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<b>Title:</b>	INFLUENCE OF THE SUPPORT CHARACTERISTICS AND THEIR FUNCTIONALIZATION ON THE CATALYTIC ACTIVITY OF Pt-Ru CATALYSTS FOR PEM FUEL CELLS				
<b>Presenting author:</b>	Juan Carlos Calderón Gómez	<b>Under 30 y.o.?</b>	NO	<b>Presentation in English?</b>	NO

**EXPECTED CLASSIFICATION:** (please, mark all the options that better define the research performed)

MAIN SESSION	
X	PEM fuel cells
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	Hydrogen
	Other

SUB-CLASSIFICATION	
	Numerical simulation
X	New materials
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# Influence of the support characteristics and their functionalization on the catalytic activity of Pt-Ru catalysts for PEM fuel cells

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## 1 Introduction

Carbon black, usually Vulcan XC-72, is the most typical carbon support for anodic catalysts in the polymer electrolyte membrane fuel cells (PEMFC) [1]. However, recent works have shown that other types of carbon materials, such as nanofibers nanotubes, aerogels, and mesoporous carbons can improve the efficiencies of the catalysts, when used as supports [1-3]. 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. With respect to the interaction between the carbon support and the catalytic particle, some authors have reported the existence of other effects, principally related with the metal-support interaction, which increases the electronic density on catalytic particles by a donor effect of the carbon support [4-5]. Nevertheless, the rise in electron density can be significant only if particle size of the microdeposit (platinum) is comparable to the thickness of the double layer between the nanoparticle and the carbon support [7]. The specific metal-support interaction is through electron transfer from platinum clusters to oxygen groups present on the surface of the support. This interaction is considered to be beneficial to the enhancement of catalytic properties and to improve stability of the electrocatalyst [7].

Carbon xerogels can be used as carbon supports, bearing in mind their mesoporous and macroporous textures and large pore volumes. These supports possess excellent characteristics like others carbon supports, such as high porosity,

high surface area, controllable pore size, and different form (monolith, thin film, or powder), depending of the desired utility [8]. On the other hand, ordered mesoporous carbons have recently received great attention because of their potential use as catalytic supports in fuel cell electrodes. They have controllable pore sizes, high surface areas and large pore volumes [8]. Nanoporous carbons with 3D ordered pore structures have been shown to improve the mass transport of reactants and products during fuel cell operation [6].

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 FAM method does not completely reduce the Ru precursor salt, due to the low dissociation constant of formic acid ( $1.8 \times 10^{-5}$ ) 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 xerogels and ordered mesoporous carbons, 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) [9]. For the physical characterization of synthesized catalysts, X-ray and (EDX, XRD) and microcopic (TEM) techniques were used. In addition, electrochemical activity of these materials, towards CO and methanol electrooxidation was studied by cyclic voltammetry and chronoamperometry. Finally, synthesized catalysts were tested in a direct methanol fuel monocell, in order to assess catalyst performance and cell power densities using catalyst supported on functionalized carbons.

## 2 Experimental

### 2.1 Carbon supports synthesis

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 mesopore diameter [8]. 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 °C (CXNA750). CMK-3 materials were obtained by incipient impregnation method using 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.

### 2.2 Synthesis of Pt-Ru catalysts

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 [9]. 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 °C 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 °C for 2 h.

### 2.3 Physical and electrochemical characterization

The catalysts were characterized physico-chemically 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 their activity towards CO and methanol oxidation.

