



Composite anode electrode based on iridium oxide promoter for direct methanol fuel cells



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ABSTRACT

A composite anode was developed to increase the performance of a direct methanol fuel cell (DMFC). High surface area IrO₂ nanopowder was synthesized by a sulfite complex method and added to a 50% PtRu/C catalyst prepared by the same procedure. A catalytic ink, composed of PtRu/C catalyst, IrO₂ and Nafion ionomer, was deposited on a carbon-cloth-based backing layer and used as composite anode in a DMFC. A significantly higher performance was recorded for the composite electrode-based MEA compared to a bare one, at 60 °C and 90 °C, confirming that the electrocatalytic activity is related to the characteristics of water displacement of IrO₂ additive, which acts as a co-catalyst for this reaction. The improvement was significantly higher by using 5 M methanol solution as the fuel. These results evidence that a multifunctional catalyst can operate better than PtRu for methanol oxidation since this multi-step process requires different functionalities to speed up the reaction rate.

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1. Introduction

Direct methanol fuel cells (DMFCs) are considered as an attractive option for the efficient and clean conversion of energy in portable applications or auxiliary power units [1–3]. Pt–Ru catalysts have shown the highest electro-catalytic activity for the oxidation of methanol when used at the anode of DMFCs, but the high cost, the sluggish kinetics and the stability of the bimetallic nanoparticles are the main drawbacks of these catalysts [4–8]. Yet, it is necessary to further enhance the catalytic activity of the anode catalyst decreasing the net amount of platinum used in the membrane-electrode assembly (MEA), and reducing thus the final stack cost. In this regard, several routes have been pursued to achieve this goal, e.g. the use of non-precious alloys, core-shell structures, alternative supports, ternary and quaternary formulation adding other metals, etc. [9–24]. However, although some progress is registered to reduce the amount of platinum used, there is no clear evidence regarding the increase of performance and stability [25].

Recently, some metal oxides have been investigated as additives, including TiO₂ [26–31], CeO₂ [32,33], SnO₂ [34], ZrO₂ [35], WO₃ [36,37], MoO₃ [38], etc. These additives have allowed achieving slightly better performance than Pt-based catalysts. The methanol oxidation process consists of two main steps, i.e. the dehydrogenation of methanol and the oxidation of CO

intermediates. The role of Ru is to oxidize CO by means of the facile formation of OH species from the water displacement process [39]. This is the rate determining step, especially at high temperature and high methanol concentration when the methanol dehydrogenation reaction on Pt is sufficiently fast. There is an important analogy among the methanol oxidation and oxygen evolution reactions since both processes require water discharging on the electrode followed by the adsorption of active oxygen species that give rise to a surface reaction with adsorbed methanolic residues, in the case of methanol oxidation, or desorbs as oxygen molecule in the electrolysis mode. Of course these processes occur in a quite different potential window and water displacement at very low potentials, as required for the methanol process, is a quite slow step. In this regard, the addition of oxygen evolution catalysts such as iridium oxide may be beneficial to provide enhanced methanol oxidation activity at lower overpotential. IrO₂ exhibits an excellent corrosion resistance in acidic medium, good electrical conductivity and high electrocatalytic activity toward oxygen evolution [40]. It belongs to platinum group metals (PGM) and is characterized by a high cost (approximately 40% lower than platinum). However, in contrast to other metal oxides mentioned herein that are more economically interesting, IrO₂ presents high electronic conductivity and high resistance in acid media. Chen et al. studied Pt particles electrodeposited on iridium oxide thin film supported on a titanium substrate for the oxidation of methanol. They obtained a potential shift for the methanol oxidation reaction of over 0.2 V when adding iridium oxide to the Ti/Pt electrode, and they correlated it with a low coverage of CO and a significant CO₂ formation at lower

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potentials applying in situ FTIR measurements [41]. Nevertheless, to maximize both platinum and iridium oxide utilization in the catalytic layer, small nanoparticles are required to obtain as high surface area as possible and a good interaction between the different phases involved in the oxidation of methanol. In the present work, an easy method to prepare a composite DMFC anode has been developed. The electrode is composed of an in-house prepared high metal surface area 50 wt% PtRu/C catalyst mixed to an in-house synthesized high surface area IrO₂. This composite electrode was investigated in a direct methanol single cell and compared to a bare one. To address the need of reduction of noble metal amount for cost-effective DMFCs, a Pt loading as low as 0.5 mg cm⁻² in the anode was used in all experiments.

2. Experimental

The in-house made 50 wt% PtRu/C catalyst was prepared as reported in Ref. [42]. Briefly, sulfite complexes of Pt and Ru, in appropriate amounts, were decomposed by hydrogen peroxide to form aqueous colloidal solutions of Pt and Ru oxides. These particles were adsorbed on carbon black to form a PtRuO_x/Vulcan XC-72 catalyst. The amorphous oxides supported on carbon were reduced in a hydrogen stream to form a metallic alloy.

IrO₂ was prepared using, also in this case, the sulfite complex route [40]. Briefly, Ir chloride salt was used to obtain the iridium sulfite complex by reaction with sodium dithionite. Afterwards, the Ir-sulfite complex obtained was decomposed in the presence of H₂O₂ to form a colloidal suspension giving rise to an amorphous oxide after flocculation that was filtered and dried at 80 °C. This amorphous Ir-oxide was subsequently treated in air at 400 °C for one hour.

