

Preparation of PtRu/Carbon hybrid materials by hydrothermal carbonization: A study of the Pt:Ru atomic ratio

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Abstract. PtRu/Carbon materials with different Pt:Ru atomic ratios (30:70, 50:50, 60:40, 80:20 and 90:10) and 5 wt% of nominal metal load were prepared by hydrothermal carbonization using $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ as metals sources and catalysts of the carbonization process and starch as carbon source and reducing agent. The obtained materials were treated at 900 °C under argon and characterized by EDX, XRD and cyclic voltammetry. The electro-oxidation of methanol was studied by cyclic voltammetry and chronoamperometry using thin porous coating technique. The PtRu/Carbon materials showed Pt:Ru atomic ratios obtained by EDX similar to the nominal ones. XRD analysis showed that Pt face-cubic centered (fcc) and Ru hexagonal close-packed (hcp) phases coexist in the obtained materials. The average crystallite sizes of the Pt (fcc) phase were in the range of 8-12 nm. The material prepared with Pt:Ru atomic ratio of 50:50 showed the best performance for methanol electro-oxidation.

Introduction

The fuel cells are devices that convert chemical energy directly into electrical energy with high efficiency and low emission of pollutants. The ideal fuel to these devices is the hydrogen, but the production, storage and delivery of this fuel present some problems. Thus, fuel cells employing alcohols directly 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 the problems related to the use of hydrogen [1-5].

Methanol has been considered the most promising fuel because it is more efficiently oxidized than others alcohols due the low complexity of its molecular structure. PtRu/C electrocatalyst (carbon-supported PtRu nanoparticles) has been considered the best electrocatalyst for methanol electro-oxidation. The performances of PtRu/C electrocatalysts are 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 conditions [9-11]. Recently, the synthesis of metal/carbon nanoarchitectures by a one-step and mild hydrothermal carbonization was reported using starch or glucose and metals salts [12-13].

In this work, PtRu/Carbon hybrid materials with Pt:Ru atomic ratios of 30:70, 50:50, 60:40, 80:20 and 90:10 and metal load of 5 wt% were prepared by hydrothermal carbonization process [12-13] and tested as electrocatalysts for methanol electro-oxidation aiming fuel cell applications.

Experimental

PtRu/Carbon materials were prepared by hydrothermal carbonization 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 metals sources and catalysts of carbonization and starch (Aldrich) as carbon source and reducing agent. An aqueous solution starch was mixed with an amount of noble metals salts. The pH of resulting mixture was adjusted using tetrapropylammonium hydroxide (TPAOH - 20 wt% in water) solutions at about 11. Then, the solution was 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 2h. The materials were thermally treated under argon atmosphere at 900°C for 3h.

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

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

The carbonization yield (wt%) was determined by gravimetry considering that all carbon atoms of starch (100 wt%) were converted on a carbonaceous 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⁻¹ was employed under dry oxygen (30 mL min⁻¹) [14].

Electrochemical studies of electrocatalysts were carried out using the thin porous coating technique [5,15,16]. 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 min, 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 0.0001g. In voltammetry cyclic experiments the current values (*I*) were expressed in amperes and were normalized per gram of platinum (A g_{Pt}⁻¹). 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.

