

Article

## PtRu Nanoparticles Deposited by the Sulfite Complex Method on Highly Porous Carbon Xerogels: Effect of the Thermal Treatment

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**Abstract:** Highly porous carbon xerogels (CXGs) were synthesized to be used as support for PtRu nanoparticles. Metal particles were deposited on CXGs by means of the sulfite complex method for the first time. Catalysts so-obtained were submitted to thermal treatment in H<sub>2</sub>, at different temperatures, in order to increase the particle size and thus the intrinsic activity. Physico-chemical characterizations included N<sub>2</sub> physisorption, X-Ray diffraction, X-ray photoelectron spectroscopy and transmission electron microscopy. Highly dispersed alloyed PtRu particles were obtained, with crystal sizes ranging from 1.6 to 2.0 nm. PtRu-catalysts were tested in half-cell for the methanol oxidation reaction (MOR). The resulting thermal treatment was effective in increasing both particle size and catalytic activity toward MOR.

**Keywords:** carbon xerogel; platinum-ruthenium catalyst; methanol oxidation reaction; sulfite complex method

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## 1. Introduction

Pt–Ru catalysts are well known for their high activity towards the electro-oxidation of methanol [1–5]. Nevertheless, drawbacks such as slow oxidation kinetics and methanol crossover make the efficiency of the Direct Methanol Fuel Cells (DMFC) still insufficient for practical applications [1]. Therefore, further optimizations of the anode material and the membrane are necessary for the development and commercialization of DMFC. In this context, an attractive approach for the anode, which appears as a possible solution to reduce metal loading and increase the catalytic efficiency, is the use of novel carbonaceous materials as electrocatalyst supports [6–9]. The nature of the support, as well as the interaction between the latter and the metal, has been demonstrated to be extremely important, given that it determines the physico-chemical properties of catalysts, such as dispersion, stability and morphology of metallic crystallites [10–12]. In addition, characteristics of the support can also determine the electrochemical properties of catalysts by altering mass transport, active electrochemical area and metal nanoparticle stability during the cell operation [13,14].

Among the numerous new carbon materials that can be found in the literature, carbon xerogels, cryogels and aerogels constitute an interesting alternative to carbon blacks [15,16]. These materials are obtained either by supercritical drying or evaporative drying of organic gels, followed by pyrolysis. Their texture is fully controllable within a wide range of pore sizes and distribution via the synthesis process of the organic gel [14]. The use of carbon gels as catalysts supports has been previously reported. Catalysts supported on carbon gels (aerogels, cryogels and xerogels) showed higher activities towards methanol oxidation and oxygen reduction, in comparison to catalysts supported on commercial carbon blacks, such as Vulcan [12,15–18]. Vulcan XC-72R, with a surface area of *ca.* 250 m<sup>2</sup> g<sup>-1</sup>, has been commonly used as a catalyst support, especially in DMFC anode catalyst preparation. However, an accessible and sufficiently large surface for maximum catalyst dispersion has been argued to be a necessary but insufficient condition for obtaining optimized carbon-supported catalysts. First of all, Vulcan has a preponderance of small pores that cannot be filled with polymer molecules. This portion inside the micropores has less or even no electrochemical activity due to the difficulty in reactant accessibility. Besides, the poor surface chemistry of this carbon material makes its impregnation with the metallic precursor difficult.

Some studies have dealt with different preparation methods of catalysts onto this kind of supports. Arbizzani *et al.* developed PtRu catalysts, prepared by both chemical and electrochemical routes, on mesoporous cryo- and xerogel carbons [18]. Their results were compared to those obtained with Vulcan-supported PtRu, resulting in almost double specific catalytic activity when Vulcan was substituted by the former carbons. Job *et al.* reported the use of the ‘Strong Electrostatic Adsorption’ (SEA) method to prepare Pt/carbon xerogel catalysts, exhibiting high Pt dispersion at high metal content [15]. Figueiredo *et al.* prepared Pt catalysts supported on carbon xerogels by impregnation with H<sub>2</sub>PtCl<sub>6</sub>, studying the effect of different reduction protocols [12].

Carbon xerogels have also been employed as catalyst supports in previous studies of our group [19–21]. Carbon xerogels were used as support for Pt and PtRu nanoparticles, synthesized by an impregnation and reduction with sodium borohydride method. Catalysts performed higher activities than commercial catalysts Pt/C, ETEK and PtRu/C, ETEK, that are supported on Vulcan carbon black [19]. In another paper, we reported the synthesis of two carbon xerogels of different textural properties, which were