### 2.4 Direct methanol fuel monocell tests

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<sup>®</sup> 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 mgcm<sup>-2</sup> was achieved. Nafion<sup>®</sup> 117 membranes were cleaned and converted into the acid form by boiling in 3 % H<sub>2</sub>O<sub>2</sub> for 1 h, followed by boiling in 0.5 M H<sub>2</sub>SO<sub>4</sub> for 2 h. Between these treatments, the membranes were washed with boiling water for 0.5 h. 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 each side of the pretreated membrane at 50 bar and 130 °C for 180 s. The MEAs were mounted into an in-house built direct methanol fuel monocell hardware. A single cell configuration was used with 25 cm<sup>2</sup> 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 70 °C for activation and polarisation curve recording. Monocells were operated with a 0.75 M CH<sub>3</sub>OH solution pumped through the anode compartment at 1.5 mL min<sup>-1</sup>. O<sub>2</sub> was fed through the cathode compartment at 0.3 L min<sup>-1</sup>. After the preconditioning procedure of the MEA described in ref. [10], polarization curves were measured.

## 3 Results

### 3.1 Carbon supports characterization

Carbon xerogel showed a mesoporous morphology (average diameter pore size = 16.5 nm) with surface areas in the range 632-754 m<sup>2</sup>g<sup>-1</sup>. Surface chemistry was found to depend on the chemical treatment used. Pore radius distribution for carbon xerogels was near to 8 nm (Fig. 1).

In contrast, CMK-3 ordered mesoporous carbons 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<sup>2</sup>g<sup>-1</sup>) and a large pore volume (0.81 cm<sup>3</sup>g<sup>-1</sup>). Pore radius distribution for these materials was close to 3 nm.

### 3.2 Physical characterization of synthesized Pt-Ru catalysts

Pt-Ru catalysts presented atomic ratios of Pt:Ru and metal content close to 1:1 and 20% respectively. XRD patterns of the synthesized catalysts on carbon xerogels are given in Fig. 2. All of them showed the characteristic peaks, (111), (200), (220) and (311), of the face centered cubic (fcc) structure of Pt, and a diffraction feature around 24.5° which corresponds to the (002) reflection of graphite basal planes attributed to the catalyst support. Table 1 summarizes the results including particle size and lattice parameters for electrocatalysts prepared on both carbon supports.

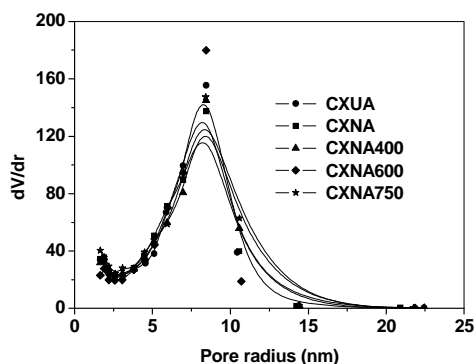


Fig. 1. Pore radius distribution for carbon xerogels

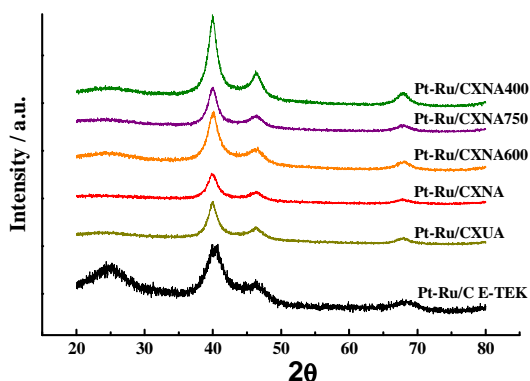


Fig. 2. XRD for synthesized Pt-Ru catalysts on carbon xerogels

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

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

### 3.3 Electrochemical characterization of Pt-Ru catalysts

Nature and treatment of the support have an influence on the morphological, physicochemical and

electrochemical properties of catalysts synthesized. Fig. 3 shows that the catalyst prepared with the chemically treated xerogel delivers higher current density during methanol oxidation than the heat treated samples. On the other hand, the increase in the severity of the heating treatment is accompanied with a decrease in the oxidation activity of the materials.

