

Synthesis and characterization of PtRu/Carbon hybrids with different metallic load by hydrothermal carbonization method

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RESUMO

Híbridos PtRu/Carbono com diferentes cargas metálicas (5, 10 e 20% em massa) foram preparados por carbonização hidrotérmica utilizando celulose como fonte de carbono e agente redutor e $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ e $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ como fontes de metais e catalisadores do processo de carbonização. Os materiais como-sintetizados foram tratados sob atmosfera de Argônio a 900 °C e caracterizados por espectroscopia por energia dispersiva de raios-X, análise termogravimétrica, difração de raios-X, microscopia eletrônica de transmissão e voltametria cíclica em meio ácido. A eletro-oxidação do metanol foi estudada por cronoamperometria. O material preparado utilizando uma carga metálica de 5% em massa apresentou a melhor eletroatividade para a eletro-oxidação do metanol comparado aos outros materiais provavelmente devido ao menor tamanho de partículas e conteúdo de óxidos superficiais.

Palavras-chave: Eletrocatalisadores; Eletro-oxidação do metanol; Células a combustível

ABSTRACT

PtRu/Carbon hybrid materials with different metallic loadings (5, 10, and 20 wt%) were prepared by hydrothermal carbonization using cellulose as carbon source and reducing agent and $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ as metals sources and catalysts of the carbonization process, respectively. The as-synthesized materials were further treated under argon atmosphere at 900 °C and characterized by energy-dispersive X-ray spectroscopy, thermogravimetric analysis, X-ray diffraction, transmission electron microscopy, and cyclic voltammetry in acidic medium. The electro-oxidation of methanol was studied by chronoamperometry. The material prepared using a metallic load of 5 wt% showed the best electroactivity for methanol electrooxidation compared to other obtained materials probably due to the smaller particle size and content of oxides on the surface of the material.

Keywords: Electrocatalysts; Methanol electro-oxidation; Fuel cells

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1 INTRODUCTION

The use of hydrogen in fuel cells still presents problems associated with the production, delivery, and primarily, storage. Thus, the use of alcohols directly in fuel cells (Direct Alcohol Fuel Cells – DAFC) is attracting interest in mobile and portable applications (GONZALEZ, 2000; WENDT, GÖTZ, LINARDI, 2000; WENDT, LINARDI, ARICÓ, 2004; SPINACÉ, LINARDI, NETO, 2005; NETO et al., 2005). The methanol, due to its low molecular complexity, is efficiently oxidized, presenting promising results. One of the catalytic systems that shows effective results for methanol oxidation is constituted by PtRu nanoparticles supported on carbon (PtRu/C electrocatalyst). The catalytic activity of PtRu/C electrocatalysts is strongly dependent on the method of preparation and is one of the major topics studied in Direct Methanol Fuel Cells (DMFC) (SPINACÉ et al., 2004; ZHOU et al., 2004; LIU et al., 2006). Besides, the use of different carbon supports as nanotubes and mesoporous carbons increases the performance of PtRu/C electrocatalysts. However, the synthesis of these supports is normally complex or involves harsh conditions (LIU et al., 2002; SERP, CORRIAS, KALCK, 2003; PARK et al., 2004; LIU et al., 2006).

Recently, the synthesis of metal/carbon nanoarchitectures by a one-step and mild hydrothermal carbonization process was reported (LIU et al., 2002; YU et al., 2002; SERP, CORRIAS, KALCK, 2003; PARK et al., 2004; QIAN et al., 2006). By this methodology, we prepared PtRu/Carbon materials (Pt:Ru with an atomic ratio of 50:50 and a nominal metallic load of 5 wt%) using different carbohydrates as carbon sources and salts of Pt(IV) and Ru(III). The obtained materials were applied as electrocatalysts for methanol oxidation showing activity (TUSI et al., 2007; TUSI et al., 2011; TUSI et al., 2012). However, studies indicate that electrocatalysts (PtRu/C) with a high metallic load (prepared by other methodologies) favor the methanol oxidation (YAN et al., 2006; MA et al., 2009; WANG et al., 2009; LEE et al., 2010).