subsequently functionalized through several oxidation treatments. These carbon xerogels were used as supports in the preparation of several Pt catalysts which were characterized and tested for CO and methanol electro-oxidation, performing higher activities than Pt supported on Vulcan [20]. In another work, PtRu catalysts were prepared using a highly mesoporous carbon xerogel submitted to different oxygen functionalization treatments: diluted and concentrated nitric acid as well as gas-phase 5% O<sub>2</sub>-N<sub>2</sub> oxidation. Catalysts with 20 wt% loading and equimolar Pt:Ru metallic phase were prepared using an impregnation procedure involving chemical reduction with formic acid. Catalysts supported on the carbon xerogel presented higher activities towards methanol oxidation than the catalyst supported on Vulcan prepared by the same procedure [21]. In comparison to the commercial carbon black Vulcan, carbon xerogel doubles the S<sub>BET</sub> value determined for Vulcan. Such features favour diffusion of reagents and products to and from active sites when using carbon xerogels as catalysts supports, instead of Vulcan, making catalysts more active. Although catalysts supported on carbon xerogels showed higher performances than when supported on Vulcan, not proper dispersion was achieved in these works for any of the methods assayed (impregnation and reduction with different reduction protocols), pointing out the need for further research in synthesis methods providing low crystallite size and high metallic dispersion.

In general, the Pt/carbon gel catalysts are classically obtained via deposition from the liquid phase; in most cases, impregnation of the support by H<sub>2</sub>PtCl<sub>6</sub> solutions is used and followed by various post-treatments, such as liquid phase reduction or drying followed by gas phase reduction under hydrogen [15]. Nevertheless, it has been noticed that the presence of chloride ions during the deposition can have a negative effect on the later performance of the catalysts for methanol oxidation [15]. In this paper a sulfite-complex based method is used for the first time for carbon xerogels, in order to avoid the use of chloride species. This preparation method presents an advantage over the straight reduction of chloride salts since no chloride ions are present during the deposition of the metals onto the support. Further, given that this method leads to small metallic particles, with a high dispersion, two thermal treatments at different temperatures were carried out, in order to slightly increase crystal and particle size, favoring catalytic activity towards methanol oxidation reaction (MOR).

## 2. Results and Discussion

### 2.1. Textural Properties of Carbon Xerogels and PtRu-Catalysts

Carbon xerogel (CXG) was synthesized by a sol-gel method consisting on the polymerization and pyrolysis of resorcinol and formaldehyde. Subsequently, this carbon material was used as support for PtRu nanoparticles deposited by a sulfite complex method, based on the formation of colloids. PtRu metallic loading was calculated to obtain a 20 wt.% on the carbon support. Catalysts so obtained were divided in three aliquots: one as-prepared and the other two were treated under a H<sub>2</sub> stream for 1 h at 200 °C and 400 °C, respectively.

Carbon xerogel shows a high surface area (see Table 1), and can be mainly considered as a mesoporous carbon, with 89% of its pore volume corresponding to mesopores, and average pore sizes of 23 nm. Textural properties of PtRu catalysts are also shown in Table 1. Catalysts were named as follows: PtRu/CXG-COL (given that the sulfite complex method is based on colloids), followed by TT-200 or TT-400 (standing for thermal treatment at 200 °C or 400 °C, respectively). Upon metallic

loading, surface area and pore volume decrease considerably, but still carbon materials conserve a highly developed porous structure. Note that mean pore size slightly decreases after metallic introduction but there is no significant selectivity regarding the deposition on micropores nor mesopores, indicating the presence of PtRu nanoparticles all over the CXG surface. It is also worthy of note that the porosity increases with thermal treatment in terms of both Brunauer-Emmet-Teller (BET) surface area and pore volume, maybe attributable to some carbon gasification from the CXG.

**Table 1.** Brunauer-Emmet-Teller (BET) surface area and pore volumes obtained from N<sub>2</sub> adsorption isotherms for the carbon xerogel and the PtRu-catalysts prepared.

| Sample             | $S_{\text{BET}}$ (m <sup>2</sup> g <sup>-1</sup> ) | $V_{\text{pore } p/p_0 \approx 1}$ (cm <sup>3</sup> g <sup>-1</sup> ) | $V_{\text{meso BJH}}$ (cm <sup>3</sup> g <sup>-1</sup> ) | $V_{\text{micro}}$ (cm <sup>3</sup> g <sup>-1</sup> ) | Mean pore size (nm) |
|--------------------|--|---|--|---|---------------------|
| CXG                | 528  | 1.79  | 1.66   | 0.14  | 23                  |
| PtRu/CXG-COL       | 271  | 0.51  | 0.59   | 0.08  | 19                  |
| PtRu/CXG-COL-TT200 | 278  | 0.57  | 0.46   | 0.09  | 18                  |
| PtRu/CXG-COL-TT400 | 332  | 0.66  | 0.55   | 0.11  | 18                  |

## 2.2. PtRu-Catalysts Characterization

PtRu crystal sizes, shown in Table 2, were calculated from the XRD patterns (shown in Figure 1) and using the Debye-Scherrer equation on the Pt (220) reflection. PtRu crystal size ranges from 1.6 to 2.0 nm.

