

Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

SciVerse ScienceDirect

journal homepage: [www.elsevier.com/locate/ije](http://www.elsevier.com/locate/ije)

## Macroporous carbon as support for PtRu catalysts



Angélica M. Baena-Moncada<sup>a</sup>, Rusbel Coneo-Rodríguez<sup>a</sup>,  
 Juan C. Calderón<sup>b</sup>, Jonathan Flórez-Montaño<sup>b</sup>, Cesar A. Barbero<sup>a</sup>,  
 Gabriel A. Planes<sup>a</sup>, José L. Rodríguez<sup>b</sup>, Elena Pastor<sup>b,\*</sup>

<sup>a</sup> Universidad Nacional de Río Cuarto, Ruta Nac. 36, Km. 601, X5804BYA Río Cuarto, Argentina

<sup>b</sup> Departamento de Química Física, Instituto de Materiales y Nanotecnología, Universidad de La Laguna, Avenida Astrofísico F. Sánchez S/N, 38071 La Laguna, Tenerife, Spain

### ARTICLE INFO

#### Article history:

Received 10 April 2013

Received in revised form

17 June 2013

Accepted 18 June 2013

Available online 20 July 2013

#### Keywords:

Macroporous porous carbon

Direct methanol fuel cells

Methanol electro-oxidation

PtRu electrocatalysts

Differential electrochemical mass spectrometry

### ABSTRACT

A high surface macroporous porous carbon (MPC) has been obtained by SiO<sub>2</sub> nanoparticles template and further used as support for PtRu catalysts. MPC supported PtRu materials show an enhanced activity for methanol electrooxidation when compared with commercial catalysts. This observation is discussed in terms of reactant accessibility to active sites. The improved diffusion through the porous matrix influences not only methanol feeding, but also removal of reaction subproducts, as clearly shown by differential electrochemical mass spectrometry (DEMS).

Copyright © 2013, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

## 1. Introduction

An efficient metal utilization in direct methanol fuel cell (DMFC) anodes requires a high dispersion of small metal nanoparticles (NP) over the surface of a conductive material. In the practice, this situation results in a high porous matrix composed by the supporting material and the catalyst. Far away from an ideal situation, the access to electrocatalyst active sites is partially hindered (or blocked) by the support, affecting severely the mass transfer rate. This effect acts in detriment of anode performance. Therefore, some transport conditions must be fulfilled by the support: it should provide appropriated fuel access to metal active sites, followed by adequate elimination of reaction products.

On the other hand, it has been shown that the morphology of the electrode material determines the performance of catalysts used in DMFC [1–5]. The dependence of the reaction mechanism (i.e. the occurrence of alternative pathways) on the mass transfer phenomena was clearly established by Z. Jusys et al. [6]. These authors demonstrated that electrochemical efficiencies, product distribution and turnover frequencies (TOF) of reactions occurring during the methanol electrooxidation (formation of formaldehyde, formic acid and CO<sub>2</sub>), depend strongly on the catalyst loading.

Recently, we have studied the methanol oxidation on mesoporous Pt (MPPt) applying thin-layer flow-cell differential electrochemical mass spectrometry (TLFC-DEMS) [5]. It was concluded that, under restricted diffusion of the soluble

\* Corresponding author. Tel.: +34 679437939; fax: +34 922318033.

E-mail address: [epastor@ull.es](mailto:epastor@ull.es) (E. Pastor).

methanol electrooxidation products (i.e. formic acid and formaldehyde), as occurs in real carbon supported catalysts, these species can interact again with the catalytic surface and readsorb, increasing the CO<sub>2</sub> efficiency. However, in these conditions the current density diminishes noticeably.

Like metals [4], carbon-based porous support can be specifically designed for the improvement of mass transport. With this purpose, the electrodes must have an interconnected porous matrix, with the porous dimension adjusted at a point between two divergent trends: the highest surface area and the larger pore size.

In the present paper, a macroporous carbon (MPC) obtained by SiO<sub>2</sub> template is used as support for PtRu nanoparticles. These NP are attached on the MPC surface via chemical reduction of a mixture of Pt<sup>+4</sup>/Ru<sup>+3</sup> by the formate ions method (SFM method [7]). The catalysts activity towards methanol electrooxidation is tested by cyclic voltammetry, chronoamperometry and TLFC-DEMS techniques.

