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Analysis of performance losses of direct methanol fuel cell with methanol tolerant PtCoRu/C cathode electrode

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ABSTRACT

The long-term stability of PtCoRu/C to methanol crossover has been evaluated in a direct methanol fuel cell (DMFC) configuration. The DMFC has been subjected to continuous operation under potential step cycles. The degradation of the DMFC with PtCoRu/C has been followed by comparison of the power density curves recorded after 0, 60 and 312 h of continuous operation, and compared to that recorded for a DMFC with Pt/C. Electrochemical Impedance Spectra (EIS) were recorded directly from the DMFCs and used to identify the main degradation phenomena responsible for the loss of performance of the used fuel cell. AC impedance spectra show that the resistance of the anode reaction increases while resistance associated to the cathode reaction decreases after the long-term stability tests; however, the analysis of the power density curves unequivocally show that the performance of the DMFCs goes down during the stability tests. This apparent contradiction can be explained by taking into account the changes between the fresh and used PtCoRu/C observed by X-ray diffraction (XRD) and transmission electron microscopy (TEM) analyses. During the potential step cycles Ru dissolves from PtCoRu/C leading to Pt-enriched catalysts which are more active for the oxygen reduction reaction (lower resistance) but less tolerant to methanol (lower power density).

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1. Introduction

Direct methanol fuel cells (DMFCs) are attracting a great deal of attention as power sources for portable devices and small vehicles [1–5]. By using methanol as fuel, DMFCs have a number of advantages over H₂-feed proton exchange

membrane fuel cells (PEMFCs). Methanol has a higher specific energy density than hydrogen and it is easier to store, transport and handle than H₂ [6]. However, important issues such as the slow kinetics of the methanol electrooxidation reaction (MOR) and methanol crossover through Nafion® membranes toward the cathode are compromising widespread

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commercialization of DMFCs [7]. In order to minimize the latter issue, efforts are mainly focused in two directions. On the one hand, the development of low methanol permeability membranes is expected to decrease the methanol crossover effect [8,9]. On the other hand, from a catalytically point of view, efforts are focused on the description of catalysts that do not absorb methanol while maintaining a high ability for catalyzing the oxygen reduction reaction (ORR) under the operation conditions of DMFCs [10,11].

Recently, we have shown that modifying Pt/C with both Co and Ru results in methanol tolerant catalysts for the ORR [12]. Carbon supported PtRu bimetallic particles are benchmark catalysts for the electrooxidation of CO and methanol [13,14], but their performance for the ORR is rather poor. However, the actual behavior of Ru is severely affected by the working environment. The remarkable performance of PtCoRu/C for the ORR in the presence of methanol accounts to the presence of Co and upper oxide Ru species [12]. On the one hand, it is well known that the performance of Pt/C for the ORR improves with the addition of Co [15]. On the other hand, such upper oxide Ru species, which are stable under ORR working conditions (potentials more positive than 0.7 V and O₂ saturated atmosphere), impede methanol adsorption on PtCoRu/C. Under these conditions, PtCoRu/C does not adsorb methanol and the ORR proceeds similarly as if PtCo/C was used in a methanol-free environment. Hitherto, the performance and stability of PtCoRu/C on a direct methanol fuel has not been studied.

Durability studies are necessary previous to commercialization of DMFCs. These studies are impractical at the laboratory scale since they require long-term operation in the range of several thousands of hours [16–20]. Therefore, accelerated stress tests (AST) have been designed to assess durability of fuel cells and to identify the main degradation patterns of the components of fuel cells [21–24]. Most of those studies focused on the effects of long-term operation for the degradation of the membrane, the gas diffusion layer, the bipolar plate or the anode catalyst. The effect of methanol crossover on the cathode catalyst has been scarcely studied in long-term analysis in DMFCs [25]. Power density losses or voltage degradation are the main parameters observed to identify fuel cell evolution during stability analysis. However, in order to pinpoint the causes of the degradation of individual components of fuel cells requires the use of EIS on the fuel cell [26–30]. EIS is a powerful diagnosis tool to identify and quantify the weight of individual contributions to the processes occurring during the operation of fuel cells and to monitor the variations of their magnitudes during long-term operation. Mueller et al. [26] have demonstrated the use of EIS under realistic operating conditions of DMFCs to identify the process taking place in the cell. EIS analysis allows the separate evaluation of anode kinetics and mass transport, cathode kinetics and mass transport and contributions from membrane conductivity.

This paper presents a thorough study of the degradation of PtCoRu/C cathode catalyst during short- and long-term operations in a DMFC single cell. PtCoRu/C is a very active electrocatalyst for the oxygen reduction reaction (ORR) in the presence of methanol as demonstrated by linear sweep voltammetry analysis. The life analyses of DMFC single cells

with PtCoRu/C or Pt/C as cathode catalysts and PtRu/C as anode ones have been studied at 400 mV (short-term analysis) or in a continuous potential cycling between 0.7 V and 0.3 V for 20 s during 312 h (long-term analysis). The degradation of the DMFC single cells is clearly observed from the polarization and power density curves recorded after the durability tests. The contribution of the methanol oxidation reaction, CO_{ad} adsorption/desorption, anodic reaction, membrane (IR) resistance and ORR to the performance of the DMFCs has been evaluated by EIS. All of the above magnitudes increased with the severity and duration of the life analysis of the DMFC single cell, except for the resistance of the ORR process. These features suggest that the PtCoRu/C becomes more active to the ORR but less tolerant to methanol during the durability tests. XRD and TEM *ex situ* analyses of the fresh and used PtCoRu/C catalyst reveal an increasing in the particle size of the cathode catalyst and that Ru dissolves from the PtCoRu/C after long-term analysis.

2. Experimental

2.1. Synthesis of PtCoRu/C

Carbon supported PtCoRu nanoparticles have been synthesized by the polyol method. Briefly, an ethylene glycol (EG) solution of the metal precursors (H₂PtCl₆, RuCl₃ and CoCl₂) was added dropwise to a dispersion of the carbonaceous support (Vulcan XC 72R) in EG under stirring. The resulting mixture was stirred for 3 h. Afterward, a solution of NaOH (2.5 M in EG) was added to adjust the pH to 13. The total amount of water was of 5 vol%. The solution was refluxed at 140 °C for 3 h under flowing N₂ to ensure the total reduction of the metallic precursors. Finally, the obtained solid was thoroughly rinsed with water and dried at 70 °C for 8 h and labeled as PtCoRu/C.

2.2. Physicochemical characterization

A 200 kV transmission electron microscope JEM 2100-F (Jeol Ltd.) was used for TEM analyses. Energy-Dispersive X-Ray Spectroscopy (EDS) were performed with an Oxford INCA-Sight detector coupled to the microscope and the spectra were analyzed with an INCA Energy software package. Specimens were dispersed in ethanol in an ultrasonic bath and few drops were deposited over a 200 mesh copper lacy carbon grid from SPI. X-ray diffraction (XRD) patterns were recorded using an X-ray diffractometer from X'Pert Pro PANalytical. Bragg's angles (2θ) between 10° and 90° were recorded at 0.02 s⁻¹ and a count time of 20 s per step. The assignment of the diffraction lines to the corresponding crystalline phases was carried out by comparison with Powder Diffraction Files (PDF) from the International Centre for Diffraction Data (ICDD) (a.k.a.) Joint Committee on Powder Diffraction Standards (JCPDS). An Extra-II TXRF spectrometer (Rich & Seifert) was used to estimate the metal loading of the samples.

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