

Preparation of PtRu/Carbon Hybrids by Hydrothermal Carbonization Process

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PtRu/Carbon hybrids were prepared by hydrothermal carbonization process using glucose or starch as carbon sources and reducing agents and platinum and ruthenium salts as catalysts of carbonization process and metals source. The obtained PtRu/Carbon materials were characterized by SEM/EDX, TGA, XRD and cyclic voltammetry. The electro-oxidation of methanol was studied by cyclic voltammetry using the thin porous coating technique aiming fuel cell application. The catalytic activity was dependent of carbon source and time used in the synthesis.

Keywords: glucose, starch, hydrothermal carbonization, electrocatalyst, fuel cell

1. Introduction

Fuel cells employing directly alcohols as fuel (Direct Alcohol Fuel Cell – DAFC) are very attractive as power source for portable, mobile and stationary applications. The alcohol is fed directly into the fuel cell, without any previous chemical modification or purification and it is oxidized at the anode while oxygen is reduced at the cathode. This characteristic avoids problems related to production, purification and storage of hydrogen¹⁻⁵.

The methanol has been considered the most promising alcohol, because it is more efficiently oxidized than others alcohols due the low complexity of its molecular structure. PtRu nanoparticles supported on carbon (PtRu/C electrocatalyst) has been considered the best electrocatalyst for methanol electro-oxidation. The catalytic activity of PtRu/C electrocatalysts is strongly dependent on the method of preparation and it is one of the major topics studied in Direct Methanol Fuel Cells (DMFC)⁶⁻⁸.

Studies have been shown that the use of carbon nanotubes and mesoporous carbon as support increase the performance of the PtRu/C electrocatalysts, however, the synthesis of these supports are normally complex or involve harsh conditions⁹⁻¹¹. Recently, the synthesis of metal/carbon nanoarchitectures by a one-step and mild hydrothermal carbonization process was reported using starch or glucose and metals salts¹²⁻¹⁴.

In this work, PtRu/Carbon materials with Pt:Ru atomic ratio of 50:50 were prepared by hydrothermal carbonization process¹²⁻¹⁴ and tested as electrocatalysts for methanol electro-oxidation aiming fuel cell applications.

2. Experimental

PtRu/Carbon materials were prepared by hydrothermal carbonization process using $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (Aldrich), $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (Aldrich), glucose (Aldrich) and starch (Aldrich). An aqueous solution of glucose or starch was mixed with an amount of noble metals salts (glucose or starch/PtRu molar ratio of 82). Then, the solution was submitted to hydrothermal treatment at 200 °C for different times in a 110 mL capacity Teflon-lined stainless steel autoclave. The ob-

tained solids were filtered, washed with ethanol and water and dried at 100 °C for 2 hours. The materials were thermally treated under argon atmosphere initially at 550 °C for 4 hours and after this period at 900 °C for 3 hours.

The XRD analyses were performed using a Rigaku diffractometer model Multiflex using Cu K α radiation source ($\lambda = 0.15406$ nm).

The atomic ratios were obtained by EDX analysis using a scanning electron microscope Phillips XL30 with a 10 and 20 keV electron beam and equipped with EDAX DX-4 microanaliser.

The carbonization yield (wt. (%)) was calculated considering that all carbon atoms of glucose or starch were converted on a carbeneous structure.

The PtRu metal loading (wt. (%)) was determined by thermogravimetric analysis (TGA) using a Shimadzu D-50 instrument and platinum pans. Heating rate of 5 °C/min was employed under dry oxygen (20 mL/min)¹⁵.