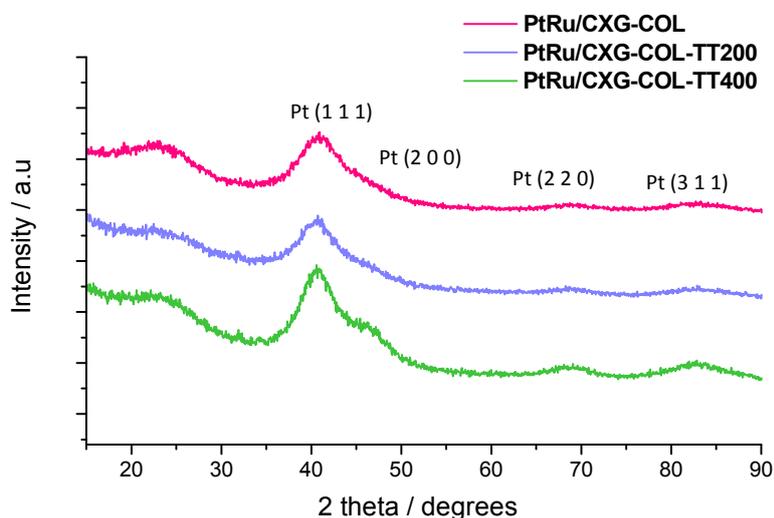
**Table 2.** PtRu crystal size obtained by XRD and PtRu concentration in the synthesized catalysts.

| Sample            | % w/w PtRu | Atomic ratio Pt:Ru | PtRu crystal size | Lattice parameter | $X_{\text{Ru}}$ in PtRu alloy |                          |
|-------------------|------------|--------------------|-------------------|-------------------|-------------------------------|--------------------------|
|                   | TGA        | XRF                | nm                | nm                | Vegard's law                  | Antolini's equation [22] |
| PtRu/CXG-COL      | 25         | 1.6                | 1.6               | 0.386             | 0.35                          | 0.49                     |
| PtRu/CXG-COLTT200 | 25         | 1.6                | 1.8               | 0.387             | 0.39                          | 0.37                     |
| PtRu/CXG-COLTT400 | 25         | 1.6                | 2.0               | 0.385             | 0.43                          | 0.50                     |

The highly developed surface area of these carbon materials is the controlling parameter determining such a low crystal size. Thermal treatment proved to be effective in increasing the catalysts crystal size. The amount of Ru alloyed with Pt ranges from 0.35 to 0.43 when calculated using Vegard's law, and slightly higher when using Antolini's equation [22]. Antolini and co-workers [22] obtained similar values of  $X_{\text{Ru}}$ , however, a little smaller. The higher  $X_{\text{Ru}}$  in the alloy in comparison to Antolini's work, might be due to the small crystal size, favoring inclusion of Ru in the fcc structure of Pt. This is confirmed by the lattice parameter that decreases from 0.392 nm (from pure Pt) to *ca.* 0.385 due to the contraction of the lattice, indicating the formation of the alloy between Pt and Ru. In the case of PtRu/CXG-COL-TT200 and PtRu/CXG-COL-TT400 catalysts, it is possible that H<sub>2</sub> treatment favored

the further inclusion of Ru in the fcc network. The metallic loading was slightly higher than the nominal 20 wt.% in all cases. X-ray fluorescence analysis yields similar to Pt/Ru ratios for all catalysts prepared.

**Figure 1.** Diffractograms obtained by XRD for the synthesized PtRu catalysts.



TEM images, shown in Figure 2, were acquired for PtRu catalysts in order to analyze the metal dispersion obtained. A uniform distribution of the active phase is obtained in all cases. The remarkably enhanced dispersion of the metal compounds achieved through this sulfite complex method lead us to conclude that, in terms of active phase dispersion, the surface of the carbon support is optimally covered by the metallic particles. Histograms obtained confirmed the results obtained from XRD. Catalysts submitted to subsequent thermal treatment produced larger particle sizes (around 2.4 nm and 3.1 nm for PtRu/CXG-COL-TT200 and PtRu/CXG-COL-TT400, respectively) as a consequence of the intended metallic particle sintering to a certain extent, in comparison to the untreated catalyst, PtRu/CXG-COL, with a particle size distribution centered at 1.9 nm.

**Figure 2.** Representative TEM micrographs of the PtRu electrocatalysts (a) PtRu/CXG-COL; (b) PtRu/CXG-COL-TT200 and (c) PtRu/CXG-COL-TT400.