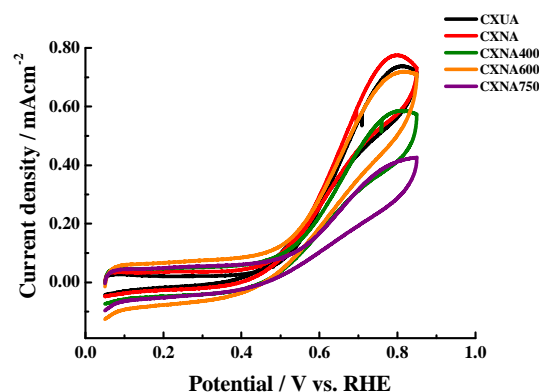


Fig. 3. Cyclic voltammograms for methanol oxidation on Pt-Ru/C (xerogels) catalysts. Scan rate: 20 mVs<sup>-1</sup>. Supporting electrolyte: 0.5 M H<sub>2</sub>SO<sub>4</sub>. Methanol concentration: 2.0 M.

### 3.4 Electrochemical characterization of Pt-Ru catalysts

Results from electrochemical characterization were confirmed by the tests conducted in a direct methanol fuel monocell. Power densities for the synthesized catalysts diminished with the increase of the temperature of the thermal treatment of the xerogel (Fig. 4). In the case of CMK-3 materials, low power densities were achieved in all cases probably due to the low conductivity showed by these carbons.

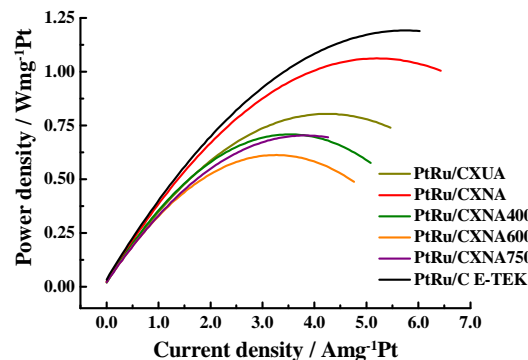


Fig. 4. Normalized power density per Pt weight vs. current density obtained in a single DMFC at 70 °C, for the Pt-Ru catalysts supported on xerogels.

## 4 Discussion

From data in Table 1, it can be concluded that Pt-Ru catalysts supported on carbon xerogels and CMK-3 ordered mesoporous carbons were obtained with metal loading and atomic Pt:Ru proportions close to nominal values (20% and 1:1, re-

spectively). Moreover, from the lattice parameters the formation of alloyed Pt-Ru nanoparticles is confirmed, with crystallite sizes between 2.9 and 4.6 nm.

Electrochemical behaviour of the catalysts after the chemical and heating treatments can be understood considering the number of oxygenated groups in the carbon supporting material as consequence of these procedures.

In the case of the xerogels, it is evident that the CXNA is the material with the major quantity of oxygenated groups, due to the chemical treatment and the absence of heat treatment for this material. When increasing the temperature, part of the carbon with the oxygenated groups is oxidized and lost, and in this way, the number of these available on the carbon surface decreases. Oxygenated groups seem to be involved in the oxidation of methanol and, accordingly, the currents decrease with increasing the temperature of the experimental procedure applied to the support.

Results obtained for Pt-Ru electrocatalysts prepared on CMK-3 materials confirm the positive effect of chemical pre-treatment on the currents obtained during methanol electrooxidation.

## 5 Conclusions

Two different mesoporous carbons were synthesized: carbón xerogels and CMK-3 ordered mesoporous carbons. These materials were heat and chemically treated and used as support for Pt-Ru electrocatalysts for CO and methanol electrooxidation. Experimental data allowed to establish a relation between the nature of the support and its chemical and/or heat treatment, and the morphological, physical and electrochemical properties of the synthesized Pt-Ru catalysts. Moreover, efficiencies obtained in direct methanol fuel monoreactor demonstrate that it is possible to design the support treatment to convert these electrocatalysts in good candidates for using them as anodes in a PEM fuel cell.

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