In this work, PtRu/Carbon hybrids with different metallic loads (5 wt%, 10 wt%, and 20 wt%) were prepared by hydrothermal carbonization. The obtained materials were characterized by energy-dispersive X-ray spectroscopy (EDX), thermogravimetric

analysis (TGA), X-ray diffraction (XRD), transmission electron microscopy (TEM), and cyclic voltammetry (CV) in acidic medium. The electro-oxidation of methanol was studied by chronoamperometry.

2 MATERIALS AND METHODS

2.1 Synthesis of PtRu/Carbon hybrids

PtRu/Carbon hybrids (Pt:Ru atomic ratio of 50:50 and metallic loads of 5 wt%, 10 wt%, and 20 wt%) were prepared by hydrothermal carbonization (TUSI et al., 2007; TUSI et al., 2011; TUSI et al., 2012) using $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (Aldrich) and $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (Aldrich) as metal sources and catalysts of carbonization process and cellulose (Aldrich) as carbon source and reducing agent, respectively. An aqueous solution of cellulose was mixed with an amount of noble metals salts. The pH of the resulting mixture was adjusted using TPAOH (20 wt% in water) solutions at approximately 11. The solution was then submitted to hydrothermal treatment at 200 °C for 6 h in a 110 mL-capacity Teflon-lined stainless steel autoclave. The obtained solids were filtered, washed with ethanol and water, and dried at 70 °C for 2 h. The materials were heated under argon atmosphere at 900 °C for 3 h aiming the carbon graphitization (SEVILLA, FUERTES, 2006). The carbonization yield (wt%) was determined by the quotient between the experimental yield and the theoretical yield (considering an initial mass of carbon source of 5 g).

2.2 EDX

The Pt:Ru atomic ratios were obtained by EDX using a scanning electron microscope (Phillips XL30) with a 20 kV electron beam equipped with EDX DX-4 microanalyzer.

2.3 TGA

The PtRu metal loading (wt%) was determined by TGA using a Shimadzu D-50 instrument and platinum pans. A heating rate of 5 °C min⁻¹ was employed under dry

oxygen (30 mL min⁻¹) (BATURINA, AUBUCHON, WYNNE, 2006; SELLIN, CLACENS, COUTANCEAU, 2010).

2.4 XRD

The XRD analyses were carried out in a Rigaku model Miniflex II diffractometer using Cu K α radiation ($\lambda=0.15406$ nm). The diffractograms were recorded with 2θ angles in the range of 20–90° with a step size of 0.05° and a scan time of 2 s per step. The average crystallite (d) size was obtained by the application of Scherrer's Eq. (1), where K is a particle-shape-dependent constant (0.9 for spherical particles), λ is the wavelength of the incident radiation (Cu K α), θ is the angle of the (220) peak, and β is the width in radians of the diffraction peak at half height (RADMILOVIĆ, GASTEIGER, ROSS, 1995). The use of peak associated with (220) reflection of Pt_{fcc} is to minimize the contributions of carbon and phases of other elements (RADMILOVIĆ, GASTEIGER, ROSS, 1995).

$$d = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

The fcc lattice parameters of electrocatalysts (a_{fcc}) were calculated using the values of the wavelength of the incident radiation (λ) and angle of Bragg (θ) to the point of higher intensity to the reflection of (220) plane according to Eq. 2:

$$a_{fcc} = \frac{\lambda\sqrt{2}}{\sin \theta} \quad (2)$$

From the values of lattice parameters, the Ru atomic fraction in PtRu alloy was calculated. The dependence of PtRu lattice parameter of unsupported alloy on Ru content follows the Vegard's law (ANTOLINI, CARDELLINI, 2001; ONODERA et al., 2010). For supported alloys, it is difficult to evaluate the degree of alloying, as the lattice constant of pure supported Pt is lower than that of unsupported Pt (due platinum-carbon interactions) and the Ru atomic fraction in fcc alloy is less than the nominal Ru content of the sample. Considering that the dependence of the lattice parameter on