Results and Discussion

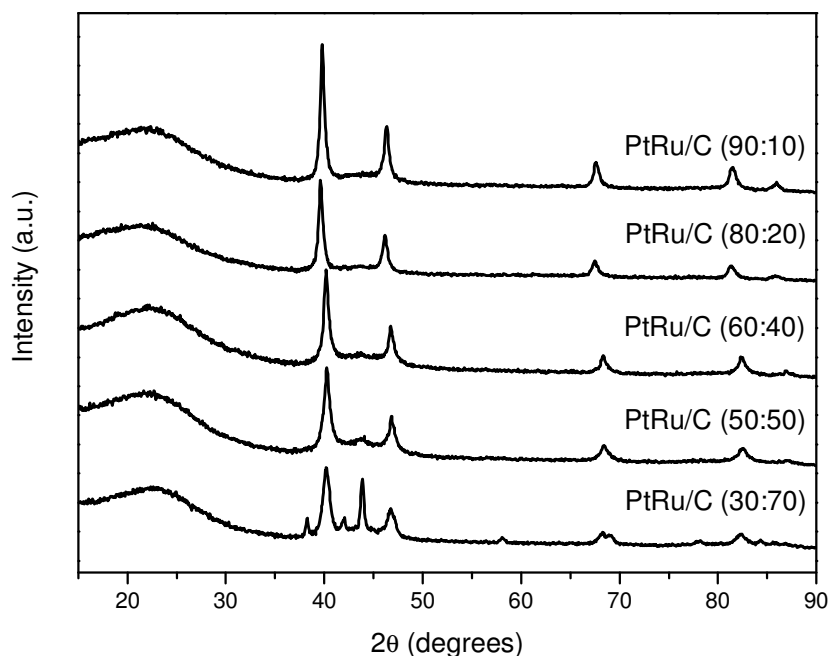
PtRu/C electrocatalysts were prepared by hydrothermal carbonization process using starch as carbon source (Table 1). In the reaction conditions, the starch hydrolyses to glucose units that acts as reducing agent of Pt(IV) and Ru(III) ions, which acts as catalysts of the carbonization process [11]. The carbonization yields of the as-synthesized materials were in the range of 60-70 wt%. After thermal treatment at 900°C a weight loss of 50wt% was observed for all prepared materials. The Pt:Ru atomic ratios of the obtained materials determined by EDX analysis after thermal treatment at 900°C were similar to the nominal ones. The obtained PtRu loadings (wt%) were around 5wt%, which were similar to the nominal value.

Table 1 - Pt:Ru atomic ratios, carbonization yield, weight lost, average crystallite size and PtRu metal load of PtRu/Carbon materials.

Pt:Ru atomic ratio [nominal]	Pt:Ru atomic ratio [EDX] ¹	Carbonization yield [wt%] ²	Weight lost [%] ¹	PtRu metal load [wt%] ¹	Average crystallite size [nm] ^{1,3}
30:70	33:67	74	51	4.3	08
50:50	51:49	71	51	4.8	12
60:40	61:39	74	55	6.1	12
80:20	74:26	62	50	4.7	10
90:10	87:13	63	50	6.0	11

¹ after thermal treatment, ² as-synthesized, ³ calculated from X-ray diffractograms using Scherrer equation.

The X-ray diffractograms of PtRu/Carbon materials after thermal treatment were shown in Fig. 1. The diffractograms of PtRu/C materials showed a broad peak at about $2\theta = 23^\circ$ associated to the carbon material and five peaks at about $2\theta = 40^\circ, 47^\circ, 67^\circ, 82^\circ$ and 87° that are associated to the (111), (200), (220), (311) and (222) planes, respectively, of the fcc structure of platinum and platinum alloys [17,18]. All samples also presented a peak at about $2\theta = 44^\circ$, which increase with the increase of the ruthenium content in the samples. This peak was attributed to a separated hexagonal close-packed (hcp) phase of metallic ruthenium [18]. It was also observed for the material prepared with Pt:Ru atomic ratio of 30:70 other two peaks at about $2\theta = 38^\circ$ and 58° of Ru (hcp) structure. The (220) reflections of Pt (fcc) crystalline structure were used to calculate the average nanoparticle size according to Scherrer formula [17] and the calculated values are in the range of 8-12 nm (Table 1). Thus, it was observed the presence of Pt(fcc) and Ru(hcp) phases for all prepared materials.

**Figure 1** – X-ray diffraction of PtRu/C hybrid materials after thermal treatment under argon atmosphere at 900 °C.

The cyclic voltammograms (CV) of PtRu/Carbon materials in acid medium are shown in Fig. 2.