## 2. Experimental

### 2.1. SiO<sub>2</sub> template, carbon support and catalysts: synthesis and characterization

The synthesis of the mesoporous carbon was recently described [8]. Briefly, SiO<sub>2</sub> NP of 400 nm in diameter were synthesized by TEOS hydrolysis in basic media [9] and further used as molds. With this purpose, SiO<sub>2</sub> NP were deposited by vertical sedimentation in the bottom of a vial [10]. After solvent evaporation, the resulting opal was expelled out of the vial and then treated at 600 °C or 1000 °C (sample K and I, respectively) for 4 h to form a connected opal. Those opals were later impregnated with the carbon precursor: a mixture of resorcinol (1 g), formaldehyde (1.6 mL) and sodium carbonate (0.4 mL 0.1 M). The resin-SiO<sub>2</sub> compound was dried in oven (105 °C) and then pyrolyzed at 850 °C in the absence of O<sub>2</sub> for a 24 h period. The SiO<sub>2</sub> pattern was then removed by treating the samples with fluorhydric acid solution.

The MPC was loaded (20% metal) with PtRu NP using the formate ions method [7], adding the metal precursors solution (H<sub>2</sub>PtCl<sub>6</sub> and RuCl<sub>3</sub>, Sigma–Aldrich) to the carbon support impregnated with 2.0 M HCOOH solution. The pH was previously adjusted to 12.0. This dispersion was heated at 80 °C under stirring, keeping the temperature constant during the addition of the metal salts solution. Reaction mixture was kept under stirring for 12 h at room temperature, and finally the mixture was filtered, washed and dried at 60 °C for 2 h.

The diameters of the SiO<sub>2</sub> NP were determined by dynamic light scattering (DLS, Malvern 4700 with goniometer and 7132 correlator) with an argon-ion laser operating at 488 nm. All measurements were made at the scattering angle of 90°. FIB-SEM images were done with a dual beam system Strata DB235 (FEI Company), following the procedure as described elsewhere [11]. BET surface area, micropore area and pore volume were obtained with a Micrometrics ASAP 2020 instrument. Metal content and PtRu atomic ratios of the synthesized catalysts were determined by Energy Dispersive X-Ray Analysis (EDX), using an Oxford Instruments

Microanalysis Group 6699 ATW scanning electron microscope at 20 kV, with a Si detector and a Be window. XRD patterns of synthesized catalysts were obtained using a Universal Diffractometer Panalytical X'Pert X-ray, operating with a Cu-K $\alpha$  radiation generated at 40 kV and 30 mA. Scans were done at 3° min<sup>-1</sup> for 2 $\theta$  values between 20 y 100°. Metal crystallite size [12] and lattice parameters [13] were calculated using the dimensions of peak (220), Scherrer's equation and Vergard's Law.

### 2.2. Electrochemical characterization

Electrochemical experiments were carried out in a thermostated three electrodes electrochemical cell, using a hydrogen reference electrode in the electrolyte solution (RHE) as the reference. All potentials in this work are given against the RHE. A small piece of high surface carbon was used as auxiliary electrode. In this study, the working electrode consists of a certain amount of the PtRu/MPC or commercial PtRu/C E-TEK deposited as a thin layer over a glassy carbon disc ( $\phi = 3$  mm). For this purpose, an aqueous suspension of 4.0 mg mL<sup>-1</sup> of the PtRu/MPC or PtRu/C E-TEK catalyst was prepared by ultrasonically dispersing it in a solution of 15  $\mu$ L of Nafion (5 wt.%, Aldrich) in 0.5 mL of MilliQ water. An aliquot (20  $\mu$ L) of the dispersed suspension was pipetted on the glassy carbon surface and dried at ambient temperature under Ar atmosphere. The currents are expressed as current densities  $J$  (A cm<sup>-2</sup>), calculated from the measured current  $I$  (A) and the real electroactive area  $S$  (cm<sup>2</sup>).  $S$  was estimated from CO (N47) stripping experiments. Electrochemical measurements were performed with a PC controlled Autolab PGSTAT30 potentiostat–galvanostat. All reagents were of analytical grade. Argon (N50) was bubbled through the solution to avoid dissolved oxygen.