X-ray diffraction (XRD) powder patterns for these materials were obtained on a Philips X'Pert X-ray diffractometer using a Cu/Kα source operating at 40 kV and 30 mA. The peak profile of the (2 2 0) reflection in the face-centered-cubic (fcc) structure of PtRu alloy was obtained by using the Marquardt algorithm. Instrumental broadening was determined by using a standard platinum sample. X-ray fluorescence (XRF) analysis of the PtRu/C catalysts was carried out with a Bruker AXS S4 Explorer spectrometer operating at a power of 1 kW and equipped with a Rh X-ray source, a LiF 220 crystal analyzer and a 0.128 divergence collimator. The Pt/Ru atomic ratio was determined by using Pt/Lα and Ru/Lα emission lines after appropriate calibration with standard samples. Transmission electron microscopy (TEM) analysis was carried out by first dispersing the catalyst powder in isopropyl alcohol. A few drops of these solutions were deposited on carbon film-coated Cu grids and analyzed with a FEI CM12 microscope.

The electrodes were prepared according to the procedure described in a previous paper [43]. A slurry composed of catalyst and water was mixed under sonication at 60 °C for 30 min. Then, the appropriate amount of IrO₂ was added to the anode slurry during the treatment under sonication at 60 °C and left for another 30 min. Two composite electrodes were prepared, having an IrO₂ content of 20 wt% and 40 wt% with respect to the catalyst (50 wt% PtRu/C) amount. Afterwards, a 15 wt% of Nafion ionomer (5 wt%, Ion Power) with respect to the catalyst was added dropwise to the slurry. The obtained ink was deposited on a commercial GDL from E-TEK (HT-ELAT). An anode electrode without IrO₂ was prepared for comparison using the same procedure. The anodes were prepared with a Pt loading of 0.5 mg cm⁻², whereas Pt black powder (Alfa Aesar) was used for cathode fabrication on a commercial GDL from E-TEK (LT-ELAT) with a Pt loading of 1 mg cm⁻². A Nafion 117 membrane was used as the electrolyte. Membrane-electrode assemblies (MEAs) were formed by hot-pressing the electrodes onto the membrane for 90 s, at 130 °C and 20 kg cm⁻², and subsequently installed

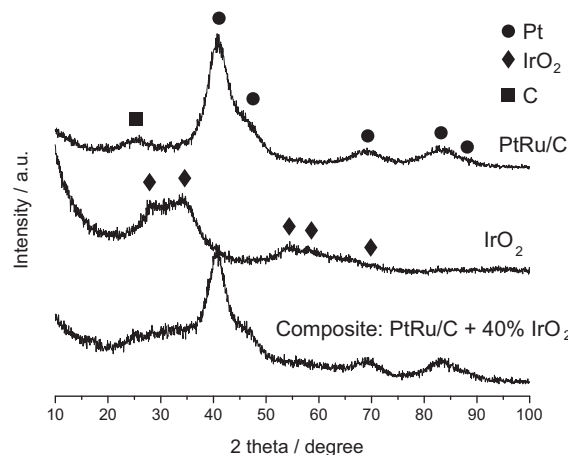


Fig. 1. XRD patterns of the 50 wt% PtRu/C catalyst, the IrO₂ additive and the composite PtRu/C + 40 wt% IrO₂.

in a fuel cell test fixture of 5 cm² active area (Fuel Cell Tech., Inc.). The cell was connected with a DMFC test station from Fuel Cell Tech., Inc., for the single cell polarization measurements. For these experiments, preheated aqueous methanol (2 or 5 M) was fed to the anode chamber of DMFC through a pump; whereas, humidified oxygen was fed to the cathode. Atmospheric pressure was maintained in both compartments for all measurements. Reactant flow rates were 2 and 100 mL min⁻¹ for methanol/water mixture and oxygen stream, respectively. Single cell performances were investigated by steady-state galvanostatic measurements.

3. Results and discussion

3.1. Physico-chemical characterization

Fig. 1 shows the XRD patterns of the 50 wt% PtRu/C catalyst, the IrO₂ additive used for the anode electrode preparation, and the composite ink. PtRu/C sample presents the typical cubic fcc crystallographic structure of Pt and its alloys. A shift toward higher Bragg angles with respect to reference Pt (JCPDS card n° 40-802) is observed in the XRD pattern of the 50 wt% PtRu/C catalyst, indicating that Ru is alloyed within the cubic structure of Pt, as expected for Ru contents below 70 at%. The physico-chemical properties of the 50 wt% PtRu/C catalyst are reported in Table 1. The degree of alloying, calculated according to the relationship described by Garcia et al. [44], was Pt₄₃Ru₅₇, close to the nominal composition (50:50) and to the XRF bulk composition of Pt₄₉Ru₅₁. Moreover, the PtRu crystallite size, determined by the Debye–Scherrer equation and considering the (2 2 0) reflection broadening, was 1.6 nm. This low PtRu crystallite size together with a high alloying degree results in a very high theoretical surface area of 226 m² g⁻¹. The IrO₂ pattern shows the presence of broadened peaks corresponding to the reflection of the tetragonal structure of IrO₂ (JCPDS card n° 15-870), indicating small crystallites. This sample was also characterized by an underlying amorphous matrix. The composite material based on the highest content of IrO₂ is also included in Fig. 1. Notice that the diffractogram of the composite material corresponds to the contribution of the patterns of both PtRu/C and IrO₂, where the IrO₂-related peaks show low intensity because IrO₂ is characterized by fine crystallites in an amorphous matrix.

TEM image of the pure 50 wt% PtRu/C catalyst is reported in Fig. 2a, showing a good coverage of the carbon support by the small PtRu nanoparticles (1.6 nm), well-dispersed on the carbon black particles of about 30 nm size. Whereas, Fig. 2b shows a TEM image of the IrO₂ nanoparticles, with an average size of 2.6 nm. Assuming spherical nanoparticles and a density of IrO₂ of 11.66 g cm⁻³, the

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