Electrochemical studies of electrocatalysts were carried out using the thin porous coating technique^{5,16,17}. An amount of 20 mg of the electrocatalyst was added to a solution of 50 mL of water containing 3 drops of a 6% solution polytetrafluoroethylene (PTFE) suspension. The resulting mixture was treated in an ultrasound bath for 10 minutes, filtered and transferred to the cavity (0.40 mm deep and 0.47 cm² area) of the working electrode. The quantity of electrocatalyst in the working electrode was determined with a precision of 0.0001 g. In voltammetry cyclic experiments the current values (I) were expressed in amperes and were normalized per gram of platinum (A/g_{Pt}). The quantity of platinum was calculated considering the mass of the electrocatalyst present in the working electrode multiplied by its percentage of platinum. The reference electrode was a RHE and the counter electrode was a platinized Pt plate. Electrochemical measurements were made using a Microquimica (model MQPG 01, Brazil) potentiostat/galvanostat coupled to a PC and using the Microquimica software. Cyclic voltammetry was performed in a 0.5 mol.L⁻¹ H₂SO₄ and 0.1, 0.5 and 1.0 mol.L⁻¹ methanol in 0.5 mol.L⁻¹ H₂SO₄ solutions saturated with N₂. For comparative purposes a commercial PtRu/C

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E-TEK (20 wt. (%), Pt:Ru molar ratio 50:50, Lot # B0011117) was used.

3. Results and Discussion

PtRu/Carbon materials were prepared by hydrothermal carbonization process using glucose or starch acts as the carbon sources and reducing agents, and platinum and ruthenium salts as catalysts for the carbonization process and source of the metals to be encapsulated¹². When starch was used as carbon source, its partial hydrolysis leads to glucose units, which acts as reducing agent for noble metals¹². The carbonization yield using glucose and starch as carbon sources reached 78 and 68 wt. (%), respectively, after 6 hours of reaction time. Using starch as carbon source and increasing the reaction time to 12 hours the carbonization yield increased to 90 wt. (%). The PtRu/Carbon materials as-synthesized did not show any activity for methanol electro-oxidation probably due to an incompletely polymerization and carbonization of the carbon sources in the reaction conditions¹². In order to obtain a graphitic structure, the materials were further treated at 900 °C and a weight loss of 51 and 52% were observed for materials prepared using glucose and starch after 6 hours of reaction time, respectively. A weight loss of 59% was observed for the material prepared using starch after 12 hours of reaction time. After thermal treatment at 900 °C the Pt:Ru atomic ratios of the obtained materials, determined by EDX analysis, were similar to the nominal atomic ratios used in preparations (Table 1). The PtRu loading (wt. (%)), determined by TGA analysis¹⁵, showed the presence of 5 wt. (%) of metals for materials prepared using glucose and starch after 6 hours of reaction time and 7 wt. (%) for the material prepared using starch after 12 hours of reaction time (Table 1 and Figure 1).

The X ray diffractograms of PtRu/Carbon materials as-synthesized and after thermal treatment were shown in Figure 2. The diffractograms of as-synthesized materials showed a broad peak at about $2\theta = 20^\circ$ associated to the carbon material. The material prepared using glucose showed peaks at about $2\theta = 40^\circ$, 47° , 67° and 82° , that are associated to the (111), (200), (220) and (311) planes, respectively, of the fcc structure of platinum and platinum alloys^{18,19}. The materials prepared using starch as carbon source showed the peaks corresponding to fcc structure broader than the ones observed for the material prepared using glucose, which suggest that the metal nanoparticles formed in these materials were smaller than the one formed in the material prepared using glucose (Figure 2a). After thermal treatment (Figure 2b) in all diffractograms the peak corresponding to the carbon material was shifted to higher 2θ angle and the peaks corresponding to fcc structure of Pt and Pt alloys become narrow and sharp indicating an increase of the average nanoparticle size. The (220) reflections of Pt (fcc) crystalline structure were used to calculate the average nanoparticle size according to Scherrer formula¹⁸ and the calculated values are in the range of 9-11 nm (Table 1). After thermal treatment it was also observed in all diffractograms a peak at about $2\theta = 44^\circ$ attributed to a separated ruthenium phase¹⁹. SEM images revealed the materials have morphology of spheres for all prepared samples (Figure 3).