### 2.3. DEMS characterization

Differential electrochemical mass spectrometry (DEMS) was used to detect volatile and gaseous products generated during the methanol electro-oxidation. Several DEMS designs have been described in details in previous publications [14,15]. For the experiments described in the present work, the electrochemical cell was connected to the chamber containing the quadrupole mass spectrometer (PFEIFFER VACUUM QMS 200). A rotary vane pump evacuates the latter, whereas the vacuum in the chamber containing the mass spectrometer is obtained from a turbomolecular pump. A DEMS cell has been described in previous papers [4,5], which works under reactant flow and allows simultaneous detection of faradaic current and gaseous species produced on the electroactive surface by means of mass spectrometry. Conventional three-electrodes arrangement was employed with a RHE prepared in the supporting electrolyte and a graphite stick as the counter-electrode. The working electrode was a gas diffusion electrode composed of a thin layer of the metal/MPC catalyst deposited over a gas diffusion layer (carbon black coated carbon cloth), which acts as interface between the electrolyte and the vacuum system, contacted with a gold wire.

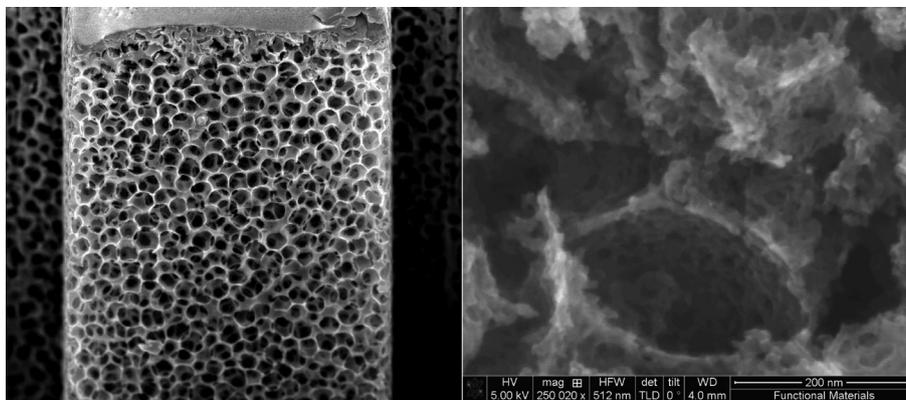


Fig. 1 – FIB-SEM image of MPC-K.

### 3. Results and discussion

#### 3.1. MPC carbon characterization

DLS experiments show a SiO<sub>2</sub> NP diameter of ca. 400 nm, with a polydispersity index of 0.0327 ( $\approx 3\%$ ) [8]. As result of NP sedimentation and subsequent oven treatment at 600 (K) or 1000 °C (I), a white solid is obtained. After impregnation and posterior pyrolysis, the resulting blue–green solid composed of SiO<sub>2</sub> and carbon is exposed to concentrated fluorhydric acid (50%) for 48 h. A typical SEM image of the resulting carbon matrix (named MPC-K due “K” template) is given in Fig. 1. This material presents a BET surface area of 102 m<sup>2</sup>/g with 64 m<sup>2</sup>/g micropore area and 0.053 cm<sup>3</sup>/g volume of pores. The SEM image in Fig. 1 left shows the cross section of a mesoporous carbon microparticle (cut in the SEM chamber with the aid of a focused ion beam). It is observed that the result of this chemical etching is a macroporous carbon inverse opal possessing interconnected “vesicles”. In a further increase of the magnification (Fig. 1 right), the vesicle reveals the mesoporous nature of the pore wall. As it was recently discussed in a previous paper, the macropores are due to the template effect of the hard silica spheres, while the mesoporosity seems to be related to the cracks produced in the carbon due to restricted contraction. The whole process produces a carbon material with hierarchical porous structure [8]. Those high surface porous microparticles will be the support for the PtRu NP deposition.

The electrochemical study of this carbon material (Fig. 2A) reveals the existence of a high electroactive surface area (ESA), capable to provide capacitive currents with values around 0.3–0.4 Ag<sup>-1</sup> (cycling at 5 mV/s) in 1 M H<sub>2</sub>SO<sub>4</sub>. From these values, a surface electroactive area around 700–900 m<sup>2</sup>/g can be roughly estimated (based on 15 mF cm<sup>-2</sup>) [16]. These values are in good agreement with the existence of a porous carbon mesh, which connects the inner surface of the microparticles with the external electrolytic medium.

