Pt-Ru CATALYSTS SUPPORTED ON MESOPOROUS CARBONS FOR POLYMER ELECTROLYTE MEMBRANE FUEL CELLS

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Abstract

Pt-Ru electrocatalysts supported on xerogels and CMK-3 ordered mesoporous carbons were synthesized by reduction with formate ions (SFM method). Some of the carbon supports were chemically treated with HNO_3 in order to generate oxygen groups on the surface, while other supports were heat treated. Physical characterization of the catalyst was obtained using X-ray dispersive energy (EDX) and X-ray diffraction (XRD) techniques. Results showed that Pt-Ru catalysts with similar metal content (20%) and atomic ratios (Pt:Ru 1:1) were obtained. The electrochemical activity was studied by cyclic voltammetry and chronoamperometry. Higher methanol oxidation current densities were found for catalyst deposited on chemically treated supports. Electrode preparation and MEA assembly allowed an in-house built direct methanol fuel to be fitted with the synthesized catalysts and supports in order to assess their performance. Cell and reactants were conditioned by a direct methanol test station. Polarisation curves were measured and confirmed data obtained by voltammetry, regarding the effect of heat treatment of the carbon support. Normalised power curves per weight of catalyst are discussed in terms of the significant impact on noble metal loading and attained cell maximum power, in comparison with results obtained with a commercial catalyst.

Keywords: carbon xerogels, CMK-3 ordered mesoporous carbons, Pt-Ru electrocatalysts, polymer electrolyte membrane fuel cells

1. Introduction

Anodic catalysts for polymer electrolyte membrane fuel cells (PEMFC) are conformed by Pt-Ru nanoparticles supported on carbon black, usually Vulcan XC-72 [1]. Recent works have shown that other types of carbon materials, such as nanofibers nanotubes, aerogels, and mesoporous carbons xerogels can improve the efficiencies of the catalysts, when used as supports [1-3]. However, the causes for such efficiency enhancement have not yet been fully determined, although it is thought that these supports can increase the dispersion of the metal, decrease the formation of nanoparticle agglomerates and improve the conductivity and the diffusion of electrochemical species.

There are different methods of reduction of metal precursors for supported catalyst nanoparticles, such as the reduction by sodium borohydride (BM) or formic acid (FAM). In particular, the method FAM does not completely reduce the Ru precursor salt, due to the low dissociation constant of formic acid (1.8 x 10-5) and the pH dependence of the reduction potential of Ru.

In this study we have used a modified FAM method for the synthesis of Pt-Ru nanoparticles on functionalized carbon, where the pH of the reaction medium was increased to 12, to ensure complete dissociation of acid formic into formate ions – intermediate species which act as reducing agent (formate ion method-SFM) [4].

Synthesized catalysts were analyzed by different techniques to study their physicochemical properties. In addition, we analyzed their activities for the electrooxidation of CO and methanol using cyclic voltammetry and chronoamperometry.

Finally, synthesized catalysts were tested in a single direct methanol fuel cell, in order to assess catalyst performance and cell power densities using catalyst supported on functionalized carbons.

2. Experimental

Mesoporous carbon materials prepared as support for Pt-Ru catalysts were carbon xerogel (CX) and ordered mesoporous carbon (CMK-3).

The xerogel was synthesized by the sol-gel method, from resorcinol and formaldehyde, followed by drying and carbonization (CXUA). pH was adjusted in order to obtain the required diameter of mesopores [5]. Samples were functionalized with 7 M nitric acid in a Soxhlet for 3 h (CXNA). Additional samples were prepared by heat treatment at different temperatures: 30 min at 400 (CXNA400), 600 (CXNA600) and 750 ºC (CXNA750).

CMK-3 materials were obtained by incipient impregnation method using an ordered mesoporous silica as a template and a furan resin as carbon precursor [6]. The impregnated silica was carbonized at 700 °C for 2 h and subsequently the silica-carbon composite was subjected to washing with NaOH + ethanol to remove silica. Then, these carbons were functionalized by treatment with either diluted or concentrated nitric acid for 0.5 h.