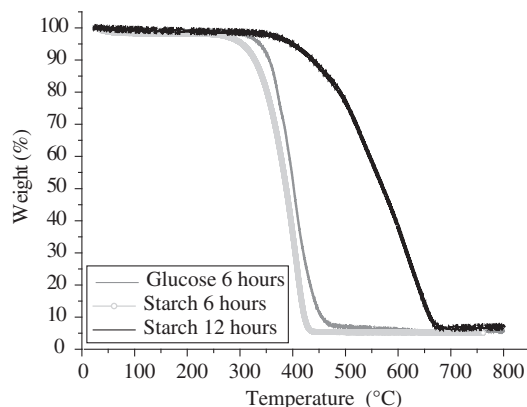


Figure 1. Thermogravimetric analysis of PtRu/Carbon materials after thermal treatment under dry oxygen (20 mL/min) and heating rate of 5 °C/min.

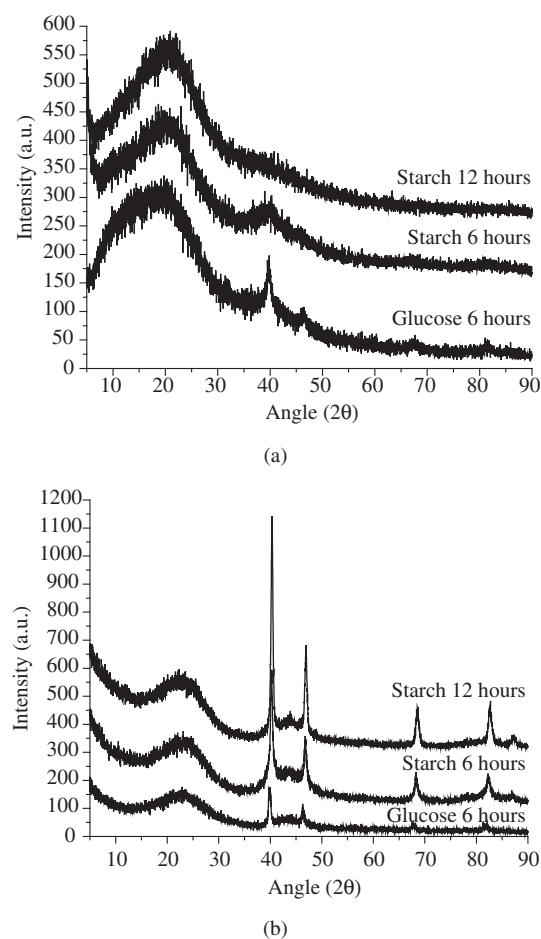
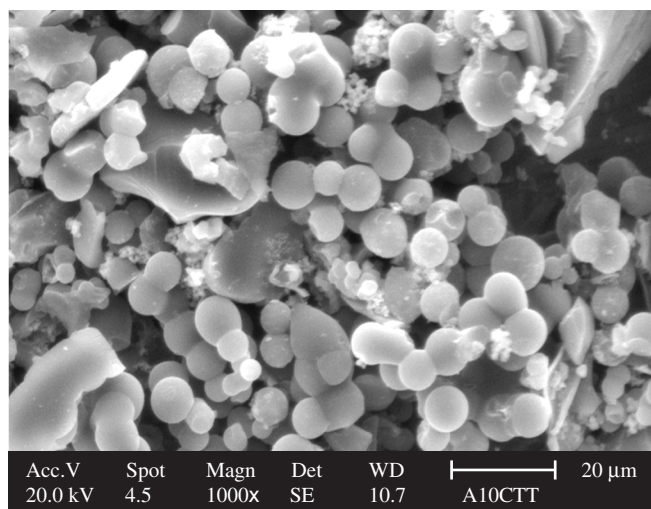


Figure 2. X ray diffractograms of PtRu/Carbon materials (a) as-synthesized and (b) after thermal treatment.