Ru content is the same for supported and unsupported Pt, the lattice constant of carbon-supported PtRu (a_{PtRu}) is calculated by Eq. 3:

$$a_{\text{PtRu}} = a_{\text{Pt}} + kx_{\text{Ru}} \quad (3)$$

where $a_{\text{Pt}} = 3,9155 \text{ \AA}$ is the lattice parameter of pure carbon-supported platinum, $k = 0,124 \text{ \AA}$ is a constant obtained from data related to unsupported alloys and x_{Ru} is the Ru fraction in the alloy (ANTOLINI, CARDELLINI, 2001; ONODERA et al., 2010). Using the values of x_{Ru} calculated by Eq. 3, Ru fraction in the alloy (Ru_{alloy}), called alloy degree, was calculated by Eq. 4:

$$Ru_{\text{alloy}} = \frac{x_{\text{Ru}}}{\left[(1 - x_{\text{Ru}}) (Ru/Pt)_{\text{nominal}} \right]} \quad (4)$$

where $(Ru/Pt)_{\text{nominal}}$ is the Pt:Ru atomic ratio obtained by EDX.

2.5 TEM

TEM was carried out using a JEOL JEM-2100 electron microscope operated at 200 kV. The particle size distributions were determined by measuring 150 nanoparticles from micrographs using Image Tool Software.

2.6 Electrochemical experiments

Electrochemical studies were carried out using the thin porous coating technique (GONZALEZ, 2000; SPINACÉ, LINARDI, NETO, 2005; NETO et al., 2007). An amount of 20 mg of the electrocatalysts was added to a solution of 50 mL of water containing three drops of 6% polytetrafluoroethylene (PTFE) suspension. The mixture was treated in an ultrasound bath for 10 min and transferred to the cavity of the working electrode. The quantity of electrocatalysts in the working electrode was determined with a precision of 0.0001 g.

CV experiments were performed in $1.0 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution saturated with N_2 using an Microquímica potentiostat/galvanostat (model MQPG 01, Brazil), while that of

the time-current curves of the methanol electro-oxidation on obtained hybrids were performed holding the cell potential at -5.4 V vs RHE in $1.0 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution containing

1.0 mol L^{-1} of methanol at room temperature.

3 RESULTS AND DISCUSSION

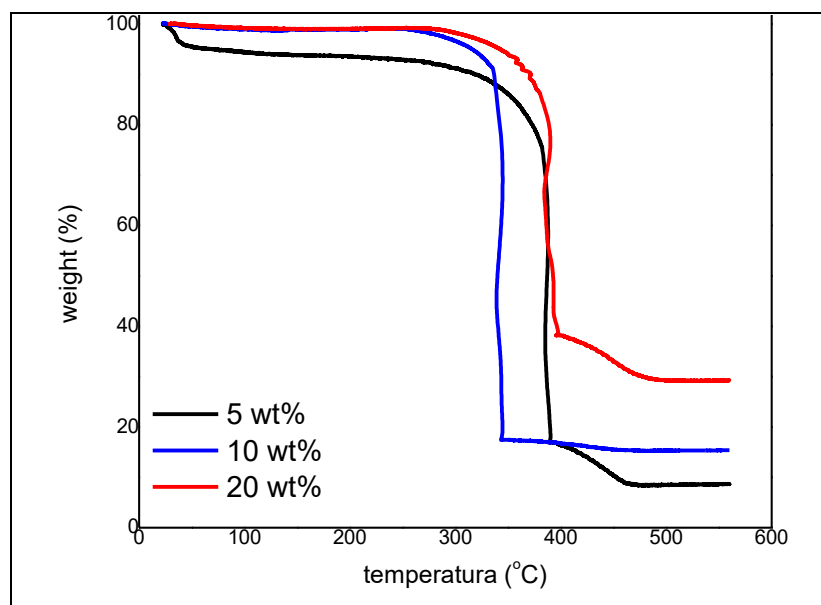
Some data on the characterization of PtRu/Carbon hybrids with different metallic loads are presented in Table 1. The Pt:Ru atomic ratios of the materials after thermal treatment were similar to the nominal ones. The carbonization yields were in the range of 60-66%, indicating that higher metallic loads result in lower carbonization yields, contrary to expectations. The weight loss values were approximately 53-59%, decreasing with the increase in metallic load. This data suggests that a higher content of metals favors the carbonization process and slightly decreases the loss of carbonaceous material (from incomplete carbonization) in thermal carbonization.

