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# Tailoring carbon xerogels' properties to enhance catalytic activity of Pt catalysts towards methanol oxidation

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## ARTICLE INFO

### Article history:

Received 16 March 2015

Received in revised form

11 May 2015

Accepted 26 May 2015

Available online xxx

### Keywords:

Carbon xerogels

Methanol electro-oxidation

Pt catalysts

## ABSTRACT

The work presented herein deals with the study of the influence of the synthesis conditions on the properties of carbon xerogels (CXGs). The study analyzes the effect of the composition of the mixture of carbon gel precursors and the pH on the porous structure, the arrangement of carbon, the surface chemistry and the electrical conductivity. Certain conditions allow obtaining CXGs with a high porosity, high ordering and polymerization degree. CXGs are used as Pt catalyst supports for the electro-oxidation of methanol. CXGs with the higher ordering and polymerization degree result in catalysts with low crystal sizes and good metallic distribution. Such catalysts show the highest activities towards methanol oxidation. CXG-supported Pt catalysts outperform a Vulcan-supported Pt catalyst prepared in the same conditions.

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## Introduction

Methanol oxidation in direct methanol fuel cells (DMFCs) is the limiting reaction of this kind of devices, due to substantially slow kinetics [1–3]. Huge efforts have been dedicated in the last decades to obtain highly active catalyst promoting this reaction [1,4–7]. Platinum-based catalysts are the most efficient, but their high cost is one of the obstacles preventing DMFCs from successful commercialization. In order to minimizing the amount of Pt and reducing the catalyst cost, several works propose the use of advanced materials as supports, allowing the control of the distribution and morphology of noble metal nanostructures, resulting in increased catalytic performance [1–15].

Over the past decades, carbon materials have attracted increasing attention for their interesting physical properties [1,2,11–17]. Recent developments in carbon nanomaterials, such as carbon nanotubes (CNTs) [18,19], carbon nanofibers [20,21], graphene [22–24] etc., have further boosted the research on high-performance DMFC electrocatalysts [1]. In comparison with traditional carbon supports (carbon blacks and activated carbons), carbon nanomaterials present unique properties that enhance catalytic activity (high specific surface area and strong interaction with metal nanoparticles, excellent stability under harsh electrochemical conditions and high electrical conductivity) [1,11]. Among the vast amount of carbon materials, carbon gels have been extensively studied as noble metals supports [25]. Carbon gels are porous materials with a reticular structure formed by

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<http://dx.doi.org/10.1016/j.ijhydene.2015.05.169>

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interconnected spherical carbon nanoparticles. These materials are obtained through the carbonization of an organic gel obtained from the polycondensation of hydroxylated benzenes (resorcinol, phenol, catechol, etc) and aldehydes (formaldehyde, furfural, etc) [26–28]. These gels are classified based on the drying method employed to dry the aqueous organic gels: carbon aerogels (super-critical drying), carbon cryogels (freeze-drying) and carbon xerogels (evaporative drying). Among the three of them, carbon xerogels, CXGs, are the cheapest and easiest to produce [28,29]. Some authors have claimed that evaporative drying leads to a high amount of shrinkage and collapse of the porous texture of the original material [26,27]. However it has been thoroughly proved that highly porous CXGs with negligible shrinkage can be produced by properly choosing the synthesis conditions, yielding the most cost-competitive material [28,30].

Carbon gels have been widely used as supports for different catalytic processes [31]. In the field of fuel cells the use of CXGs as catalysts supports has led to catalysts with enhanced performance towards methanol oxidation in comparison to conventional carbon supports [25]. For instance, Figueiredo et al. [32] observed a remarkable increase in the activity for methanol electro-oxidation when Pt–Ru catalysts were supported on oxidized CXGs. These catalysts were twice more active than those supported on the untreated xerogels. The explanation for this different performance was based on the higher contents of metallic Ru on the surface and on the oxidation state of the two metals. Arbizzani and co-workers [33] studied the specific catalytic activity of DMFC anodes based on PtRu catalysts deposited by chemical and electrochemical route on mesoporous cryo- and xerogel carbons. Their results were compared to those obtained with PtRu supported on Vulcan, being the specific catalytic activity more than double when Vulcan is substituted by former carbons. The higher activity was attributed to the presence of large mesopore or macropore volumes, which facilitates methanol diffusion.

