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Performance of carbon-supported palladium and palladium–ruthenium catalysts for alkaline membrane direct ethanol fuel cells

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ABSTRACT

The activity of carbon supported palladium-based catalysts towards ethanol oxidation reaction in alkaline medium is investigated. To this end, Pd and Pd_xRu (x = 1, 6, 12) materials are synthesized supported on Vulcan XC72R by a modified impregnation method. These materials are characterized physicochemically and their composition varies between 40 and 50 wt. % of metal content. The mean size of nanoparticles is below 4 nm, and the size of the majority of particles ranges from 2 to 6 nm. The catalytic activity of these samples is also tested in half-cell and alkaline membrane direct ethanol fuel cell (AMDEFC). Lower onset potential and higher oxidation current densities is observed in palladium-rich bimetallic catalysts. By using the prepared samples as anode of AMDEFC and a commercial membrane of polybenzimidazole as solid electrolyte, the maximum power density is observed for Pd₁₂Ru/C, 97 mW cm⁻², almost doubling the value achieved by the catalyst Pd/C (50 mW cm⁻²), and above the obtained by commercial PtRu/C catalyst (89 mW cm⁻²).

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Introduction

Polymer electrolyte membrane fuel cells (PEMFC) are devices that are attracting great interest in recent decades due to the high power densities that are capable of reaching at relatively low temperatures. Hydrogen and methanol have been the most common fuels used in these devices. However, both have certain drawbacks, such as the problems of production, storage and distribution of hydrogen or the toxicity of

methanol [1]. An alternative to these fuels is the use of ethanol, cheaper and less toxic than methanol. The oxidation of ethanol has been the topic of numerous research papers in recent years [2–7]. It is mainly due to the high energy density and thermodynamic efficiency of this fuel, in addition to the fact that ethanol is considered a green chemical. It can be produced in large quantities as a renewable biofuel from the fermentation of biomass and, in addition, both ethanol and its final oxidation products (CO₂ and water) are relatively non-toxic.

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Direct ethanol fuel cells (DEFCs) meet some requirements for a sustainable energy conversion technology, such as high electrical efficiency, easy handling of ethanol, or low operation temperature, and they are attractive power sources for portable electronic devices. However, the slow electrode kinetics, the poisoning and high cost of electrocatalysts are some of challenges to be overcome [8,9]. In this regard, platinum-based materials are considered the best catalysts for the oxygen reduction and for the oxidation of small organic molecules in acidic media, and the most of studies on the oxidation of ethanol have been focused on Pt, PtRu or PtSn [2,10–12]. Nevertheless, the higher pH of alkaline membrane DEFCs can improve the reaction kinetics with respect to acidic DEFCs. It facilitates the use of a range of non-precious metal catalysts both in the cathode and in the anode, reducing the dependence of platinum [13]. For example, Ag and MnO₂ are good catalysts for the oxygen reduction reaction and present high tolerance to alcohols, which makes them good candidates as cathodes [14]. On the other hand, Pd electrocatalysts can be highly active for the oxidation of a large variety of small molecules in basic media, where also other non-noble metals are enough stable for electrochemical uses [15]. Palladium is cheaper and more abundant than platinum, and the dilution of Pd with non-noble metals in adequate amounts leads to catalysts with promising activity in the potential range practical for fuel cell applications. The use of these catalysts is expected to decrease the cost of electrodes and therefore the total cost of devices. The main issue of the improvement of electrocatalysts for alkaline DEFCs was the limited development of the anion exchange polymeric membranes. Nevertheless, the recent advances in polymeric membranes with good anionic conductivity led to the increasing interest in Pd-based electrocatalysts.

