W. Powdered samples were deposited on a carbon tape. XPS data have been interpreted by using the on-line library of oxidation states implemented in the PHI MULTIPAK 6.1 software and the PHI Handbook of X-ray photoelectron spectroscopy [31].

Electrochemical characterization

Cyclic voltammograms were collected in acidic and alkaline media to determine the electrochemical response of PtCu/C and Pt/C (E-TEK) electrocatalysts. Electrochemical experiments were performed in a three-electrode electrochemical cell with a BioLogic VSP Potentiostat. A glassy carbon electrode (Basi[®]), a Hg/Hg₂SO₄ electrode saturated in K₂SO₄ (for the acidic medium), a Hg/HgO electrode in 1 M KOH (for the

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