

Research Article

Investigation of IrO₂/Pt Electrocatalysts in Unitized Regenerative Fuel Cells

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Received 4 April 2011; Revised 16 May 2011; Accepted 8 June 2011

Academic Editor: Elena Pastor Tejera

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IrO₂/Pt catalysts (at different concentrations) were synthesized by incipient wetness technique and characterized by XRD, XRF, and SEM. Water electrolysis/fuel cell performances were evaluated in a 5 cm² single cell under Unitized Regenerative Fuel Cell (URFC) configuration. The IrO₂/Pt composition of 14/86 showed the highest performance for water electrolysis and the lowest one as fuel cell. It is derived that for fuel cell operation an excess of Pt favours the oxygen reduction process whereas IrO₂ promotes oxygen evolution. From the present results, it appears that the diffusion characteristics and the reaction rate in fuel cell mode are significantly lower than in the electrolyser mode. This requires the enhancement of the gas diffusion properties of the electrodes and the catalytic properties for cathode operation in fuel cells.

1. Introduction

A Unitized Regenerative Fuel Cell (URFC) is an energy storage system useful to be connected to renewable sources such as solar energy or wind energy [1]. Such a system consists of a water electrolyser and a fuel cell combined in one stack, allowing a significant cost and volume reduction compared to the two devices separated. During electrolysis mode, water is electrolyzed to hydrogen and oxygen which are used to produce electrical energy in the subsequent fuel cell mode. Compared with conventional secondary batteries, the URFC has the advantage of long-term energy storage, being free of self-discharge, and higher energy density [2, 3]. Instead, compared with the conventional Regenerative Fuel Cell (RFC), which usually consists of separate fuel cell and electrolyser, the URFC is a simpler and more compact system because it uses only one electrochemical cell [4, 5]. Nevertheless, the design of an electrode to be used in an electrolyser is inherently different than that of a fuel cell electrode [6]. For example, for the oxygen electrode in a polymer electrolyte fuel cell, the Gas Diffusion Layer (GDL) is usually a highly hydrophobized carbon paper or carbon

cloth. However, they cannot be used as the GDL of a URFC for the following two reasons: (i) the carbon material tends to corrode at high potential on the oxygen electrode side during the water electrolysis operation and (ii) GDLs have to achieve an appropriate balance between the hydrophobic and hydrophilic properties for both the fuel cell and water electrolysis operation [7]. While the electrode for water electrolyser is generally designed to be flooded or partially flooded, the fuel cell must repel water. From these considerations it arises clearly that the URFC is not the simple linear combination of electrodes used in fuel cells with those used in electrolysis cells. For instance, the hydrogen electrode must not only contribute to the hydrogen evolution reaction but also must do it in the opposite direction. Nevertheless, the most critical point is the oxygen electrode, which displays the greater difficulties for its design [8]. To date, bifunctional electrocatalysts for oxygen redox reaction of URFCs include Pt-Ir [9], Pt-Ru-Ir [10], Pt-IrO₂ [11–15], and Pt-IrO₂-RuO₂ [16, 17], among which IrO₂ and RuO₂ are mainly prepared by using Adams fusion method [18]. Most of the above described bifunctional oxygen electrode catalysts are obtained by mixing an efficient electrocatalyst for oxygen

reduction (Pt black) and an efficient electrocatalyst for oxygen evolution (Ir or IrO_2 or $\text{IrO}_2\text{-RuO}_2$), which may result in poor combination between Pt black and Ir or IrO_2 or $\text{IrO}_2\text{-RuO}_2$ and thus lower bifunctional performance of oxygen electrode electrocatalysts. In this work, our approach was the use of an impregnation method to support IrO_2 onto Pt surface in order to reduce the amount of metal oxide maintaining good performance in electrolysis mode. Moreover, a hydrophobized Ti grid was used [19, 20] as diffusion layer, instead of the carbon-based GDL commonly used in fuel cells, at the oxygen electrode compartment in order to have a stable support [21, 22] and suitable reactants distribution/products removal.

2. Experimental

2.1. Preparation of IrO_2/Pt Electrocatalysts. The preparation of IrO_2/Pt was carried out by incipient wetness technique, which consists in the impregnation of commercial IrO_2 (Spectrum) onto a commercial Pt black (Johnson Matthey). The electrocatalysts were prepared at three different concentrations (weight ratios of 7/93, 11/89, and 14/86). Such compositions were precisely determined by X-ray fluorescence (XRF) analyses.