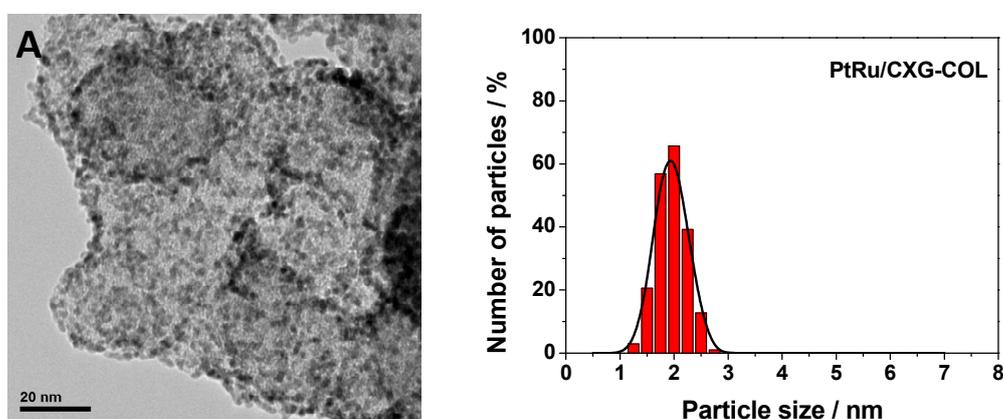
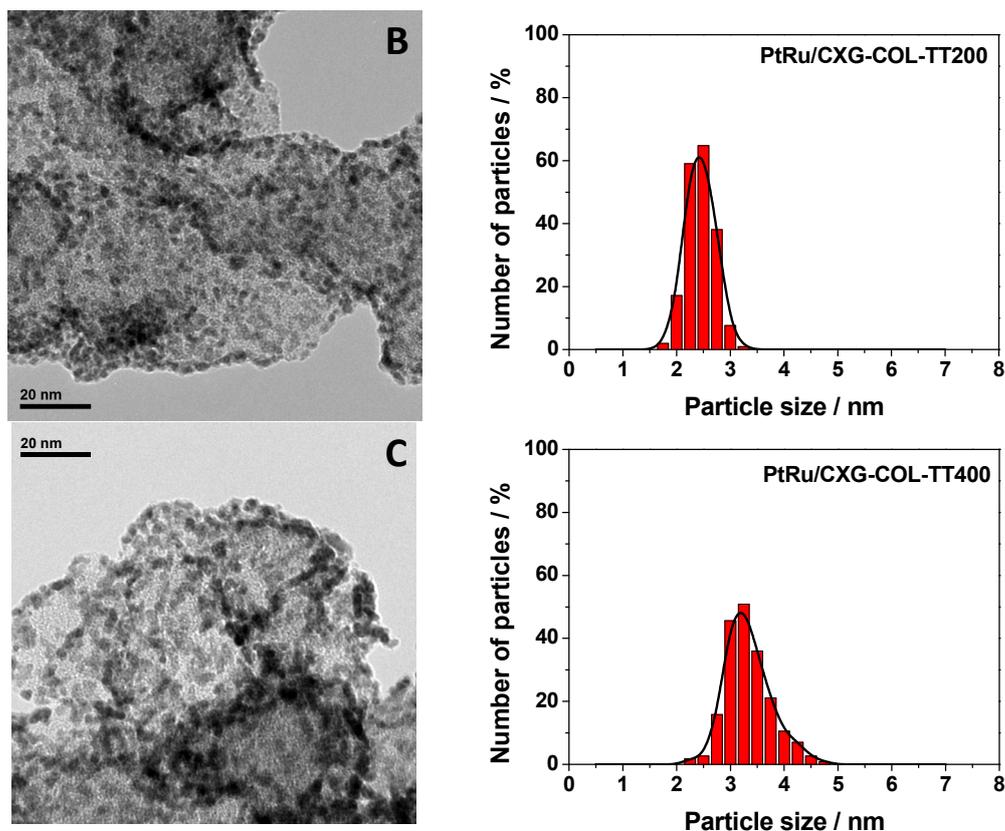


Figure 2. Cont.



XPS was used to identify the oxidation state of Pt and Ru on the surface of the different catalysts prepared. Pt and Ru peaks were deconvoluted as described in [23]. Figure 3 shows an example of the deconvolution of Pt  $4f_{7/2}$  and Ru  $3p_{3/2}$  signals for the catalyst PtRu/CXG-COL, whereas Table 3 shows the results of this deconvolution.

Figure 3. XPS signals for (a) Pt and (b) Ru for the catalyst PtRu/CXG-COL.

