

Available at [www.sciencedirect.com](http://www.sciencedirect.com)journal homepage: [www.elsevier.com/locate/he](http://www.elsevier.com/locate/he)

# Performance of carbon-supported PtPd as catalyst for hydrogen oxidation in the anodes of proton exchange membrane fuel cells

Francisco Alcaide<sup>a,\*</sup>, Garbiñe Álvarez<sup>a</sup>, Pere L. Cabot<sup>b</sup>, Oscar Miguel<sup>a</sup>, Amaia Querejeta<sup>a</sup>

<sup>a</sup>Dpto. de Energía, CIDETEC-IK4, P<sup>o</sup> Miramón, 196, 20009 San Sebastián, Spain

<sup>b</sup>Laboratori d'Electroquímica de Materials i del Medi Ambient, Dept. Química Física, Universitat de Barcelona, Martí i Franquès, 1-11, 08028 Barcelona, Spain

## ARTICLE INFO

### Article history:

Received 9 December 2009

Received in revised form

12 February 2010

Accepted 3 March 2010

Available online 3 April 2010

### Keywords:

PEMFC

Membrane electrode assembly

CO tolerance

Hydrogen oxidation reaction

PtPd catalyst

## ABSTRACT

In this work, the replacement of platinum by palladium in carbon-supported catalysts as anodes for hydrogen oxidation reaction (HOR), in proton exchange membrane fuel cells (PEMFCs), has been studied. Anodes with carbon-supported Pt, Pd, and equiatomic Pt:Pd, with various Nafion<sup>®</sup> contents, were prepared and tested in H<sub>2</sub>/O<sub>2</sub> (air) PEMFCs fed with pure or CO-contaminated hydrogen. An electrochemical study of the prepared anodes has been carried out in situ, in membrane electrode assemblies, by cyclic voltammetry and CO electrooxidation voltammetry. The analyses of the corresponding voltammograms indicate that the anode composition influences the cell performance. Single cell experiments have shown that platinum could be replaced, at least partially, saving cost with still good performance, by palladium in the hydrogen diffusion anodes of PEMFCs. The performance of the PtPd catalyst fed with CO-contaminated H<sub>2</sub> used in this work is comparable to Pt, thus justifying further work varying the CO concentration in the H<sub>2</sub> fuel to assert its CO tolerance and to study the effect of the Pt:Pd atomic ratio.

© 2010 Professor T. Nejat Veziroglu. Published by Elsevier Ltd. All rights reserved.

## 1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are attractive power sources for portable, automotive, and stationary applications, due to their high energy density, high efficiency and low operating temperature, amongst other technical advantages. However, some cost and durability issues, not yet resolved, are delaying the large-scale commercialization of these systems [1].

Platinum is the mostly used catalyst in the electrodes of PEMFCs. However, it is essential to reduce the loading of this noble metal in the entire cell because of its high cost and low

availability [2]. The main strategies to attain this requirement are dispersing Pt on high surface area carbonaceous materials, the use of alloys, and the optimization of catalyst layer structure in the gas diffusion electrodes of the membrane electrode assemblies (MEAs) [3–7].

In general, the reduction of costs has been focused primarily on PEMFC cathodes, because the oxygen reduction reaction kinetics limits the fuel cell performance. Alternatively, there is great potential to reduce cost by optimizing the anode catalyst layer [8].

With respect to the anode of PEMFCs, the main challenge is to design catalysts which exhibit high activity towards

\* Corresponding author. Tel.: +34 943 309 022; fax: +34 943 309 136.

E-mail address: [falcaide@cidetec.es](mailto:falcaide@cidetec.es) (F. Alcaide).

0360-3199/\$ – see front matter © 2010 Professor T. Nejat Veziroglu. Published by Elsevier Ltd. All rights reserved.

doi:10.1016/j.ijhydene.2010.03.011

hydrogen oxidation reaction (HOR), and high tolerance to impurities as well, because of the technical hydrogen used as anode feed gas is mainly produced by reforming and thus, it inevitably contains small amounts of impurities such as carbon monoxide [9,10]. It is known that CO poisons Pt catalyst and reduces the cell performance, even at low concentrations (<5 ppm) [11]. To this respect, one of the most important advances was the development of bimetallic PtRu catalysts that exhibit superior activity in the oxidation of CO-contaminated H<sub>2</sub> compared to pure Pt [12–15]. However, the main shortcomings of PtRu catalysts are their high cost, instability at high positive potentials, and limited natural resources of Ru.

On the other hand, palladium is more widespread in the Earth crust than platinum (abundance of  $1.5 \times 10^{-2}$  vs.  $5 \times 10^{-3}$  parts per million by mass, respectively [16]), it is less expensive than Pt, and it also exhibits interesting electrocatalytic properties for HOR [17–20]. As a consequence, PtPd bimetallic catalysts have been proposed as an attractive alternative to Pt to reduce its amount in PEMFC anodes [21–24]. In addition, to assess their CO tolerance, the hydrogen electrooxidation in the presence of CO on these catalysts has been studied with encouraging results [25–27]. Nevertheless, no attempts have been made to optimize the composition of the anode catalyst layers. It is known that the optimum anode operation requires not only a high activity electrocatalyst but also an optimized anode catalyst layer. Catalyst layers of practical electrodes used in PEMFC contain some Nafion<sup>®</sup> ionomer, which has significant influence on the thin-film electrode performance [28–31]. Then, further optimization of the catalyst layer composition is clearly necessary.