Table 1 Pt:Ru atomic ratios, carbonization yields, weight loss after thermal treatments, and metallic loads obtained by TGA of PtRu/Carbon hybrids

Nominal metallic Load (wt%)	Pt:Ru atomic ratio EDX	Carbonization Yield (%)	Weight loss (%)	Metallic load TGA (%)
5	56:44	66	59	6
10	50:50	63	57	15
20	56:44	60	53	29

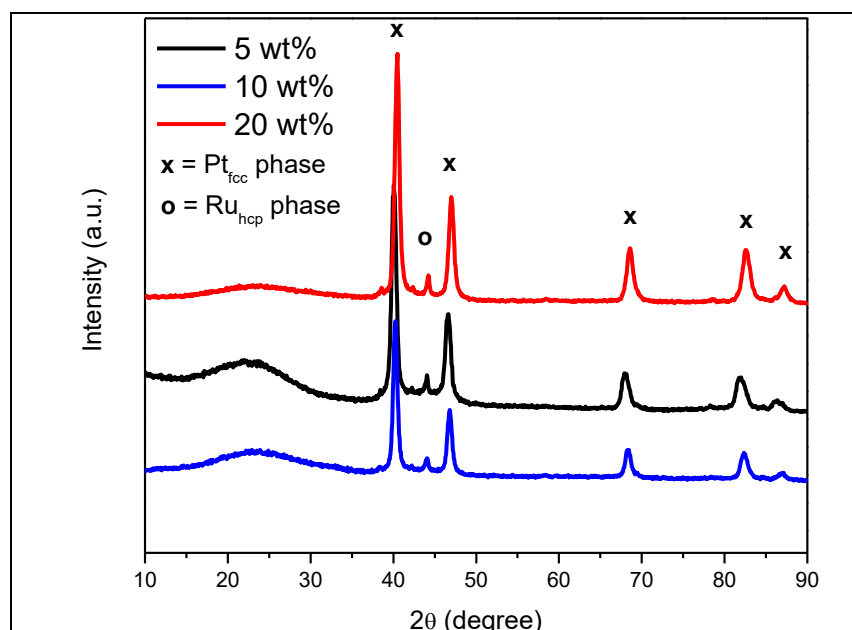
The metallic load values determined by TGA of thermally treated PtRu/Carbon hybrids (Figure 1) presented discrepancies when compared to nominal values, except in the case of materials with a metallic load of 5 wt%. The PtRu/Carbon hybrids with nominal metallic loads of 10 wt% and 20 wt% showed metallic loads approximately 50% higher than the nominal values.

Figure 1 - TGA of PtRu/Carbon hybrids obtained by hydrothermal carbonization and thermal treatment at 900 °C.



The X-ray diffractograms of thermally treated PtRu/Carbon hybrids are presented in Figure 2. All materials showed a broad peak at approximately $2\theta = 23^\circ$ associated to the carbon and five peaks at approximately $2\theta = 40^\circ, 47^\circ, 67^\circ, 82^\circ$, and 87° associated to the (111), (200), (220), (311), and (222) planes, respectively, of the fcc structure of platinum and platinum alloys (RADMILOVIĆ, GASTEIGER, ROSS, 1995; ANTOLINI, CARDELLINI, 2001; LUA, GUO, 2000). All samples also presented a peak at approximately $2\theta = 44^\circ$ attributed to a separated hexagonal close-packed phase of metallic ruthenium (RADMILOVIĆ, GASTEIGER, ROSS, 1995; SIERRA et al., 1995; TUSI et al., 2007). Peaks associated with RuO_2 were not observed, indicating the presence of this compound in the amorphous phase (ANTOLINI, CARDELLINI, 2001; GUO et al., 2005).

Figure 2 - X-ray diffractograms of PtRu/Carbon hybrids with different metallic loads.



The mean particle sizes and the alloy degrees of PtRu/Carbon hybrids with different metallic loads are presented in Table 2.