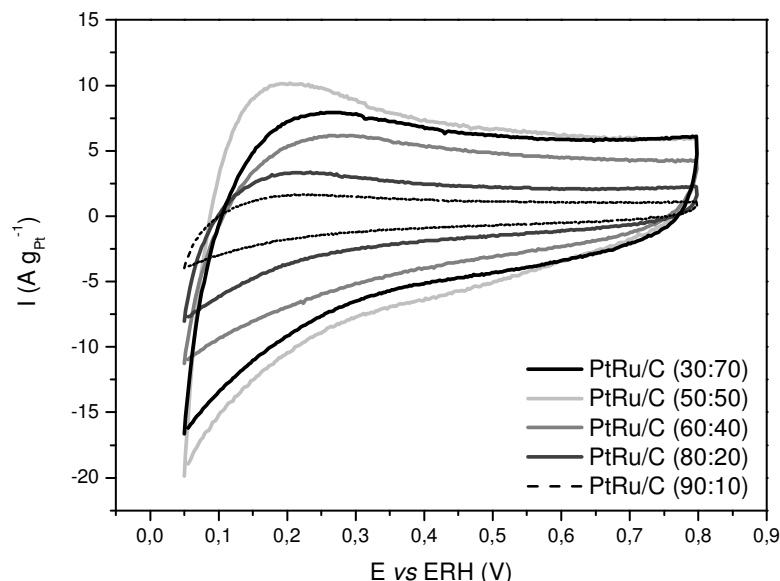


Figure 2 - Cyclic voltammograms of PtRu/Carbon materials in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ with a sweep rate of 10 mV s^{-1} .

For all materials the CVs do not have a well-defined hydrogen adsorption-desorption region (0.05-0.4V) and the currents in the double layer (0.4-0.8V) increase with the increase of the ruthenium content in the samples. The increase of the currents in the double layer could be attributed to the increase of the Ru oxide species on the surface [8].

The PtRu/Carbon materials performances in methanol oxidation were studied by cyclic voltammetry and chronoamperometry and the results are shown in Fig. 3 and 4, respectively.

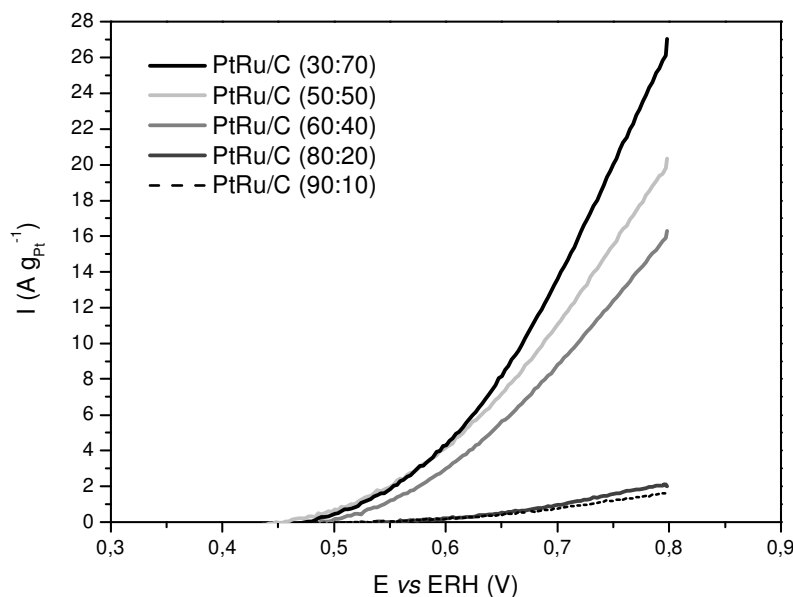


Figure 3 – Cyclic voltammograms of PtRu/Carbon materials in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ containing 1.0 mol L^{-1} of methanol with a sweep rate of 10 mV s^{-1} , considering only the anodic sweep.

The anodic cyclic voltammetry responses (Fig. 3) were plotted after subtracting the background currents [1,15,16] and the currents values were normalized per gram of platinum, considering that methanol adsorption and dehydrogenation occur only on platinum sites at ambient temperature [1]. The electro-oxidation of methanol started in the range of 0.45 – 0.55 V and an increase of current values was observed with the increase of Ru content in samples. Gasteiger *et al.* [19] using well characterized PtRu alloys surfaces described that the activity of Ru towards the dissociative adsorption of methanol was a strong function of temperature. It was found that the optimum surface had an Ru content which increased with increasing temperature, from close to 10 atomic percent of Ru at 25°C to a value in the vicinity of 30 at 60°C. Thus, contrary to the observed for PtRu alloys, our materials that contain Pt(fcc) and Ru(hcp) phases showed good activities for methanol oxidation at room temperature increasing the Ru content. This showed that the performances of PtRu/C electrocatalysts are strongly dependent on the method of preparation [6-8].