#### 3.2. PtRu/MPC characterization

After the PtRu NP deposition in MPC-I and MPC-K, the metal content and Pt:Ru atomic ratio were determined by EDS

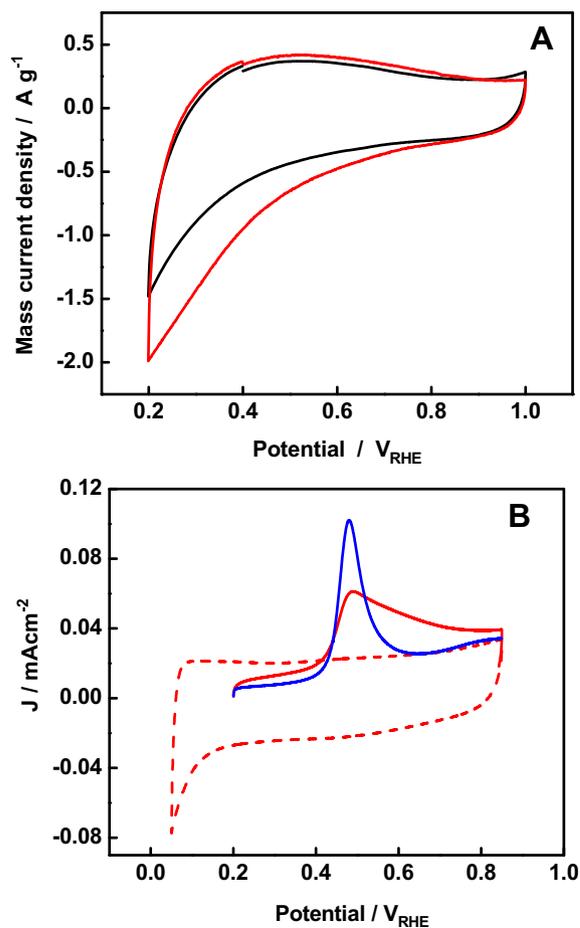


Fig. 2 – (A) Cyclic voltammogram of the porous carbon at 5 mV/s, 1 M H<sub>2</sub>SO<sub>4</sub>. MPC-I (dashed line) and MPC-K (solid line). T = 25 °C. (B) Cyclic voltammogram for PtRu/MPC-I (dashed red line), and CO stripping for PtRu/MPC-I (red line) and PtRu/MPC-K (blue line). E<sub>ad</sub> = 0.2 V<sub>ERH</sub>, v = 20 mV/s, 1 M H<sub>2</sub>SO<sub>4</sub>. T = 25 °C. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

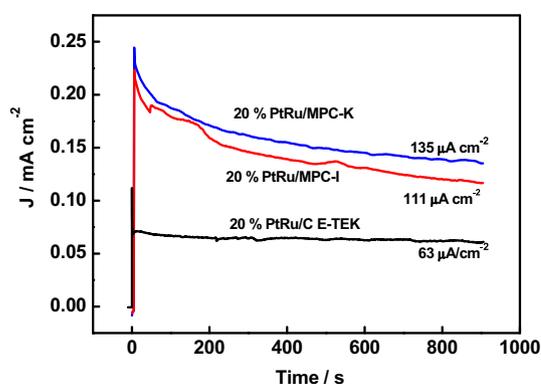
analysis. All catalysts present a metal loading around the nominal value of 20% (27, 23 and 20 for MOC-I, MOC-K and E-TEK, respectively). The composition of PtRu/MPC-K and PtRu/C E-TEK was 45:55 for Pt:Ru ratio (similar to the nominal 50:50), whereas PtRu/MPC-I catalyst exhibits higher Ru content (32:68 for Pt:Ru ratio). XRD patterns of the synthesized materials (not shown, see [Supplementary Information](#)) present characteristic peaks corresponding to the (111), (200) and (220) planes of the face centered cubic (fcc) structure of Pt, as well as a diffraction peak around  $24^\circ$  for PtRu/C E-TEK, which corresponds to the (002) reflection of graphite basal planes of the carbon support. The absence of this peak in synthesized catalysts indicates a low graphitization degree of the MPC used as support. Metal average crystallite size and lattice parameters were determined from (220) reflection peak (3.8 and 3.901 nm for PtRu/MPC-I and 4.9 and 3.905 nm for PtRu/MPC-K, respectively). These values are closed to those for the commercial E-TEK material (4.4 and 3.898 nm).

As shown in [Fig. 2B](#) (dashed red line), the addition of PtRu to the MPC changes notoriously the aspect of the cyclic voltammograms (CVs), especially in the interval from 0.05 V to 0.4 V<sub>RHE</sub>. The curves recorded are characteristic for low-loaded carbon supported PtRu materials [17]. Looking for a more precise characterization of the catalyst surface, CO stripping experiments was performed.