Table 2 - Mean crystallite size and alloy degrees of PtRu/Carbon with different metallic loads

Nominal metallic load (%)	Mean crystallite size ^{1,2} (nm)	Alloy degree ^{1,3} (%)
5	8	13
10	12	35
20	12	66

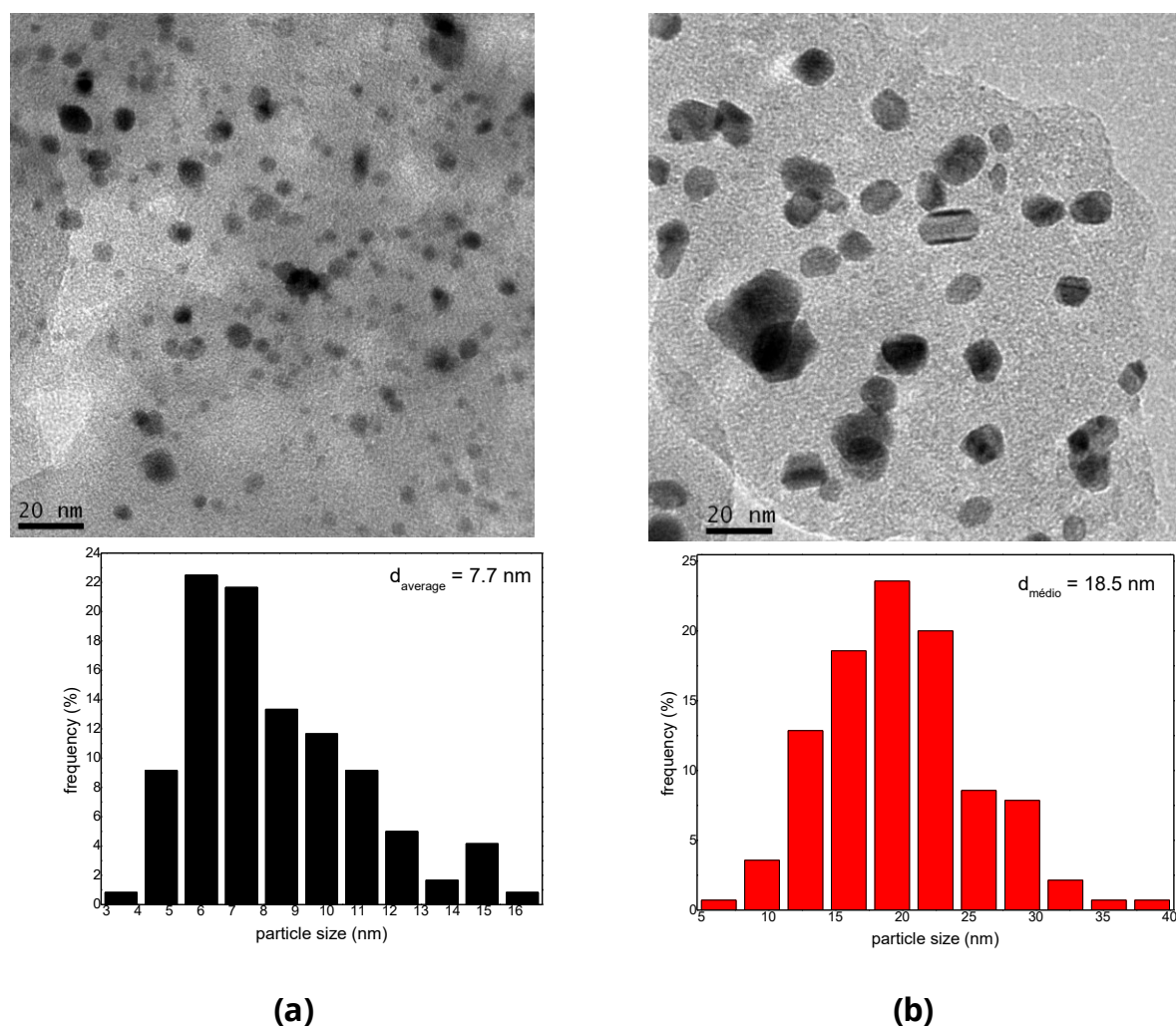
¹after thermal treatment, ²calculated by Scherrer formula, ³calculated by Vegard's law.

