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Searching for suitable catalysts for a passive direct methanol fuel cell cathode

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ABSTRACT

Trimetallic PtMRu/C cathode catalysts with M = Co or Fe obtained by an impregnation procedure using ethylene glycol and NaBH₄ as reducing agent, with suitable activity for the oxygen reduction reaction (ORR) and improved tolerance to methanol, have been physically characterized by HRTEM, EDS and XPS. The examined nanoparticles have a small particle size and are well spread on the carbon support. Pt is mainly found as Pt(0) and Co, Fe and Ru are mostly oxidized. To study their durability and performance for ORR and methanol tolerance over time, the catalysts were subjected to an electrochemical accelerated stress test (AST), consisting in cycling the potential 2000 times. Polarization curves for ORR with and without methanol were recorded. After the AST the trimetallic PtMRu/C catalysts are able to keep their performance for ORR in the presence of methanol.

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Introduction

Proton exchange membrane fuel cells (PEMFCs) are promising electrochemical devices that convert the fuel-chemical energy into electrical energy in a clean and efficient way. Among PEMFCs, direct methanol fuel cells (DMFCs) have become increasingly attractive because they utilize a liquid fuel at the anode that has high density energy and is easy to handle,

store and transport. In portable applications, passive DMFCs are one of the most prospective power sources [1–3].

In passive DMFCs, methanol, water and oxygen are passively supplied from the methanol container and from the air to the membrane electrode assembly (MEA) by capillary forces, gravity and concentration gradients thus, making it unnecessary to use auxiliary components, which consume part of the energy generated, for feeding reagents to the cell. Passive DMFCs require the use of high alcohol concentration to feed the anode. Consequently, a technical obstacle to

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overcome in these devices is methanol crossover, a phenomenon in which methanol diffuses from the anode to the cathode through the Nafion[®] membrane dragged by water because of the miscibility between methanol and water [1,4]. The crossover of methanol causes a considerable loss of fuel cell efficiency, since both the oxygen reduction reaction (ORR) and the methanol oxidation reaction (MOR) occur simultaneously on the cathode. Pt is the most widely employed cathode catalyst for the ORR, though its catalytic activity towards the oxygen reduction reaction is still insufficient [5].

One approach to solving the alcohol crossover issue in DMFCs consists in the substitution of Pt by a catalyst with high activity for the ORR and low activity for the MOR [6]. Many attempts to improve the cathode performance for the ORR, such as the employment of Pt-based catalysts with transition metals that change Pt oxophilicity and electron availability, have been successfully made [5,7–10]. Despite the amount of research carried out to establish the role of co-catalysts in the kinetic improvement of ORR, no definitive conclusion has been reached yet [11]. One of the difficulties to determine the effect of transition metals on ORR improvement is that the activity of a supported catalyst has a wide range of values depending on its microstructure and preparation procedure [4,12–15]. It has been claimed that a selective dissolution of the less-noble component from the nanoparticles (NPs) typically results in either the formation of coreshell structures or porous noble-metal-rich NPs with higher catalytic activity for ORR [16]. Summarizing, the intrinsic activity of NPs depends on their particle size, shape, composition, etc. [15,17].

In our previous works related to the search of a methanol-tolerant cathode catalyst for DMFCs, we built bimetallic PtCo/C and PtFe/C catalysts with a noteworthy performance for ORR, and trimetallic PtCoRu/C and PtFeRu/C catalysts that were also methanol-tolerant [18,19]. To obtain suitable cathode catalysts for passive DMFCs, it is important that the catalysts keep their electrochemical performance for ORR and their methanol-tolerance ability not only initially but over time. Therefore, once a suitable cathode catalyst with high methanol tolerance is obtained, long-time durability tests are required [20–22].

The aim of this work is to study the durability and performance of PtCoRu/C and PtFeRu/C synthesized methanol-tolerant cathode catalysts employing electrochemical accelerated stress tests (AST) to examine their catalytic behavior and methanol-tolerance decrease over time, prior to their widespread use in passive DMFCs.

Experimental

Catalyst preparation

Methanol-tolerant cathodes with suitable activity for ORR, i.e., PtMRu/C catalysts, with M = Co or Fe, were prepared by an impregnation method (IM) via seed-mediated growth, employing ethylene glycol and NaBH₄ as reducing agent; a more detailed description of the methodology is found in Refs. [23,19]. Briefly, in the IM procedure, H₂PtCl₆, MCl_x (M = Fe and Co), RuCl₃ and functionalized carbon support (Vulcan[®] XC-72R) were dissolved separately in ethylene glycol and ultrasonicated under N₂ flow during the whole synthesis

procedure. Then, the pH was changed to 10 by adding NH₄OH and subsequently, a small volume of the Pt precursor and 0.1 M NaBH₄ solution were added to form Pt seeds. After a few minutes, the remaining precursor and NaBH₄ solutions were added with further stirring for 2 h. The solid obtained by vacuum filtering was thoroughly washed and dried at 70 °C. The catalysts are denoted as PtMRu/C IM.

In this paper, a homemade PtCo/C catalyst that showed an outstanding behavior for ORR [18] is taken as comparison catalyst. We previously obtained the catalyst by a slightly modified impregnation method with a thermal treatment in a reducing atmosphere [24].

Characterization

The distribution and size particles of the supported catalysts were examined by a Tecnai F20 G2 high resolution transmission electron microscope (HRTEM), their bulk compositions by energy-dispersive X-ray spectroscopy (EDS), and the surface composition and chemical state of the active components by X-ray photoelectron spectroscopy (XPS).

Catalysts activity and durability evaluations

The electrochemical characterization of the synthesized catalysts was performed using a standard three-electrode electrochemical cell. A rotating disk electrode (RDE) of glassy carbon (0.071 cm² geometric area) covered with a thin layer of catalyst powder, attached by a 0.1 μm Nafion[®] thin film, was used as working electrode. The catalyst loading on the RDE was adjusted to 28 μg_{Pt} cm⁻² therefore, the quantity of catalyst on the electrode was around 5 μg. A Pt foil of 1 cm² geometric area was used as counterelectrode and a saturated calomel electrode (SCE) as reference electrode. In this work, all potentials are referred to that of the reversible hydrogen electrode (RHE). The active area of Pt in cm²_{Pt} was obtained from the CO stripping assuming 420 μCcm⁻² for one monolayer oxidation of adsorbed carbon monoxide.

The working solution was an O₂-saturated 0.5 M H₂SO₄ solution with or without CH₃OH. Though different alcohol concentrations were employed, the polarization curves are shown with 0.1 M CH₃OH. The electrochemical experiments were conducted at room temperature. Previous to ORR experiments, the potential of a fresh working electrode was cycled at a rate of 0.1 Vs⁻¹ in a N₂-purged 0.5 M H₂SO₄ solution between 0.05 V and 0.8 V, until a stable voltammetric profile was attained. The polarization curves for ORR were recorded starting from the open circuit potential value up to 0.05 V at a scan rate of 0.005 Vs⁻¹ and a disk rotation rate ω = 2000 rpm. The current densities of the polarization curves shown were calculated taking into account the geometric area of the electrode.

Degradation of the catalysts was evaluated by cycling the electrode potential 2000 times between 0.05 and 0.8 V at 0.05 Vs⁻¹ under N₂ bubbling [25]. In addition, polarization curves for ORR before and after AST were recorded with and without CH₃OH.

The onset potential for the ORR, at which the current for oxygen reduction is first observed, was determined by the point of intersection of two lines, one drawn extending the

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