The oxidation of an adsorbed CO monolayer (CO<sub>ad</sub>) gives an estimation of the final electroactive area. The metal surface area, calculated assuming 420  $\mu\text{C}/\text{cm}^2$  for CO stripping, is close to 48  $\text{m}^2 \text{g}^{-1}$  for PtRu/MPC-I and 36  $\text{m}^2 \text{g}^{-1}$  for PtRu/MPC-K. These surface values are lower than that obtained recently with the same support (MPC-K), but using a different modification of the formic acid method for fixing the PtRu nanoparticles inside the carbon support [8]. Probably, the method of synthesis influences the degree of agglomeration, finally determining the metal surface area.

As can be deduced from a simple inspection of [Fig. 2B](#), the presence of Ru shifts the onset and the peak position of the CO electrooxidation toward more negative potentials, when compared with Pt [5]. Note that the shape of the CO stripping peak is more symmetric for PtRu/MPC-K than for PtRu/MPC-I. It is well known that sulfate adsorbs strongly on Pt surface [14], so the observed current tail in PtRu/MPC-I can be attributed to a stronger sulfate adsorption on this catalyst surface, which blocks the CO diffusion towards the most catalytic sites. The different content of Pt and Ru in these catalysts could also have an influence on the CO oxidation peak. However, it is interesting to remark that this effect is also observed for 20 wt.% PtRu/C E-TEK [3,18], but absent for the PtRu/MPC-K sample (both catalysts with the same Pt:Ru atomic ratio). This result suggests that the support structure is also conditioning the catalytic response modifying the surface environment of the reactive adsorbed molecule.

A further way to test the synthesized catalysts activity involves the chronoamperometric measurement of current densities ( $\text{A cm}^{-2}$ ) for methanol oxidation at 60 °C. The response of each electrode to a potential step from 0.05 V (a potential where methanol adsorption and oxidation are negligible) to 0.55 V (a potential similar to that achieved during operation conditions in a fuel cell) can be seen in [Fig. 3](#).



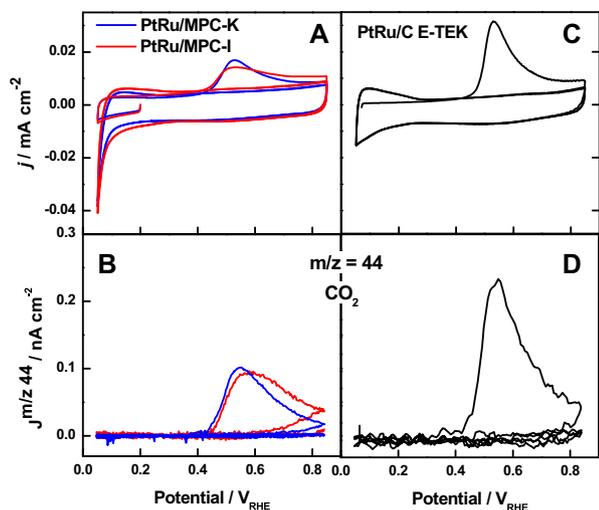
**Fig. 3 – Current transients for methanol electrooxidation on PtRu/MPC-K (blue line), PtRu/MPC-I (red line), and PtRu/C E-TEK (black line) at 0.55 V<sub>RHE</sub>, 1 M CH<sub>3</sub>OH + 1 M H<sub>2</sub>SO<sub>4</sub>, T = 60 °C. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)**

Commercial carbon supported PtRu catalyst (20 wt.% PtRu/C E-TEK) was also tested for the sake of comparison. A catalytic enhancement becomes clear from the recorded curves: the catalytic activity towards methanol oxidation at  $t = 900$  s is twice higher for PtRu/MPC (0.135  $\text{mA cm}^{-2}$  and 0.111  $\text{mA cm}^{-2}$  for K and I supports, respectively) than for PtRu/C E-TEK (0.063  $\text{mA cm}^{-2}$ ) at the same experimental conditions. For the catalysts studied here, it is assumed that most of the PtRu NP are anchored to the internal porous surface of the carbon grain. This hypothesis is based on the statement that the external surface area ( $\text{cm}^2 \text{g}^{-1}$ ) is very small for granular porous carbon (grain size 5–50  $\mu\text{m}$ ). On the other hand, considering the carbon black structure, it can be assumed that the majority of the PtRu NP in the commercial catalyst are attached over the external surface of the support. Taken in mind this fact, it is noteworthy that metal NP supported inside a granular porous-carbon are able to improve catalysts activity, measured as current density for methanol electrooxidation, with respect to the catalysts NP supported on the external surface of carbon nanoparticles.