2.2. Physicochemical Characterization. The powders were characterized by X-Ray Diffraction (XRD), X-Ray Fluorescence (XRF), and Scanning Electron Microscopy (SEM). X-ray diffraction powder (XRD) patterns for these catalysts were obtained on a Philips X'Pert X-ray diffractometer using $\text{Cu K}\alpha$ -source operating at 40 kV and 30 mA. The peak profiles of the (2 2 0) reflection in the face-centered-cubic (fcc) structure were obtained by using the Marquardt algorithm, and it was used to calculate the crystallite size by the Debye-Scherrer equation due to the fact that there are not convolution of other peaks, as it may occur with the (1 1 1), (2 0 0), and (3 1 1) reflections. Instrumental broadening was determined by using a standard platinum sample. Catalysts were placed on a silicon substrate for XRD analysis. The diffraction patterns were fitted to JCPDS (Joint Committee on Powder Diffraction Standards) and crystal size distribution calculated using LBA (line broadening analysis). XRF analysis of the catalysts was carried out by a Bruker AXS S4 Explorer spectrometer operating at a power of 1 kW and equipped with a Rh X-ray source, a LiF crystal analyzer, and a 0.12° divergence collimator. SEM analysis of the catalysts was carried out by an FEI XL-30 Field Emission Electron Gun instrument. SEM images showed both secondary and backscattering electrons.

2.3. Electrodes and MEA Preparation. A commercial 30% Pt/Vulcan XC-72 (E-TEK-PEMEAS, Boston, USA) was used as the catalyst for the H_2 evolution reaction (electrolyser) and for H_2 reduction process (fuel cell). The electrode was prepared by directly mixing in an ultrasonic bath a suspension of Nafion ionomer in water with the Pt/C catalyst powder (catalyst/dry ionomer = 2/1 wt.); the obtained paste was spread on carbon cloth backings (GDL ELAT from E-TEK).

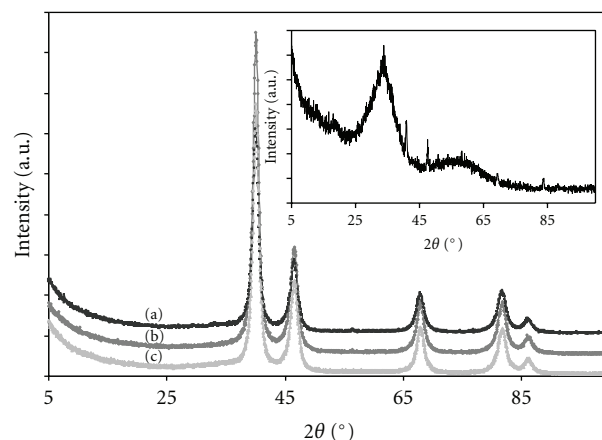


FIGURE 1: XRD patterns of (a) 14/86, (b) 11/89, (c) 7/93 IrO_2/Pt catalysts, and (inset) commercial IrO_2 .

For membrane-electrode assembly (MEA) fabrication, the oxygen electrode was prepared by hot-spray technique, depositing the IrO_2/Pt catalyst directly onto Nafion 117 membrane (Ion Power). A slurry composed of 67 wt.% catalyst and 33 wt.% Nafion solution (5 wt.% Ion Power) in deionised water and anhydrous ethylic alcohol (Carlo Erba) was prepared by mixing under ultrasounds. This slurry was deposited onto one face of the membrane by using a spray technique. The catalyst loading was about $6 \text{ mg}\cdot\text{cm}^{-2}$ for IrO_2/Pt and $1 \text{ mg}\cdot\text{cm}^{-2}$ for 30% Pt/Vulcan XC-72 (E-TEK). Nafion 117 was used as the solid polymer electrolyte. Complete MEAs were formed directly in the cell housing by tightening at $9 \text{ N}\cdot\text{m}$ using a dynamometric wrench. A hydrophobised Ti grid (Franco Corradi, Italy) backing layer was used at the oxygen compartment [23, 24].

2.4. Electrochemical Characterization. We have evaluated water electrolysis/fuel cell performance using a single-cell test fixture with a geometric area of 5 cm^2 . During fuel cell operation, the cell temperature was controlled at 80°C and a back pressure of 2 atm, for H_2 and O_2 reactant gases, was applied. Both gases were fully humidified. During water electrolysis operation, the cell was controlled at 80°C under atmospheric pressure and the water tank temperature was 85°C . The polarization curves were recorded by using an Autolab PGSTAT 302 Potentiostat/Galvanostat (Metrohm).