Bianchini and Shen published a survey of Pd-based electrocatalysts for alcohol oxidation in 2009 [15]. It collects the most representative electrodes for methanol, ethanol and 2-propanol oxidation in alkaline media, such as Pd, Pd-metal or Pd-oxide supported mainly on various carbon materials. It is pointed out that both the presence of co-catalysts and the support material can affect the catalytic performance in terms of electrochemical activity and stability. Since then, there is an increasing number of studies of the alcohol oxidation in alkaline media using Pd or Pd-based catalysts [16]. There are bimetallic catalysts with Ag [17], Au [18], Co [19], Cu [20–22], Ni [23,24], and Sn [8] among others, which are been used to study the ethanol oxidation reaction. Ruthenium is also a good promoter for alcohol oxidation in alkaline media and, as PtRu, bimetallic PdRu catalysts also show high activity towards alcohol oxidation. Recently, this bimetallic system has attracted the attention of several research groups and there are studies of PdRu systems supported on various carbonaceous materials and prepared by using different synthetic routes [13,25–27], although studies containing fuel cell measurements are rare.

In the present research, we report a facile method of synthesis of C-supported Pd and Pd_xRu nanoparticles, and a comparative study of their catalytic behavior towards ethanol oxidation in alkaline medium in half-cell and fuel cell. We have prepared a series of Pd-based nanoparticles from metallic salts with different Pd:Ru atomic ratio (1:1, 6:1, 12:1

and 1:0) and high metal loading (36–50%). Vulcan XC-72R is used as support to obtain a well dispersed catalyst toward ethanol oxidation reaction. These materials have characterized structural and morphologically in order to relate the presence of ruthenium to the catalytic behaviors. The influence of small amounts of Ru on the oxidation activity is discussed. Ethanol oxidation reaction (EOR) has been studied by electrochemical techniques in half-cell. In addition, we evaluate the performance of these materials as anode in alkaline membrane direct ethanol fuel cells (AMDEFC) by using KOH-doped commercial PBI membranes.

Experimental

Materials

Palladium(II) chloride (PdCl₂ 99.9%) and ruthenium(III) chloride hydrate (RuCl₃ 99.9%) were purchased from Alfa Aesar. Hydrochloric acid (32%), trisodium citrate 2-hydrate (99%), absolute ethanol (99.5%) and potassium hydroxide were purchased from Panreac. Sodium borohydride (99%) and Nafion solution (5 wt. %) were purchased from Aldrich. Used carbon support (Vulcan XC72R: BET surface area of 250 m² g⁻¹ and average particle size of 40–50 nm) was donated by Cabot Corp. All reagents were used as received without further purification. Ultrapure water was used throughout the experiments (Milli-Q system, Millipore, 18.2 MΩ cm). PtRu/C (45 wt. % Johnson Matthey) was used for comparison purposes.

Preparation of Pd/C and PdRu/C catalysts

Pd/C with 50 wt. % of palladium and Pd_xRu/C (x = 1, 6, 12) catalysts with 40 wt. % of metal loading and supported on Vulcan XC72R were prepared by a modified impregnation method and the procedure is described below. A solution of chloropalladic acid (0.06 M) was prepared by dissolving stoichiometric amounts of PdCl₂ and HCl in water. Similarly, a solution of ruthenium chloride 0.06 M in water was prepared. A calculated amount of sodium citrate was dissolved in the appropriate amount of these solutions (Na₃Cit:M = 2:1) and added to a suspension of Vulcan XC72R in water (180 ml) to act as protective agent. This suspension was kept under vigorous stirring for 5 h. Stoichiometric excess of 1.0 M NaBH₄ solution was added dropwise to the stirred suspension to reduce the metallic precursors. Reaction was continued for 12 h before the slurry was filtered, washed with water, and dried for 12 h at 60 °C.

Physicochemical characterization

X-ray diffractograms (XRD) were collected on a Seifert 3000 powder diffractometer operating with Cu Kα radiation (λ = 0.15418 nm) generated at 40 kV and 40 mA. Scans were recorded at 0.02° s⁻¹ for 2θ values between 10° and 90°.

X-ray photoelectron spectra (XPS) of the samples were acquired with a VG Escalab 200R spectrometer fitted with a Mg Kα (hν = 1253.6 eV) 120 W X-ray source. The energy regions of the photoelectrons of interest were scanned until an acceptable signal-to-noise ratio was achieved. Intensities were

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