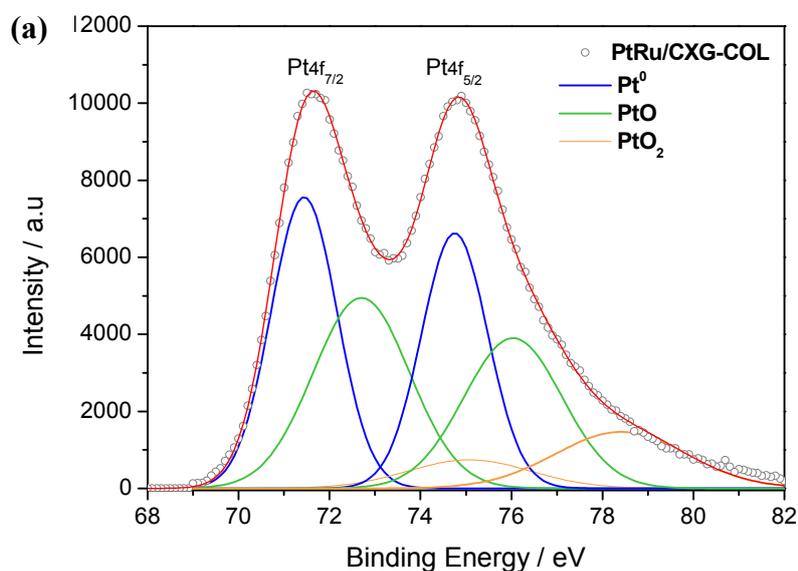
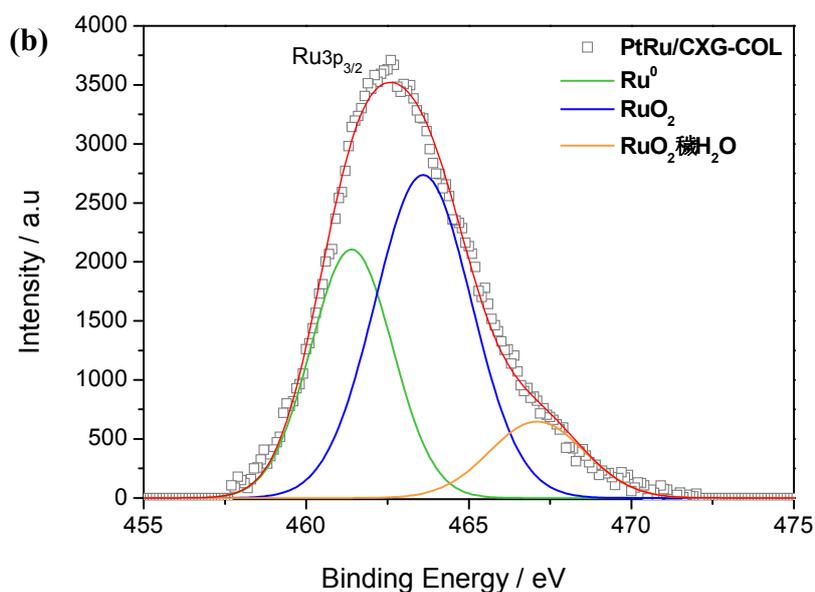


Figure 3. Cont.



For all the catalysts studied,  $\text{Pt}^0$  was found to be the predominant species on their surface. There is, however, an important contribution of oxidized  $\text{Pt}^{2+}$ , as well as of  $\text{Pt}^{4+}$ , to a lower extent. In contrast,  $\text{RuO}_2$  is the predominant species in all catalysts, followed by  $\text{Ru}^0$ . Catalysts submitted to thermal treatment in reducing atmosphere present higher amounts of reduced metals, as expected, increasing with treatment temperature. Pt/Ru atomic ratios determined by XPS are similar, and in all cases superior, to the values obtained by XRF, showing a surface particularly enriched in Pt.

**Table 3.** Binding energies of the Pt  $4f_{7/2}$  and Ru  $3p_{3/2}$  signals for catalysts prepared, determined by XPS.

| Sample             | Pt $4f_{7/2}$          |               | Ru $3p_{3/2}$                          |               | Pt/Ru |
|--------------------|------------------------|---------------|--|---------------|-------|
|                    | Species                | Intensity (%) | Species                                | Intensity (%) |       |
| PtRu/CXG- COL      | <i>Pt</i>              | 46.8          | <i>Ru</i>                              | 34.6          | 2.2   |
|                    | <i>PtO</i>             | 44.7          | <i>RuO<sub>2</sub></i>                 | 53.0          |       |
|                    | <i>PtO<sub>2</sub></i> | 8.5           | <i>RuO<sub>2</sub>·xH<sub>2</sub>O</i> | 12.4          |       |
| PtRu/CXG-COL-TT200 | <i>Pt</i>              | 54.2          | <i>Ru</i>                              | 38.2          | 2.2   |
|                    | <i>PtO</i>             | 36.6          | <i>RuO<sub>2</sub></i>                 | 50.2          |       |
|                    | <i>PtO<sub>2</sub></i> | 9.2           | <i>RuO<sub>2</sub>·xH<sub>2</sub>O</i> | 11.6          |       |
| PtRu/CXG-COL-TT400 | <i>Pt</i>              | 63.9          | <i>Ru</i>                              | 48.1          | 1.9   |
|                    | <i>PtO</i>             | 21.1          | <i>RuO<sub>2</sub></i>                 | 44            |       |
|                    | <i>PtO<sub>2</sub></i> | 15            | <i>RuO<sub>2</sub>·xH<sub>2</sub>O</i> | 7.9           |       |

### 2.3. Catalytic Activity towards MOR

Electrochemical surface areas were determined by CO stripping for the three catalysts under study, as shown in Table 4.