The mean crystallite sizes calculated by Scherrer formula were in the range of 8-12 nm, the higher values corresponded to higher metallic loads. The alloy degrees of PtRu/Carbon were in the range of 13 to 66% and the higher values were observed in the materials with a higher metallic load. Such data are in accordance with the related literature about the increase in particle sizes of electrocatalysts with high metallic load (STARZ et al., 1999; RALPH, HOGARTH, 2002).

Images obtained by TEM of PtRu/Carbon hybrids with 5 wt% and 20 wt% of metal loads are presented in Figure 3. The obtained micrographs of PtRu/Carbon hybrids indicate that both materials have a good dispersion of metal nanoparticles on the carbon support. The material PtRu/Carbon (5 wt%) presented a mean particle size of

7.7 nm, while the material with a nominal metallic load of 20 wt% showed a mean particle size of 18.5 nm, indicating that the increase of metallic load results in larger particle sizes.

Figure 3 - Micrographs obtained by TEM of PtRu/Carbon, thermally treated, with nominal metallic load of (a) 5 wt% e (b) 20 wt%



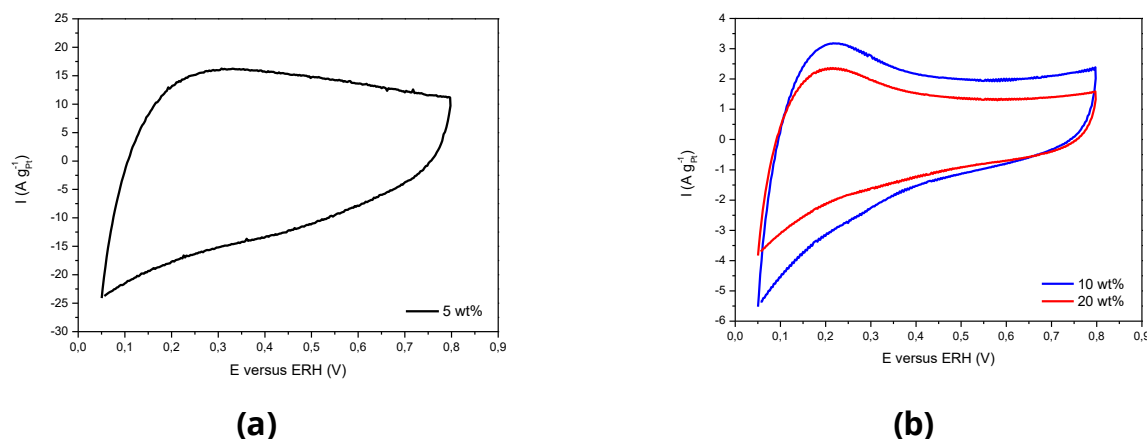
The CV of PtRu/Carbon hybrids in 0.5 mol L⁻¹ H₂SO₄ solution is presented in Figure 4a and b. The current values were normalized per gram of Pt, considering that the adsorption and dehydrogenation of methanol, at room temperature, occur only on the Pt sites (SPINACÉ, LINARDI, NETO, 2005; KIRUBAKARAN, JAIN, NEMA, 2009). All materials do not have a well-defined hydrogen adsorption-desorption region (0.0-0.4 V) and an increase in currents in the double-layer region (0.4-0.8 V) is characteristic of materials with Pt:Ru atomic ratio of 50:50 (SPINACÉ et al., 2004; TUSI

et al., 2011). The inhibition of hydrogen adsorption-desorption, probably, is due to the incorporation of Ru in the structure of Pt. The increase in the currents in the double-layer region is associated with capacitive currents and redox process of RuO_2 (BANDA et al., 2006; PROFETI et al., 2006). Such an increase in current can be attributed to the transition between Ru(III) and Ru(IV) oxidation states. Due to the different oxidation states of Ru in the range of potentials, Ru oxides are able to adsorb high amounts of OH species during the polarization process. These Ru oxides have oxidation states varied by the exchange of proton with the solution according to Equation 5 (PROFETI et al., 2006; PROFETI, PROFETI, OLIVI, 2009):