### 3.3. DEMS characterization

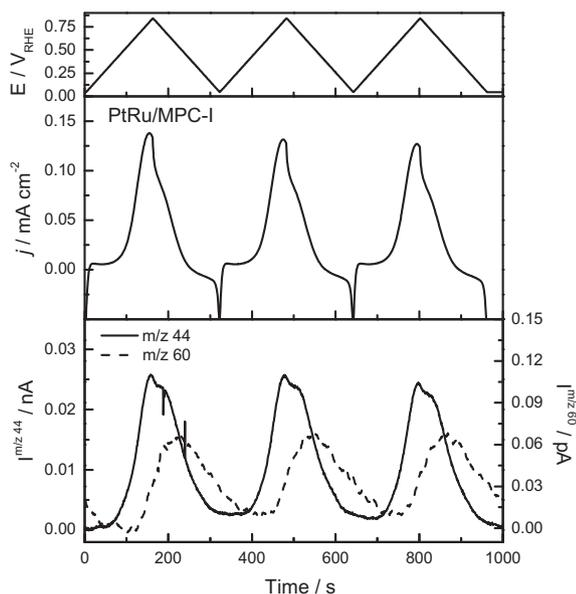
For quantitative detection of the CO<sub>2</sub> generated during methanol oxidation, experiments were carried out to calibrate the DEMS system ([Fig. 4](#)), calculating the mass spectrometer constant for the production of CO<sub>2</sub>,  $k^{\text{CO}_2}$ . Further details for these calculations are given in previous works [4,5]. CVs and mass spectrometer cyclic voltammograms (MSCVs) related to the production of CO<sub>2</sub> ( $m/z = 44$ ) during the electrooxidation of a CO adsorbed monolayer on PtRu/MPC-I and PtRu/MPC-K were simultaneously recorded (red and blue curves) at 5 mV/s. The curves confirm the onset for CO oxidation as described above. Similar experiments were performed adsorbing CO at commercial catalyst PtRu/C E-TEK (black curves) in order to compare the results.

The curves for methanol oxidation on PtRu/MPC-I in 2 M CH<sub>3</sub>OH + 0.5 M H<sub>2</sub>SO<sub>4</sub> solution and the corresponding

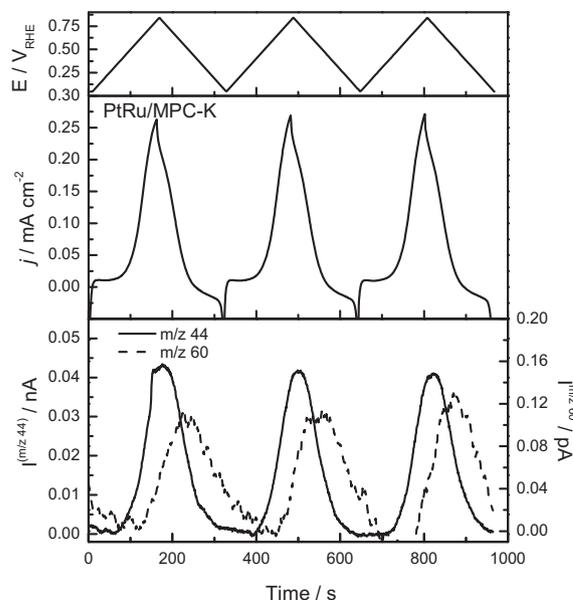


**Fig. 4** – CVs (A, C) and MSCVs (B, D) for CO<sub>2</sub> ( $m/z = 44$ ) during the stripping of CO monolayer at PtRu/MPC-I (dashed line) and PtRu/MPC-K (solid line) (A, B) and PtRu/C E-TEK (C, D).  $E_{\text{ad}} = 0.20 \text{ V}$ ;  $v = 5 \text{ mV/s}$ ;  $0.5 \text{ M H}_2\text{SO}_4$ .  $T = 25 \text{ }^\circ\text{C}$ .

successive recorded MSCVs for  $m/z = 44$  (corresponding to the electrooxidation of methanol to CO<sub>2</sub>) and  $m/z = 60$  (corresponding to the production of formic acid which is detected as methylformate) at room temperature are displayed in Fig. 5. Then, it is concluded that during the methanol oxidation, CO<sub>2</sub> and methylformate were on-line detected by mass spectrometry. Methylformate is formed through the chemical reaction between methanol and electrochemically formed



**Fig. 5** – Potential program for methanol electrooxidation on PtRu/MPC-I (up), current density (middle) and MSCVs for CO<sub>2</sub> ( $m/z = 44$ ) and HCOOCH<sub>3</sub> ( $m/z = 60$ ) (down).  $E_{\text{ad}} = 0.20 \text{ V}$ ;  $v = 5 \text{ mV/s}$ ;  $2 \text{ M CH}_3\text{OH} + 0.5 \text{ M H}_2\text{SO}_4$ .  $T = 25 \text{ }^\circ\text{C}$ .