In this study, the application of carbon-supported equiatomic PtPd as catalyst in practical electrodes for hydrogen oxidation in PEMFCs has been tested, and compared to carbon supported Pt and Pd, by means of half-cell and single cell electrochemical measurements involving cyclic voltammetry and chronopotentiometry. Special interest is devoted to the catalyst utilization, its performance in front of H<sub>2</sub> and CO-contaminated H<sub>2</sub> oxidation, and the effect of the ionomer content. The structural properties of the catalysts have been examined by X-ray diffraction (XRD).

## 2. Experimental

### 2.1. Materials

The anode catalysts used in this work were Pt, PtPd alloy with atomic ratio 1:1, and Pd, all supported at 20 wt. % on Vulcan XC-72 (VC), from Premetek Co, which will be denoted as Pt/VC, PtPd/VC, and Pd/VC, respectively. The cathode catalyst was Pt supported at 20 wt. % on Vulcan XC-72, from E-Tek, Inc. The XRD technique was used to characterize the catalysts. The XRD diffractograms were obtained by a Bruker D8 Advance diffractometer operating with Cu K<sub>α</sub> radiation ( $\lambda = 1.5406 \text{ \AA}$ ) and a  $2\theta$  scan from 30 to 100° (at  $0.02^\circ \text{ min}^{-1}$ ). Diffraction peaks were assigned according to the International Centre for Diffraction Data (ICDD) cards in PDF-2 database. The XRD data were used to determine the lattice parameter (from the

interplanar distances) and the average crystallite size (by using Scherrer equation) [32].

### 2.2. Fabrication and testing of the MEAs

Square shape MEAs with 16 cm<sup>2</sup> in section were prepared using the decal method [33–36]. Briefly, a catalyst ink for each of the different electrodes was prepared by mechanical stirring of the supported catalyst, appropriate amounts of 5 wt. % Nafion<sup>®</sup> dispersion (Aldrich), tetrabutylammonium hydroxide (Sigma–Aldrich, RG), and glycerol (Panreac, RG). The corresponding ink was painted onto a clean fiberglass-reinforced Teflon decal blank and put it in a drying oven. The procedure was repeated until the desired catalyst loading was achieved: 0.30 mg<sub>metal</sub> cm<sup>-2</sup> for the anodes and 0.20 mg<sub>Pt</sub> cm<sup>-2</sup> for the cathodes. These catalyst charges were tentatively used considering previous results showing that the anode Pt loadings in state-of-the-art MEAs operated with H<sub>2</sub>/air can be reduced without significant voltage losses to 0.05 mg<sub>Pt</sub> cm<sup>-2</sup>, while cathode Pt loadings can be reduced to 0.2 mg<sub>Pt</sub> cm<sup>-2</sup> with a voltage loss of only 20 mV up to 1.0 A cm<sup>-2</sup> [37]. The Nafion<sup>®</sup> content ranged between 10 and 40 wt. % (dry weight) in anodes and was a 30 wt. % (dry weight) in all cathodes.

Then, the painted side of two decals were placed facing each other on each side of a Nafion<sup>®</sup> NR212 membrane, which had been previously cleaned and transformed into the Na<sup>+</sup> form. The assembly was pressed at 210 °C and 50 bar for 5 min. After the hot-pressing, the decal substrates were peeled away from the membrane, and the catalyst coated membrane was reprotonated by boiling it in sulfuric acid. Finally, gas diffusion layers LT2500 W ELAT<sup>®</sup> GDL and LT1400 W ELAT<sup>®</sup> GDL (both from E-TEK, Inc.) were placed beside the cathode and the anode electrodes, respectively.

Single cell experiments were performed placing a MEA in a commercial fuel cell hardware FCT 16SCH (Fuel Cell Technologies, Inc.), which was assembled using a uniform torque of 15 N m [38]. The MEA performance was evaluated by measuring the current–voltage curves (potentiostatic polarization plots at steady-state condition) and the current–power characteristics using a fuel cell test station FCT-50S (Biologic).

Polarization curves were recorded after the MEA was activated at 0.60 V with humidified H<sub>2</sub> at 1.5× stoichiometric flow rate,  $\lambda(\text{H}_2) = 1.5$ , and O<sub>2</sub> at 2.0× stoichiometric flow rate,  $\lambda(\text{O}_2) = 2.0$ , until constant current was reached. The cell temperature was set at 80 °C. The anode feed was either H<sub>2</sub> (99.9996%, Praxair) or H<sub>2</sub>/CO (10 ppm v/v, Praxair). In some experiments the anode feed was diluted with pure N<sub>2</sub> (99.999%, Praxair). The cathode feed was O<sub>2</sub> (99.999%, Praxair) or synthetic air. The stoichiometries were 1.5 and 2.0 for anode and cathode, respectively. All gases were humidified at the cell temperature.

Furthermore, the electrochemical characterization of the catalysts was performed in the MEA. In the cyclic voltammetry measurements of the anode, which was fed with humidified nitrogen at 50 cm<sup>3</sup> min<sup>-1</sup>, the anode was the working electrode. The cathode was fed with humidified hydrogen at 200 cm<sup>3</sup> min<sup>-1</sup> and it was taken as the reference electrode and the counter electrode at the same time [39]. Cyclic voltammograms were recorded at a scan rate of 20 mV s<sup>-1</sup> at 80.0 °C. Carbon monoxide stripping experiments were performed

Download English Version:

<https://daneshyari.com/en/article/1276766>

Download Persian Version:

<https://daneshyari.com/article/1276766>

[Daneshyari.com](https://daneshyari.com)