3. Results and Discussion

XRD analyses were carried out on the prepared catalysts (Figure 1) and compared to commercial IrO_2 (Figure 1, inset). The XRD pattern of IrO_2 shows a prevailing amorphous structure and some crystalline peaks associated to metallic Ir (Figure 1, inset), whereas the bifunctional catalysts showed the face-centered-cubic (fcc) structure typical of Pt due to the large amount of this metal compared to IrO_2 (which is, in any case, in an amorphous phase). Three different compositions were prepared and identified by XRF analysis (Table 1).

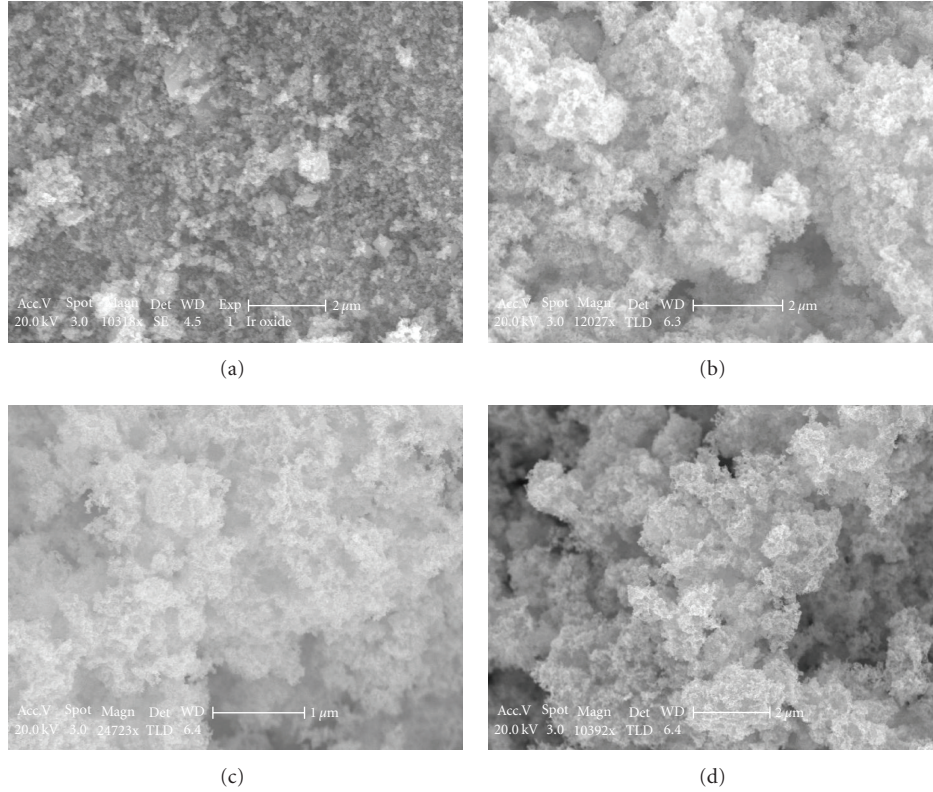


FIGURE 2: Scanning electronic micrographs of (a) amorphous IrO_2 , (b) 7/93, (c) 11/89, and (d) 14/86 IrO_2/Pt catalysts.

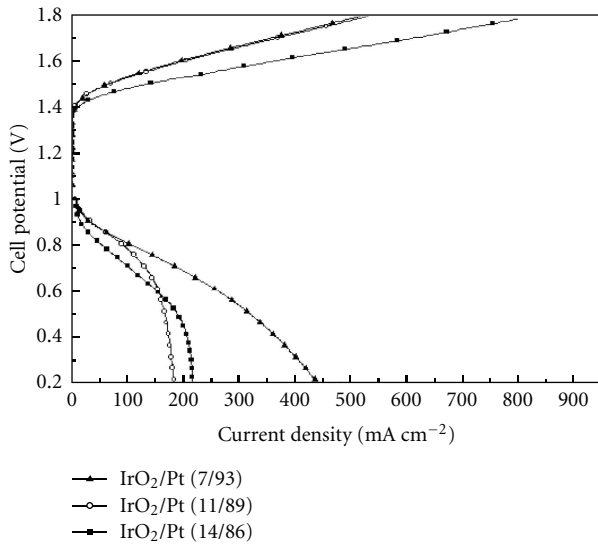


FIGURE 3: Cell potential versus current density curves for MEAs based on IrO_2/Pt catalysts at different compositions (7/93, 11/89, and 14/86) under URFC conditions.