**Table 4.** Electrochemical active surface area (ECSA) for PtRu catalysts, determined by CO stripping.

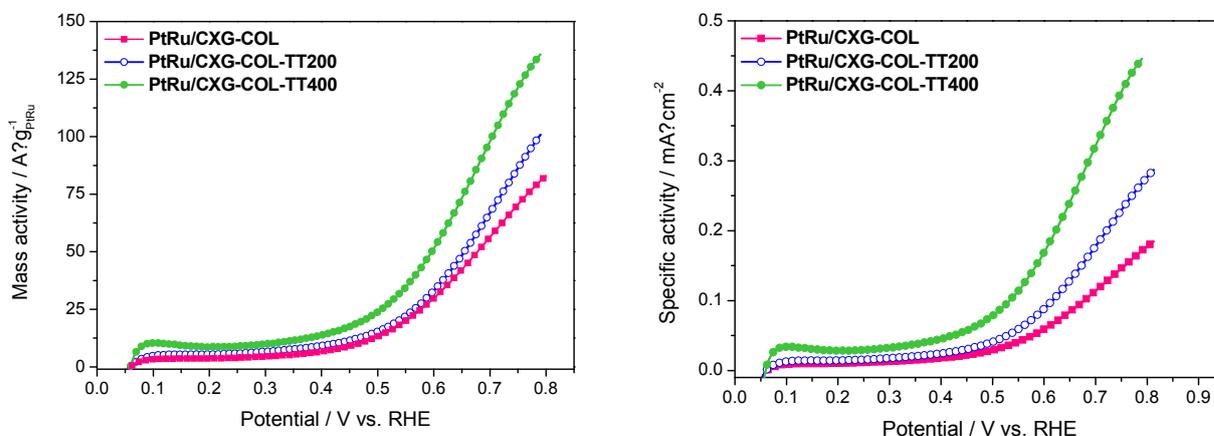
| Sample            | ECSA/m <sup>2</sup> ·g <sup>-1</sup> PtRu |
|-------------------|---|
| PtRu/CXG-COL      | 56.9                                      |
| PtRu/CXG-COLTT200 | 35.9                                      |
| PtRu/CXG-COLTT400 | 30.4                                      |

ECSA decreases when catalysts are submitted to thermal treatment, due to the increase in the particle size and the agglomeration of the metallic particles.

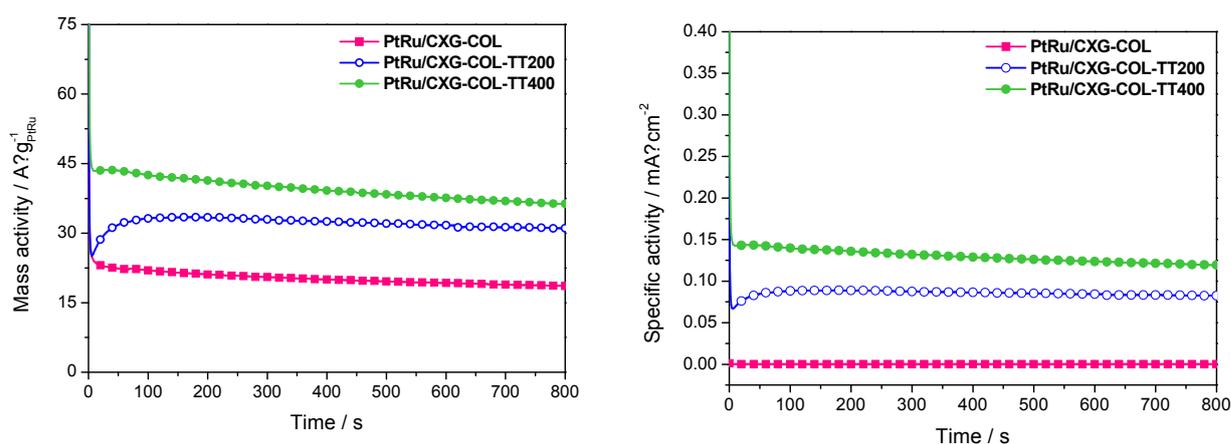
Methanol electro-oxidation polarization curves, obtained at room temperature, are shown in Figure 4. PtRu/CXG-COL-TT400 presents the highest mass activity towards methanol oxidation, as a result of its higher crystal size and amount of reduced metals, Pt<sup>0</sup> and Ru<sup>0</sup>. It is clear that crystal/particle size has a huge influence on the electrocatalytic activity. Methanol electro-oxidation is in fact a structure-sensitive process. Several studies point to a loss of effective surface area as particle size increases, resulting in lower catalytic activity. However, other authors state that there is an optimal particle size for achieving maximal catalytic activity, in a certain system. Frelink *et al.* [24] evaluated different Pt/Vulcan carbon black supported catalysts prepared through different methods and stated that for Pt particle sizes (determined by TEM) in the range 1.2–4.5 nm, a decrease in size resulted in a decrease in methanol oxidation activity, whereas for sizes larger than 4.5 nm, the methanol oxidation activity remained almost constant. They explained this fact in terms of a high affinity towards oxygen of very small particles, resulting in a largely covered Pt-OH surface which left insufficient sites for methanol adsorption. Even if it is also true that higher particle sizes may offer a higher amount of exposed crystal active phases—(111) planes have been claimed to be the most active [25]—differences in catalytic activity towards methanol oxidation may not only be related to the effect of particle size, but also to surface chemistry in the different catalytic systems [26]. Pt and Ru oxidation state can strongly determine the catalytic activity. In fact, Garcia and co-workers [26] proved that the presence of Pt and Ru oxides do not permit the dehydrogenation step, *i.e.*, breaking of C–H bonds, in the molecule of methanol.