**Fig. 6** – Potential program for methanol electrooxidation on PtRu/MPC-K (up), current density (middle) and MSCVs for CO<sub>2</sub> ( $m/z = 44$ ) and HCOOCH<sub>3</sub> ( $m/z = 60$ ) (down).  $E_{\text{ad}} = 0.20 \text{ V}$ ;  $v = 5 \text{ mV/s}$ ;  $2 \text{ M CH}_3\text{OH} + 0.5 \text{ M H}_2\text{SO}_4$ .  $T = 25 \text{ }^\circ\text{C}$ .

formic acid. From Fig. 6, it is established that the oxidation to CO<sub>2</sub> starts first and the onset for formic acid production is shifted approx. 50 mV to more positive potentials, once part of active surface sites becomes free from adsorbed species. Note that Fig. 5 makes use of a non-conventional way to show the information obtained from DEMS. The employment of time in the x axis has been chosen with the aim to show in a clear way the time delay between CO<sub>2</sub> and methylformate generation.

After calibrating the DEMS setup, the current efficiency for CO<sub>2</sub> can be determined. The conversion efficiency  $E^{\text{CO}_2}$  for methanol electrooxidation to CO<sub>2</sub> can be calculated by the equation [4,5]:

$$E^{\text{CO}_2} = \frac{6 \times Q_i^{\text{CO}_2}}{k^{\text{CO}_2} \times Q_f^i}$$

where  $Q_i$  is the ionic charge involved in the curve recorded for  $m/z = 44$  during methanol electrooxidation, and  $Q_f$  the corresponding faradaic charge. In the case of PtRu/MPC-I a value of 80% was calculated for the efficiency to CO<sub>2</sub>.

Similarly, Fig. 6 shows the curves obtained during the electrooxidation of methanol on PtRu/MPC-K. Similar behavior was also observed for this catalyst with higher currents than PtRu/MPC-I but with conversion efficiency to CO<sub>2</sub> of 55%. Comparing the results for the materials prepared in the present work with the commercial catalyst PtRu/C E-TEK (not shown), it can be established that the commercial one presents current densities and conversion efficiency (84%) quite similar to the PtRu/MPC-I catalyst (80%). In contrast, for the PtRu/MPC-K material, the conversion efficiency to CO<sub>2</sub> is visibly lower (55%) and the current density noticeably higher than the other two. Again, the effect of the higher Ru content

in PtRu/MPC-I is not determining the results, as Ru cannot oxidize methanol at room temperature but this catalyst shows higher efficiencies to CO<sub>2</sub>.

The higher current developed by the PtRu/MPC-K catalysts during the methanol oxidation is originated, in a first stage, by the faster elimination of the adsorbed CO, as shown in Fig. 2B. Another possible cause is the improved condition for reactant and products diffusion through the porous layer of catalysts. Moreover, the decrease at the conversion efficiency from methanol to CO<sub>2</sub>, together with the intensification of the methylformate signal, suggests that the reaction is mainly enhanced by the existence of alternative paths for methanol electrooxidation to formic acid, which do not involves the formation of adsorbed CO [2,5]. In addition, it was observed a better performance for the PtRu/MPC-K than the PtRu/MPC-I toward the methanol oxidation, indicating that the temperature during the preparation of the carbon materials has also an influence in the final behavior of the electrocatalysts.

#### 4. Conclusions

PtRu catalysts were prepared using a high surface macroporous porous carbon (MPC) as support. The carbonaceous material has been obtained using SiO<sub>2</sub> nanoparticles as template and presents a high surface area and interconnected pores with hierarchical distribution. Highest activity for methanol electrooxidation was obtained for the PtRu catalyst prepared with the MPC synthesized at 600 °C (PtRu/MPC-K). This activity can be explained, in general, by the improved diffusion through the porous matrix for MPCs supported PtRu, and in particular, taking into account the fast CO oxidation observed for this material.