The crystallite size of Pt in the bifunctional catalysts was estimated from the broadening of (220) reflections by the Scherrer equation. The values were about 6.5 ± 0.2 nm for all samples (Table 1).

TABLE 1: Composition and crystallite size of the catalysts.

Catalyst	Crystallite Size nm	Pt (wt. %)	IrO_2 (wt. %)
(a)	6.5	93	7
(b)	6.5	89	11
(c)	6.7	86	14

Figure 2 shows scanning electron micrographs of IrO_2/Pt at different compositions (7/93, 11/89, 14/86) and bare IrO_2 . Amorphous IrO_2 (Figure 2(a)) showed agglomerates of about 50–100 nm. The BET surface area for this IrO_2 catalyst is quite low, about $23 \text{ m}^2 \text{ g}^{-1}$ with the occurrence of micropores as confirmed by the porosity measurements reported in [25] whereas an adequate porous structure was observed for IrO_2/Pt bimetallic catalysts. All bimetallic catalysts show similar structure due to the fact that they are composed of the same materials with a larger presence of Pt [26].

The cell potential versus current density (calculated using the geometrical area of 5 cm^2) curves for MEAs based on the three compositions of IrO_2/Pt (7/93, 11/89, 14/86) under URFC conditions are shown in Figure 3. The IrO_2/Pt composition of 14/86 has the highest performance for water electrolysis and the lowest performance as fuel cell. It is derived that for fuel cell operation an excess of Pt favours the oxygen reduction process whereas IrO_2 promotes oxygen evolution. In fact, the results achieved in this work in electrolysis mode are similar to those obtained by using a pure

IrO₂ in a PEM electrolyser [22, 23]. This is probably due to the good dispersion of this metal oxide onto the Pt support. Thus, the utilization of IrO₂ is maximized. However, the presence of a larger amount of IrO₂ produces better results in the electrolysis process. Thus, it appears necessary to optimize the relative content of the two materials in order to have suitable performance in both processes.

On the contrary, in fuel cell mode, the performance is lower than that recorded in a conventional PEM fuel cell equipped with Pt catalysts in particular in the ohmic and diffusion regions [27–29]. This is probably due to the presence of the hydrophobized Ti-grid as gas diffusion layer/current collector. In fact, fuel cell tests are performed after the electrolysis process, and the fuel cell cathode could be completely flooded after operation as electrolyser, although a hydrophobized Ti-grid is used. Accordingly, oxygen is hindered by the presence of water inside the cathode compartment, and this diffusion drawback determines the loss of potential observed in Figure 3. For what concerns the amount of Pt in the bimetallic catalysts, it is observed that a higher amount produces lower potential losses as observed in the activation region (low current density) of the polarization curve. Accordingly, the performance at 0.65–0.7 V (region of interest from a point of view of the efficiency [29]) is higher for the IrO₂/Pt catalysts with increasing amounts of Pt (7/93 > 11/89 > 14/86). By using IrO₂/Pt (14/86) catalyst the performance decreased also in the activation region indicating that IrO₂ covered Pt sites reducing in this way the catalytic activity of the bimetallic catalyst for the oxygen reduction reaction. Since this formulation showed a better behaviour for the electrolysis process, it appears necessary to increase further the catalytic properties of this sample to be used as bifunctional catalyst.

4. Conclusions

IrO₂/Pt catalysts (at different concentrations) were synthesized and characterized in Unitized Regenerative Fuel Cell (URFC) configuration. These oxide-metal mixtures were prepared by incipient wetness technique and characterized by XRD, XRF, SEM, and electrochemical measurements under water electrolysis/fuel cell conditions. For fuel cell operation an excess of Pt favours the oxygen reduction process whereas IrO₂ promotes oxygen evolution. From the present results, it appears that the diffusion characteristics and the reaction rate in fuel cell mode are significantly lower than in the electrolyser mode. This requires the enhancement of the gas diffusion properties of the electrodes and the catalytic properties for cathode operation in fuel cells.

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