However, generally only textural properties or surface chemistry have been taken in consideration in the design of CXGs to be applied as catalysts supports [25,32,34–36]. Other properties, such as their structure, ordering degree and electrical conductivity have been ignored, even though being of great importance in determining the characteristics of the catalyst obtained. In a previous work, Alegre et al. [37] showed that all these parameters are of key importance in the preparation of active catalysts for the oxygen reduction reaction (ORR). In the present study, a series of CXGs having very different physico-chemical properties were used as support in the preparation of catalysts for the oxidation of methanol. A mono-metallic system, Pt, was preferred in order to center this study in the influence of the supports' properties, avoiding the influence of other parameters in this reaction, such as the Pt:Ru ratio, the oxidation state of Ru, etc [38].

## Experimental

### Synthesis methods

The synthesis procedure employed in this work was based on the ones described by Lin [39] and Czakkel [40]. Briefly,

reactants were mixed in the corresponding amounts and, after 30 min stirring, pH was adjusted to 6, with HNO<sub>3</sub> 2 M. Subsequently, the mixture was poured in closed vials, and kept for 24 h at room temperature, at 50 °C for the next 24 h and 120 h at 85 °C. The so-obtained hydrogels were subcritically dried in an oven for 5 h at 65 °C and 5 h at 110 °C. Pyrolysis of the organic xerogels was carried out in a tubular furnace at 800 °C for 3 h under a N<sub>2</sub> flow of 100 mL min<sup>-1</sup>. Some previously synthesized carbon xerogels (CXGs) [37] were selected for the present study. Table 1 summarizes their synthesis conditions.

Pt was deposited on the synthesized carbon xerogels and on Vulcan XC-72R carbon black (for comparison purposes) by an impregnation method, using formic acid as reducing agent. The amount of metallic precursor (H<sub>2</sub>PtCl<sub>6</sub>) was calculated to obtain a metal loading of 20% w/w. A 2 M HCOOH solution was heated at 80 °C, prior to the addition of the corresponding carbon material. Subsequently an aqueous solution of H<sub>2</sub>PtCl<sub>6</sub> (Sigma–Aldrich) was added dropwise. The solution was left under stirring for 1 h. Finally catalysts were filtered, thoroughly washed with deionized water, and dried overnight at 60 °C.

### Physico-chemical characterization

Textural properties of carbon xerogels were determined by nitrogen physisorption at –196 °C (Micromeritics ASAP 2020). Specific surface area was calculated applying the Brunauer–Emmet–Teller (BET) equation to the adsorption–desorption isotherms, t-plot method was used for the calculation of the pore volume along with the Barrett–Joyner–Halenda (BJH) method.

The carbon ordering degree of CXGs was evaluated by Raman spectroscopy, measuring the relative intensities of D (ca. 1350 cm<sup>-1</sup>) and G (ca. 1590 cm<sup>-1</sup>) peaks. Raman spectra of carbon xerogels were obtained with a Horiba Jobin Yvon HR800 UV, using the green line of an argon laser ( $\lambda = 514.53$  nm) as excitation source. Electrical conductivity was determined submitting the carbonaceous powder to pressure that allows increasing the conductive phase relative volume and consequently, both the average number of contacts and the apparent electronic conductivity increase. The electrical conductivity was determined applying electrical current scans up to 20 mA and measuring the voltage drop. The electrical resistance was then calculated by Ohm's law, where the system resistance is subtracted. The conductivity was then obtained from the sample resistance and geometric considerations [41]. The composition of CXGs was studied by temperature programmed desorption (TPD) and X-ray photoelectron spectra (XPS). During TPD experiments, the concentration of desorbed CO and CO<sub>2</sub> between 150 °C and 1050 °C was monitored with an HP 5890 gas chromatograph with a thermal conductivity detector, packed columns Porapak N 10 ft and molecular sieve, assigning CO and CO<sub>2</sub> to different surface oxygen groups as in Ref. [42]. C1s bands obtained from the XPS spectra were analyzed to determine the composition of carbon xerogel's surface, with an ESCAPlus Omicron spectrometer equipped with a Mg (1253.6 eV) anode, 150 W (15 mA, 10 kV) power, over an area of sample of 1.75 × 2.75 mm. This technique was also used in the case of Pt catalysts, to

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