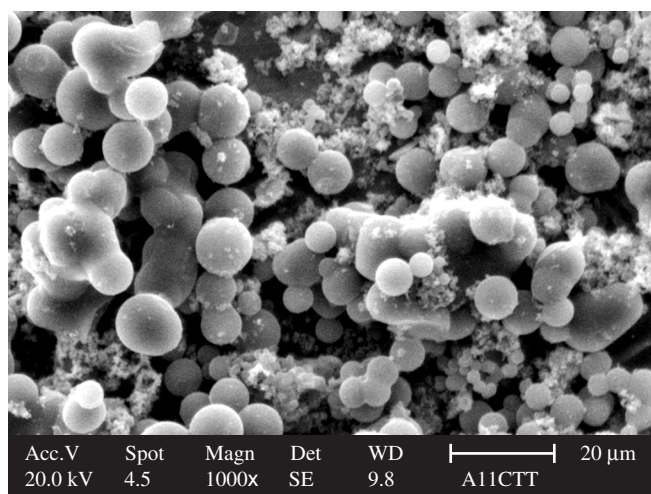
Table 1. Pt:Ru atomic ratios, average particles size and PtRu metal loading of PtRu/Carbon materials (200 °C, glucose or starch/PtRu molar ratio of 82 and Pt:Ru nominal atomic ratio of 50:50).

Carbon source	Synthesis time (h)	Carbonization yield (%) ¹	Atomic ratio Pt:Ru – EDX ²	PtRu Metal loading (wt. (%)) ²	Particle size (nm) ^{2,3}
Glucose	6	78	44:56	5	9
Starch	6	68	39:61	5	11
Starch	12	90	48:52	7	11

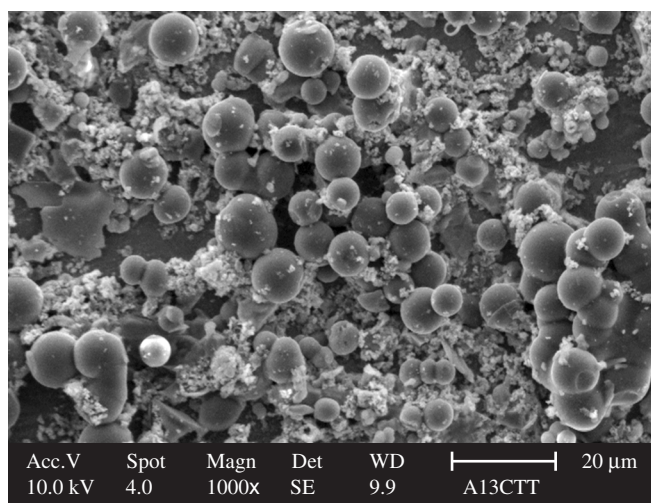
¹as-synthesized; ²after thermal treatment; and ³ average particle size calculated from XRD using Scherrer equation.



(a)



(b)



(c)

Figure 3. SEM micrographs of PtRu/Carbon materials after thermal treatment a) glucose 6 hours; b) starch 6 hours; and c) starch 12 hours.

The cyclic voltammograms of PtRu/Carbon materials in sulfuric acid medium are shown in Figure 4. For all materials the cyclic voltammograms do not have a well-defined hydrogen adsorption-desorption region (0 – 0.4 V), as observed for materials with Pt:Ru atomic ratio of 50:50⁸. The currents in the double layer (0.4 – 0.8 V) are larger for materials prepared using starch as carbon source, suggesting the presence of more oxide species on the nanoparticles surface⁸. The electro-oxidation of methanol was studied varying the concentration from 0.1 to 1.0 mol.L⁻¹ (Figure 5). In a general manner, for all samples in the hydrogen region (0-0.2 V), the currents values decrease with the increase of methanol concentration probably due to the increase of methanol adsorption on the surface⁸. For potentials more positive than 0.25 V, the currents values increase with methanol concentration, even for 1.0 mol.L⁻¹.