Carbon materials used as catalysts supports were analyzed by different techniques to study their physicochemical properties.

Both carbon materials were used to prepare Pt-Ru catalysts with a nominal metal loading of 20% and an atomic ratio Pt:Ru of 1:1, using the method of reduction with formate ions. Briefly, the carbon materials were dispersed in a 2.0 M HCOOH solution under sonication. The pH of the HCOOH solution was previously adjusted to 12.0. The mixture was then heated at 80 ºC and the metal salts solution was slowly added under stirring. The temperature was kept constant during the addition of metal salts solution, and subsequently for one hour. The reaction medium was kept under stirring for 12 h, and finally the mixture was filtered, washed and dried at 60 ºC for 2 h.

The catalysts were characterized physicochemically by X-ray techniques (energy dispersive X-ray EDX, X-ray diffraction XRD) in order to determine the crystallite size, degree of alloying and its composition, and electrochemically (cyclic voltammetry, Tafel plot and chronoamperometry) to determine the electroactive area and the reactivity of the catalysts towards CO and methanol oxidation.

Electrodes used to prepare membrane electrode assemblies (MEAs) consist of a diffusion layer and a catalyst layer. The gas diffusion layers were prepared from carbon black Vulcan XC-72 R for the anodes and the cathodes. Pt-Ru catalysts were used as anodes and 10 wt. % Pt/C catalyst were used as cathodes. To fabricate the catalyst layer, an ink was prepared by suspending the material in isopropanol, and stirring in an ultrasonic bath for 10 min to thoroughly wet and disperse it. A 5 % Nafion® dispersion solution (Electrochem, Inc) was then added to the mixture. The catalyst inks were dispersed onto the gas diffusion layer with a brush, and dried at 50 °C, until a catalyst loading of 4 mg cm^{-2} was achieved. Nafion® 117 membranes were cleaned and converted into the acid form by boiling in 3 % H_2O_2 for 1 h, followed by boiling in 0.5 M H_2SO_4 for 2 h. Between these treatments, the membranes were washed with boiling water for 30 minutes. The cleaned membranes were stored in ultrapure water, and dried before use. Each MEA was assembled by hot-pressing the prepared anode and cathode on either side of the pretreated membrane at 50 bar, 130 °C for 180 s.

The MEAs were mounted into an in-house built direct methanol fuel cell hardware. A single cell configuration was used with 25 cm^2 of active area and a single serpentine flow field design drawn on graphite plates. A test station allowed conditioning of the cell and reactants at temperatures up to 70ºC for activation and polarisation curve recording. Single cells were operated with a 0.75 M aqueous CH_3OH solution pumped through the anode compartment at 1.5 mL min^{-1}. O_2 was fed through the cathode compartment at 0.3 L min^{-1}. After the preconditioning procedure of the MEA described in ref. [7], polarization curves were measured.

3. Results

Carbon xerogel showed a mesoporous morphology (average diameter pore size = 16.5 nm) with surface areas in the range 632-754 m^{2}g^{-1}. Surface chemistry

was found to depend on the chemical treatment used.

In contrast, CMK-3 materials presented an ordered structure, with carbon rods of uniform size arranged in the same direction, leaving mesopores between them, generating higher surface area (1163 m^2g^{-1}) and a large pore volume (0.81 cm^3g^{-1}). Pore size distribution was close to 3 nm.

Pt-Ru catalysts on all materials presented atomic ratios of Pt: Ru and metal content close to 1:1 and 20% respectively. XRD patterns of the synthesized catalysts are shown in Figure 1.