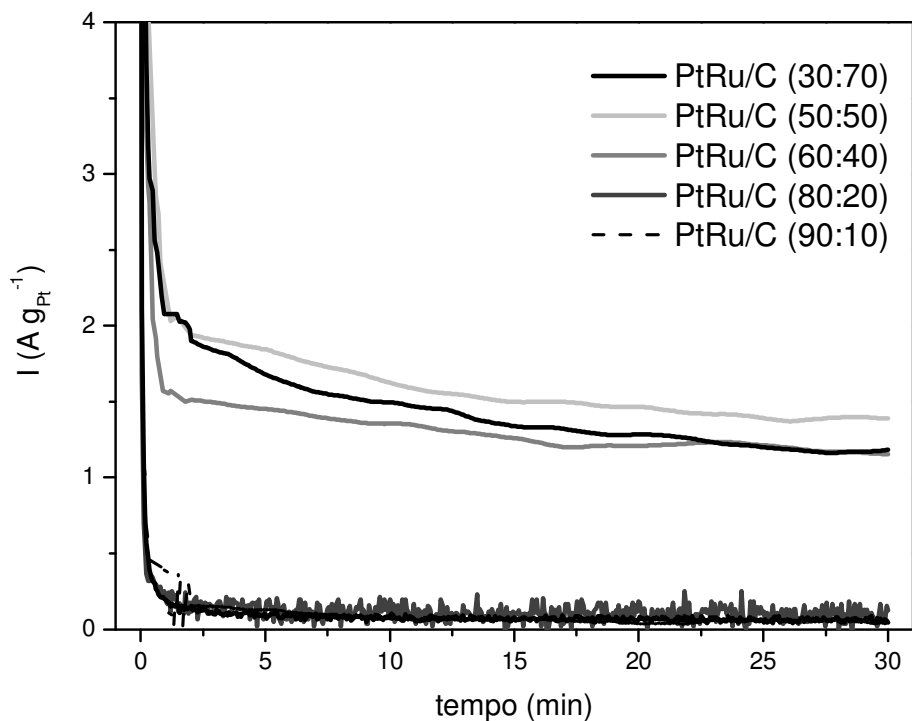


Figure 4 - Chronoamperometry of PtRu/Carbon materials in 0,5 mol L⁻¹ H₂SO₄ containing 1.0 mol L⁻¹ of methanol with a fixed potential of 500 mV.

The chronoamperometry experiments were carried out to examine the electrochemical performance and stability of the electrocatalysts (Fig 4). In agreement with cyclic voltammetry experiments (Fig. 3) the activity of the PtRu/Carbon materials also increase with the Ru content in the samples; the materials prepared with Pt:Ru atomic ratio of 50:50, 30:70 and 60:40 showed higher currents values than the materials prepared with 90:10 and 80:20. On the other hand, the stability of the material prepared with Pt:Ru atomic ratio of 30:70 was smaller than the materials prepared with Pt:Ru atomic ratio of 50:50 and 60:40.

Conclusions

The hydrothermal carbonization using starch as carbon source produces active PtRu/Carbon materials for methanol electro-oxidation. The metal load and Pt:Ru atomic ratios values of the obtained PtRu/Carbon materials were similar to the nominal values. X-ray diffractograms of

obtained materials showed that Pt(fcc) and Ru(hcp) phase coexist in the catalysts. The average crystallite sizes of the Pt(fcc) phase were in the range of 8-12 nm. The PtRu/Carbon material with Pt:Ru atomic ratio of 50:50 showed the best performance for methanol oxidation compared to the others prepared materials. Further work is necessary to characterize our materials by other techniques like X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM) and BET surface area.

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