The PtRu/Carbon materials performances in methanol oxidation are shown in Figure 6. The anodic cyclic voltammetry responses were plotted after subtracting the background currents^{1,16,17} and the currents values were normalized per gram of platinum, considering that methanol adsorption and dehydrogenation occur only on platinum sites at ambient temperature¹. The electro-oxidation of methanol started at approximately 0.25 V for the materials prepared by hydrothermal carbonization while for the commercial electrocatalyst it started at 0.30 V. The material prepared using starch and 6 hours of reaction time showed the best performance in the potential range of interest for direct methanol fuel cell (0.2 – 0.6 V).

4. Conclusions

The hydrothermal carbonization process using starch or glucose as carbon sources produces active PtRu/Carbon materials for methanol electro-oxidation. The Pt:Ru atomic ratios observed in the obtained materials were similar to the nominal atomic ratios used in the preparations. The X ray diffractograms of obtained materials showed the typical fcc structure of platinum and platinum alloys. The materials as-synthesized did not show electrocatalytic activity probably due to an incompletely polymerization and carbonization of the carbon sources in the reaction conditions. After thermal treatment an increase of the average nanoparticle size occurs and a peak at about $2\theta = 44^\circ$ attributed to a ruthenium phase appears. The material prepared using starch and 6 hours of reaction time showed the best performance in the potential range of interest for direct methanol fuel cell (0.2 – 0.6 V). Further work is however necessary to study the

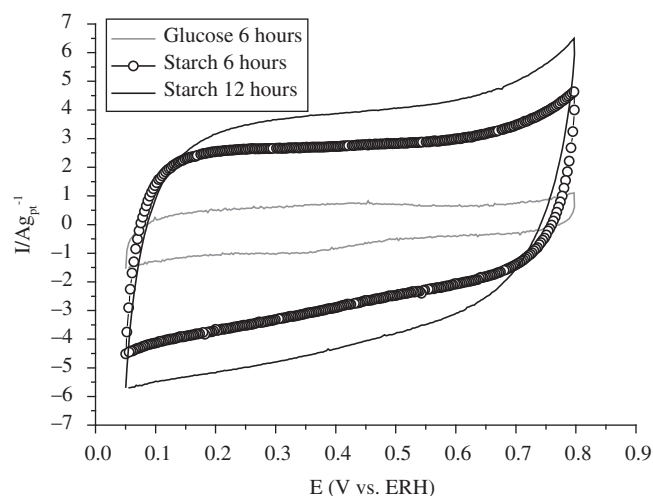
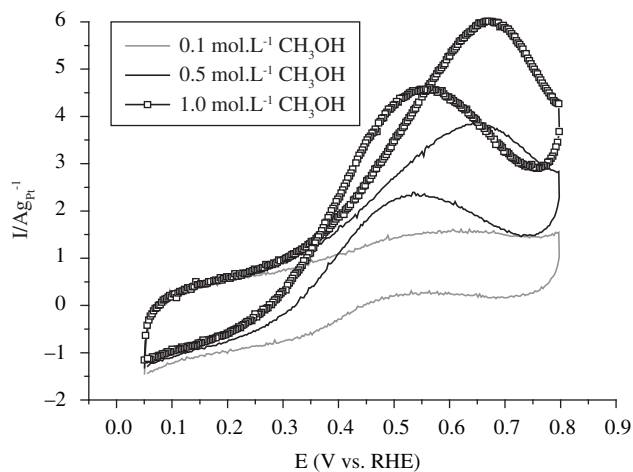
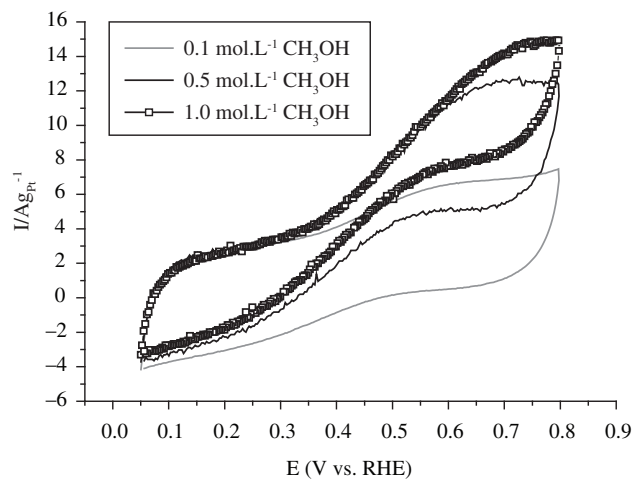


