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## Macroporous carbon as support for PtRu catalysts



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### 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).

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## 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

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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.

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