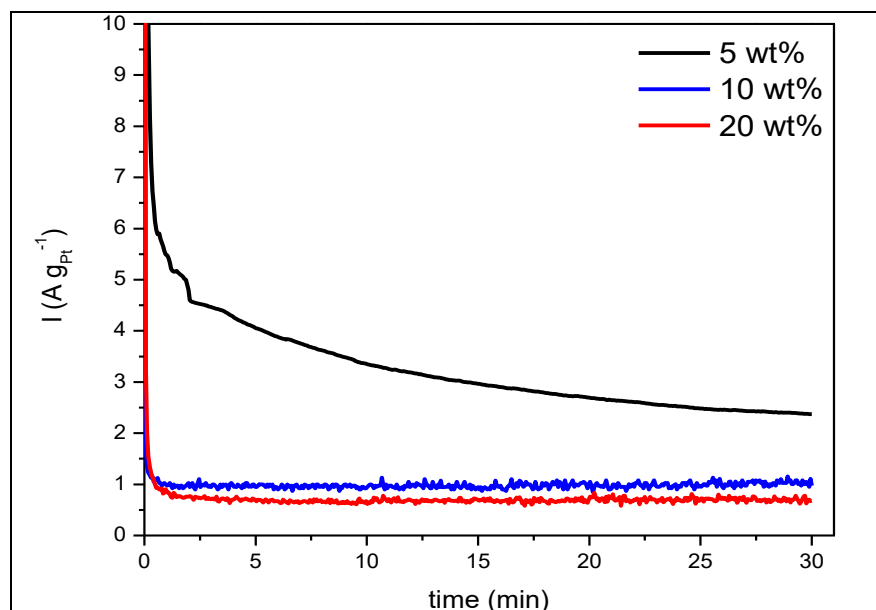
The PtRu/Carbon hybrid 5% presented the higher enlargement in the double-layer region, indicating a higher amount of surface oxides. This data corroborates with the alloy degrees presented in Table I. Apparently, higher amounts of Ru on the surface of materials result in lower definition of the hydrogen adsorption-desorption region and higher enlargement of CV; such data is in accordance with the literature (GOJKOVIĆ, VIDA KOVIĆ, DUROVIĆ, 2003; PROFETI, PROFETI, OLIVI, 2009; TUSI et al., 2011).

Figure 4 - Cyclic voltammetry of PtRu/Carbon in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution and sweep rate of 10 mV s^{-1}



The current-time curves for methanol oxidation on PtRu/Carbon hybrids are presented in Figure 5.

Figure 5 - Current-time curves of methanol electro-oxidation on PtRu/Carbon materials, in 0.5 mol L⁻¹ H₂SO₄ solution containing 1.0 mol L⁻¹ of methanol at 0.5 V for 30 min



The following order of electroactivity to the methanol oxidation was observed: PtRu/Carbon (5 wt%) > PtRu/Carbon (10 wt%) > PtRu/Carbon (20 wt%). Such results can be explained by the crystallite size (STARZ et al., 1999; GAN et al., 2010) and content of segregated Ru (ROLISON et al., 1999; LONG et al., 2000; LU et al., 2005; PROFETI, PROFETI, OLIVI, 2009). The Ru species adsorbed oxygenated species assisting the Platinum in the methanol oxidation process by a bifunctional mechanism (NETO, LINARDI, GONZALEZ, 2003; ROTH et al., 2005; WENDT et al., 2005; LIU et al., 2006; ROTH et al., 2008).

4 CONCLUSION

In this work, PtRu/Carbon hybrids with Pt:Ru atomic ratio of 50:50 and different metallic loads were prepared by the hydrothermal carbonization method. The Pt:Ru atomic ratio of the obtained materials were similar to the nominal values. On the

other hand, the metallic loads, except the material with 5 wt% of metals, presented discrepant values compared to the nominal values. The XRD analysis of these materials showed peaks associated with the Pt_{fcc} and Ru_{hcp} . The mean crystallite sizes were in the range of 8-12 nm and the alloy degrees increased with an increase in the metallic load. The chronoamperometric curves of the methanol oxidation on the PtRu/Carbon materials indicated that the material with a metallic load nominal of 5 wt% presents higher electroactivity possibly due to its smaller crystallite size and higher content of segregated Ru, resulting in a higher amount of surface oxides on the material according to CV data.

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