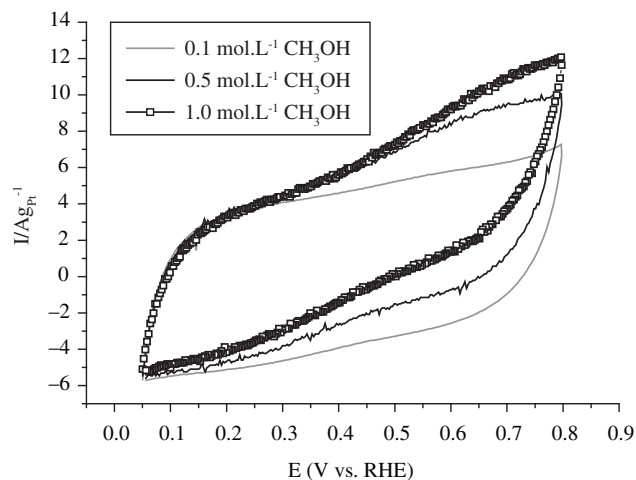
Figure 4. Cyclic voltammograms of PtRu/Carbon materials in 0.5 mol.L⁻¹ H₂SO₄ with a sweep rate of 10 mV.s⁻¹.



(a)



(b)



(c)

Figure 5. Cyclic voltammograms of PtRu/Carbon materials in $0.5 \text{ mol.L}^{-1} \text{ H}_2\text{SO}_4$ and different concentrations of methanol with a sweep rate of 10 mV.s^{-1} : a) glucose 6 hours; b) starch 6 hours; and c) starch 12 hours.

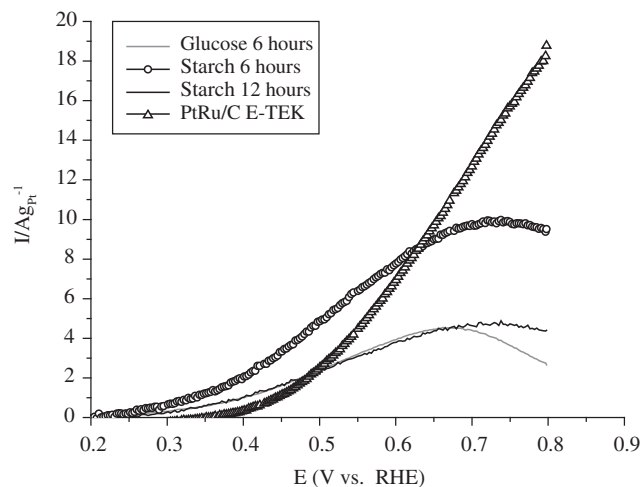


Figure 6. Cyclic voltammograms of PtRu/Carbon materials in $0.5 \text{ mol.L}^{-1} \text{ H}_2\text{SO}_4$ containing 1.0 mol.L^{-1} of methanol with a sweep rate of 10 mV.s^{-1} , considering only the anodic sweep.

synthesis conditions in more details and to characterize the obtained materials by other techniques like transmission electron microscopy and chronoamperometry.

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