The results of chronoamperometric tests of methanol oxidation are shown in Figure 5. The results at constant 0.60 V *vs.* RHE follow the same trend as the one observed in the methanol oxidation polarization curves. The catalyst PtRu/CXG-COL-TT400 shows the highest catalytic activity, followed by the catalyst PtRu/CXG-COL-TT200 and PtRu/CXG-COL; this is, in increasing order of PtRu particle size. Taking into account the decrease of electrochemical surface area from both the increase of PtRu particle size and the slight degree of agglomeration, the increase of MOR activity is attributed to the better intrinsic activity of the biggest particles, in this study 2.0 nm according to XRD and 3.1 nm according to TEM analysis [26].

**Figure 4.** Polarization curves for the electro-oxidation of methanol in a 2 M CH<sub>3</sub>OH + 0.5 M H<sub>2</sub>SO<sub>4</sub> solution at room temperature for the PtRu carbon-supported catalysts. Scan rate = 0.02 V s<sup>-1</sup>.



**Figure 5.** Current density vs. time curves recorded in a 2 M CH<sub>3</sub>OH + 0.5 M H<sub>2</sub>SO<sub>4</sub> solution at room temperature for the PtRu carbon-supported catalysts at  $E = 0.60$  V vs. RHE.



### 3. Experimental Section

#### 3.1. Carbon Xerogel Synthesis

CXG was synthesized as described in [27] by the pyrolysis at 800 °C of an organic gel obtained by the polycondensation of resorcinol and formaldehyde in stoichiometric ratio (2 mol of formaldehyde per mol of resorcinol). The gelation and curing process took place at an initial pH of 6.0 and using sodium carbonate as catalyst (0.04 mol% with respect to total content of resorcinol + formaldehyde). Curing of the organic gel was carried out for 24 h at room temperature, 24 h at 50 °C and 120 h at 85 °C. Subsequently, remaining water was exchanged with acetone and the gel was dried under subcritical conditions before its pyrolysis. Pyrolysis took place at 800 °C under a nitrogen atmosphere for 3 h.

### 3.2. Catalysts Preparation

PtRu nanoparticles were deposited on the synthesized carbon xerogels by the sulfite complex method (a type of colloidal method) never reported before for carbon xerogels. A 20 wt.% nominal metal concentration on CXGs was chosen. Sulfite complexes of Pt and Ru, in appropriate amounts, were decomposed by hydrogen peroxide to form aqueous colloidal solutions of Pt-Ru oxides. These particles were adsorbed on CXGs. The amorphous oxides on CXGs were thus reduced in a hydrogen stream to form metallic particles. The reduction process was considered complete when no significant H<sub>2</sub> consumption was detected in the outlet stream by using a thermal conductive detector (TCD). Two aliquots of this catalyst were further treated in hydrogen atmosphere at 200 °C and 400 °C for 1 h, with the aim of evaluating the effect of this thermal and reducing treatment in the features of the catalysts, mostly in terms of increased metallic crystal size. These catalysts were named PtRu/CXG-COL-TT200 and PtRu/CXG-COL-TT400, respectively.