#### Acknowledgments

Authors thank the MINECO (Spain, project CTQ2011-28913-CO2-02) and ANPCyT (Argentina, project PICT-2010-2421) for financial support AECID for sustaining the cooperation between both universities (PCI A/3040514/11). C.A.B. and G.A.P. are permanent research fellow of CONICET. J.F. acknowledges ACIISI (Gobierno de Canarias) for the predoctoral fellowship. M. Bruno is acknowledged for the BET, micropore surface area and pore volume measurements.

#### Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.ijhydene.2013.06.085>.

#### REFERENCES

- [1] Wang H, Wingender C, Baltruschat H, Lopez M, Reetz MT. Methanol oxidation on Pt, PtRu, and colloidal Pt electrocatalysts: a DEMS study of product formation. *J Electroanal Chem* 2001;509:163–9.
- [2] Wang H, Löffler T, Baltruschat H. Formation of intermediates during methanol oxidation: a quantitative DEMS study. *J Appl Electrochem* 2001;31:759–65.
- [3] Yu JS, Kang S, Yoon SB, Chai G. Fabrication of ordered uniform porous carbon networks and their application to a catalyst supporter. *J Am Chem Soc* 2002;124:9382–3.
- [4] Planes GA, García G, Pastor E. High performance mesoporous Pt electrode for methanol electrooxidation. A DEMS study. *Electrochem Commun* 2007;9:839–44.
- [5] García G, Florez-Montañón J, Hernandez-Creus A, Pastor E, Planes GA. Methanol electrooxidation at mesoporous Pt and Pt–Ru electrodes: a comparative study with carbon supported materials. *J Power Sources* 2011;196:2979–86.
- [6] Jusys Z, Kaiser J, Behm RJ. Methanol electrooxidation over Pt/C fuel cell catalysts: dependence of product yields on catalyst loading. *Langmuir* 2003;19:6759–69.
- [7] dos Santos L, Colmati F, Gonzalez ER. Preparation and characterization of supported Pt–Ru catalysts with a high Ru content. *J Power Sources* 2006;159:869–77.
- [8] Baena-Moncada AM, Planes GA, Moreno MS, Barbero CA. A novel method to produce a hierarchical porous carbon as a conductive support of PtRu particles. Effect on CO and methanol electrooxidation. *J Power Sources* 2013;221:42–8.
- [9] Wang W, Gu B, Liang L, Hamilton W. Fabrication of two- and three-dimensional silica nanocolloidal particle arrays. *J Phys Chem B* 2003;107:3400–4.
- [10] Velev OD, Lenhoff AM. Colloidal crystals as templates for porous materials. *Curr Opin Colloid Interface Sci* 2000;5:56–63.
- [11] Jiménez-Piqué E, Ramos A, Muñoz-Tabares JA, Hatton A, Soldera F, Mücklich F, et al. Focused ion beam tomography of zirconia degraded under hydrothermal conditions. *J Eur Ceram Soc* 2012;32:2129–36.
- [12] Warren BE. X-ray diffraction. 1st ed. Mineola: Addison-Wesley Publishing Co; 1969.
- [13] Gasteiger HA, Ross Jr PN, Cairns EJ. LEIS and AES on sputtered and annealed polycrystalline PtRu bulk alloys. *Surf Sci* 1993;293:67–80.
- [14] Baltruschat H. Differential electrochemical mass spectrometry. *J Am Soc Mass Spectrom* 2004;15:1693–706.
- [15] Wang H, Alden LR, DiSalvo FJ, Abruña HD. Methanol electrooxidation on PtRu bulk alloys and carbon-supported PtRu nanoparticle catalysts: a quantitative DEMS study. *Langmuir* 2009;25:7725–35.
- [16] Zhao X, Tian H, Zhu M, Tian K, Wang JJ, Kang F, et al. Carbon nanosheets as the electrode material in supercapacitors. *J Power Sources* 2009;194:1208–12.
- [17] Salgado JRC, Alcaide F, Álvarez G, Calvillo L, Lázaro MJ, Pastor E. Pt–Ru electrocatalysts supported on ordered mesoporous carbon for direct methanol fuel cell. *J Power Sources* 2010;195:4022–9.
- [18] Kolics A, Wieckowski A. Adsorption of bisulfate and sulfate anions on a Pt(111) electrode. *J Phys Chem B* 2001;105:2588–95.