All of them showed the characteristic peaks, (111), (200), (220) and (311), of the face centered cubic (fcc) structure of Pt. Moreover, all of them showed a diffraction feature around 24.5º which corresponds to the (002) reflection of graphite basal planes which is attributed to the catalyst support.
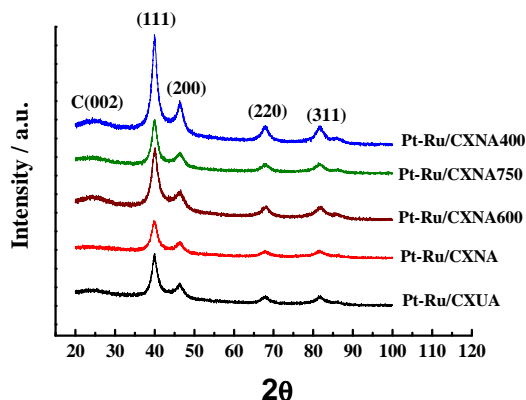

Fig. 1 XRD diffractograms for Pt-Ru catalysts.

Table 1 summarizes the results including particle size and lattice parameters.

Table 1 Composition, particle size and lattice parameters for Pt-Ru catalysts

Support/catalyst synthesis method	Pt-Ru (EDX)	Metal loading (% wt.)	Particle size (nm)	Lattice parameter (Å)
CXUA/SFM	58-42	21	4.3	3.904
CXNA/SFM	55-45	19	4.1	3.913
CXNA400/SFM	55-45	20	4.6	3.906
CXNA600/SFM	49-51	18	3.6	3.902
CXNA750/SFM	55-45	20	4.0	3.900
CMK-3/SFM	55-45	20	3.8	3.914
CMK-3 Nd05/SFM	55-45	19	2.9	3.902
CMK-3 Nc05/BM	57-43	19	2.9	3.913

It was found that both the nature and treatment of the support have an influence on the morphological, physicochemical and electrochemical properties of materials prepared.

Figure 2 also shows that the chemically treated support delivers a higher current density for methanol oxidation than the heat treated samples.
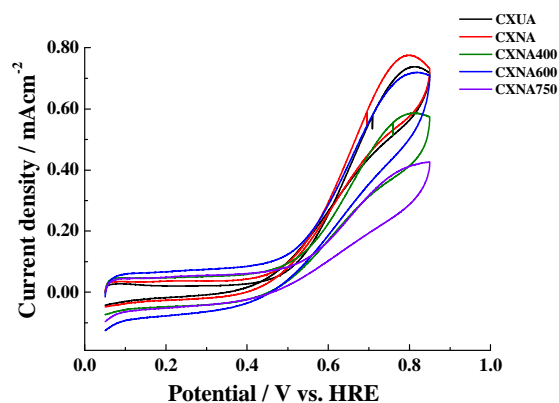

Fig. 2. Cyclic voltammograms for methanol oxidation on Pt-Ru/C (xerogels) catalysts. Scan rate: 20 mVs^{-1}. Supporting electrolyte: 0.5 M H_2SO_4. Methanol concentration: 2.0 M.

This fact was confirmed by the tests conducted in a single direct methanol fuel cell. Power densities for the synthesized catalysts diminished with the increase of the temperature of the thermal treatment of the carbon, see figure3.
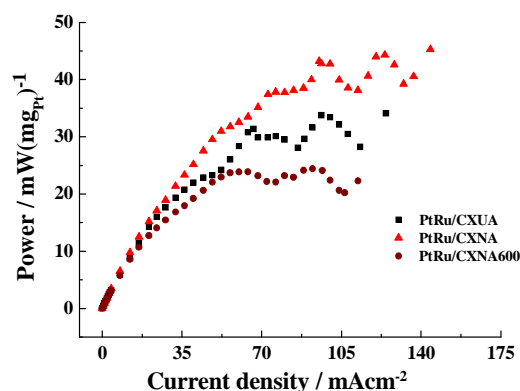

Fig.3. Normalized power densities per weight of catalyst vs. current density for single cell DMFC at 70 ºC, for some of the catalysts supported on xerogels.

Comparison with a commercial catalyst confirmed the significant impact of the use of functionalized carbons in the performance of the Pt-Ru catalysts, evident in the whole range of temperature studied, from 20 to 70ºC. Furthermore, it is to be noticed that results were obtained for a relatively low oxygen flow rate, 0.3 mL.min^{-1}.

Results regarding CMK-3 materials will be also discussed.

Acknowledgements

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