### 3.3. Physico-Chemical Characterization

The textural and morphological features of the different carbon supports and catalysts prepared were determined by means of nitrogen physisorption at −196 °C (Micromeritics ASAP 2020). Textural properties such as specific surface area, pore volume and pore size distribution were calculated from each corresponding nitrogen adsorption-desorption isotherms applying the Brunauer-Emmet-Teller (BET) equation, Barrett-Joyner-Halenda (BJH) and t-plot methods. Thermogravimetric complete oxidation in air of both the carbon support and PtRu catalysts was used to determine the total amount of metal deposited, in a Setaram Setsys evolution thermogravimetric analyzer at atmospheric pressure, with a temperature program from room temperature to 950 °C with a constant rate of 5 °C min<sup>−1</sup>. X-ray fluorescence (XRF) measurements were also used to determine the Pt:Ru atomic ratio, by using a Bruker AXS S4 Explorer spectrometer. Catalysts were as well characterized by X-Ray Diffraction (XRD), using a Bruker AXS D8 Advance diffractometer, with a  $\theta$ - $\theta$  configuration and using Cu-K $\alpha$  radiation. Crystallite sizes were calculated from the Scherrer's equation on the (220) peak for platinum. X-ray photoelectron spectrometry (XPS) analysis were performed using a 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. C 1s (280–295 eV), O 1s (526–540 eV) and Pt 4f (65–84 eV) signals were obtained at 0.1 eV step, 0.5 s dwell and 20 eV pass energy. Spectra were deconvoluted using CasaXPS software. Particle sizes were evaluated from TEM images obtained in a JEOL 2100F microscope operated with an accelerating voltage of 200 kV and equipped with a field emission electron gun providing a point resolution of 0.19 nm. The standard procedure involved dispersing 3 mg of the sample in ethanol in an ultrasonic bath for 15 min. The sample was then placed in a Cu carbon grid where the liquid phase was evaporated.

### 3.4. Electrochemical Experiments

A cell with a three-electrode assembly and an AUTOLAB potentiostat-galvanostat were used to carry out the electrochemical characterization. The counter electrode consisted on a pyrolytic graphite rod, while the reference electrode was a reversible hydrogen electrode (RHE). Therefore, all potentials in

the text are referred to the latter. The working electrode consisted of a pyrolytic graphite disk (7 mm) with a thin layer of the electrocatalyst under study deposited onto it. For the preparation of this layer, an aqueous suspension consisting of 3.6 mg of PtRu/CXG catalyst was obtained by ultrasonically dispersing it in Nafion solution 10% w/w (Sigma-Aldrich, St. Louis, MO, USA) (14.7  $\mu\text{L}$ ) and a mixture of ultrapure water (240  $\mu\text{L}$ ) (Millipore) and ethanol (240  $\mu\text{L}$ ) (Merck). Subsequently an aliquot of 40  $\mu\text{L}$  of the dispersed suspension was deposited on top of the graphite disk and dried under inert atmosphere prior its use.

Polarization curves were performed to study the electro-oxidation of methanol, in a 2 M  $\text{CH}_3\text{OH}$  + 0.5 M  $\text{H}_2\text{SO}_4$  solution, at scan rate of 20  $\text{mV}\cdot\text{s}^{-1}$ , between 0.05 and 0.8 V vs. RHE. Chronoamperometries were performed at 0.60 V vs. RHE in a 2 M  $\text{CH}_3\text{OH}$  + 0.5 M  $\text{H}_2\text{SO}_4$  solution, in order to evaluate the evolution of the electrocatalytic activity with time of the prepared catalysts in the electro-oxidation of methanol. All the experiments were carried out at room temperature, and current was normalized with respect to each catalyst metal amount (A/g PtRu).

#### 4. Conclusions

PtRu nanoparticles were deposited on a highly mesoporous carbon xerogel for the first time by a sulfite complex method. Thermal treatments at 200 °C and 400 °C in  $\text{H}_2$  for 1 h were carried out, in order to increase the crystal size. This sulfite complex method led to catalysts with low crystal sizes (from 1.6 to 2.0 nm). Thermal treatment proved to be effective increasing the catalysts crystal size and the extent of metallic phase reduction.

It was observed, by means of XRF and XPS, that Pt segregated towards the surface of the metallic crystallites deposited on the carbon xerogel.

A certain extent of pore blockage was observed upon the loading of the active phase, but catalysts still maintained the initial mesopore-enriched structure of the carbon xerogel.

Methanol electro-oxidation was found to be dependent mainly on the crystal size and the extent of reduced metals ( $\text{Pt}^0$  and  $\text{Ru}^0$ ) on the composition of the catalyst. The most active catalysts were those treated at 400 °C, PtRu/CXG-COL-TT400, with the highest crystal size and the highest amount of reduced metals. The high segregation extent of Pt towards the surface of the particles/crystallites deposited, on the surface of the carbon xerogel, may have resulted in an optimal combination of Pt and Ru atoms enhancing the progress of the different controlling steps of methanol electro-oxidation mechanism at room temperature; starting from methanol dehydrogenation and completing the oxidation of the intermediate  $\text{CO}_{\text{ads}}$  species by means of nearby  $\text{OH}_{\text{ads}}$  on Ru sites.

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## Conflicts of Interest

The authors declare no conflict of interest.

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