

PtRu/C ELECTROCATALYSTS PREPARED USING ELECTRON BEAM IRRADIATION

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ABSTRACT

PtRu/C electrocatalysts (carbon-supported PtRu nanoparticles) were prepared submitting water/ethylene glycol solutions containing Pt(IV) and Ru(III) ions and the carbon support to electron beam irradiation. The water/ethylene glycol ratio (v/v) was evaluated as synthesis parameters. The PtRu/C electrocatalysts were prepared with a nominal Pt:Ru atomic ratio of 50:50 and were characterized by energy dispersive X-ray analysis (EDX) and X-ray diffraction (XRD) and tested for methanol electro-oxidation using cyclic voltammetry and chronoamperometry. The obtained PtRu/C electrocatalysts showed the typical fcc structure of platinum-ruthenium alloys and the electrocatalytic activity depends on the water/ethylene glycol ratio used in the preparation.

1. INTRODUCTION

Fuel cells convert chemical energy directly into electrical energy with high efficiency, low emission of pollutants and are extremely attractive as power sources for mobile, stationary and portable applications. In the proton exchange membrane fuel cell (PEMFC) the anodic oxidation of hydrogen and the cathodic reduction of oxygen should be catalyzed to occur at adequate rates at low temperatures [1-4]. Carbon-supported platinum or platinum-based nanoparticles are the best electrocatalysts for anodic and cathodic reactions. However, the use of hydrogen as combustible continues to present problems especially for mobile and portable applications [4,5]. Thus, there has been an increasing interest in the use of alcohols directly as combustible (Direct Alcohol Fuel Cell – DAFC). Methanol has been considered the most promising alcohol and carbon-supported PtRu nanoparticles (PtRu/C electrocatalyst) the best electrocatalyst [6-8]. 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 Cell (DMFC) [9,10].

Recently, Spinacé et al. [11] prepared in a single step carbon-supported PtRu nanoparticles submitting water/2-propanol solutions containing Pt(IV) and Ru(III) ions and the carbon support to γ -irradiation. After 6 h of irradiation (total dose 3 kGy) all of the Pt(IV) and Ru(III) ions were reduced and deposited on the carbon support. However, the obtained PtRu/C electrocatalysts showed inferior performance compared to commercial PtRu/C E-TEK, which is considered as reference for methanol electro-oxidation [9]. This inferior performance was attributed principally due to the fact that the obtained PtRu nanoparticles have their surfaces enriched in Ru atoms [11,12]. On the other hand, PtRu/C electrocatalysts with superior performance than commercial PtRu/C electrocatalyst were prepared submitting water/ethylene glycol solutions containing the metal ions and the carbon support to γ -

irradiation, however, the time necessary to reduce the metal ions increased and not all of the Ru(III) ions were reduced even if a total dose of 48 kGy was applied [11,12]. In this work, PtRu/C electrocatalysts were prepared with different water/ethylene glycol ratios (v/v) using electron beam irradiation, which permits high dose (kGy) within a few minutes. The obtained PtRu/C electrocatalysts were tested for methanol electro-oxidation aiming fuel cell application.

2. EXPERIMENTAL

2.1. Preparation and characterization of PtRu/C electrocatalysts

PtRu/C electrocatalysts (20 wt%, Pt:Ru atomic ratio of 50:50) were prepared using $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (Aldrich) and $\text{RuCl}_3 \cdot 1.5\text{H}_2\text{O}$ (Aldrich) as metal sources, which were dissolved in water/ethylene glycol solutions (v/v). After this, the Carbon Vulcan[®] XC72R, used as support, was dispersed in the solution using an ultrasonic bath. The resulting mixture was submitted under stirring to electron beam source (Electron Accelerator's Dynamitron Job 188 – IPEN/CNEN – SP) and the total dose varied between 144 and 432 kGy. After irradiation the mixture was filtered and the solid (PtRu/C electrocatalyst) was washed with water and dried at 70°C for 2 h [11-13].

The Pt:Ru atomic ratios were obtained by EDAX analysis using a Philips XL30 scanning electron microscope with a 20 keV electron beam and provided with EDAX DX-4 microanalyser.

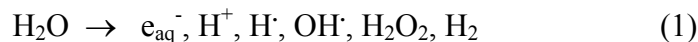
The XRD analyses were performed using a Rigaku diffractometer model Multiflex with a $\text{CuK}\alpha$ radiation source. The mean particle size was calculated using Scherrer equation [14].

2.2. Methanol electro-oxidation

Electrochemical studies of the electrocatalysts were carried out using the thin porous coating technique [15]. An amount of 20 mg of the electrocatalyst was added to a solution of 50 mL of water containing 3 drops of a 6% polytetrafluoroethylene (PTFE) suspension. The resulting mixture was treated in an ultrasound bath for 10 min, filtered and transferred to the cavity (0.30 mm deep and 0.36 cm² area) of the working electrode. The quantity of electrocatalyst in the working electrode was determined with a precision of 0.0001 g. In cyclic voltammetry experiments the current values (I) were expressed in amperes and were normalized per gram of platinum ($\text{A g}_{\text{Pt}}^{-1}$). 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 Microquímica (model MQPG01, Brazil) potentiostat/galvanostat coupled to a personal computer and using the Microquímica software. Cyclic Voltammetry and chronoamperometry were performed at 25°C using 1.0 mol L⁻¹ of methanol in 0.5 mol L⁻¹ H_2SO_4 .

3. RESULTS AND DISCUSSION

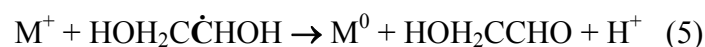
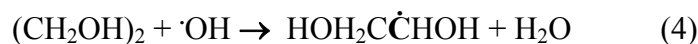
PtRu/C electrocatalysts were prepared in a single step submitting water/ethylene glycol solutions containing Pt(IV) and Ru(III) ions and the carbon support to electron beam irradiation at room temperature under stirring. The radiolysis of aqueous solutions leads to ionization and excitation of water forming the species showed in Eq. 1 [16].



The solvated electrons, e_{aq}^- , and H^\cdot atoms are strong reducing agents and reduce metal ions down to the zero-valent state (Eq. 2 and 3)



Similarly, multivalent ions, like Pt(IV) and Ru(III), are reduced by multistep reactions. On the other hand, OH^\cdot radicals could oxidize the ions or the atoms into a higher oxidation state counterbalance the reduction reactions (2) and (3). Thus, an OH^\cdot radical scavenger is added to the solution, in this case ethylene glycol, which reacts with these radicals leading to the formation of radicals exhibiting reducing power that are able to reduce metal ions (Eq. 4 and 5) [16,17].



In this manner, the atoms produced by the reduction of metals ions progressively coalesce leading to the formation of carbon-supported PtRu nanoparticles (PtRu/C electrocatalyst).

In the preparation of PtRu/C electrocatalysts the reactional mixture (water/ethylene glycol solutions containing Pt(IV) and Ru(III) ions) was initially dark brown. After irradiation and separation of the solid (PtRu/C electrocatalyst) by filtration, the reaction medium becomes colorless when a total reduction of Pt(IV) and Ru(III) ions occurs. This was already observed for PtRu/C electrocatalyst prepared in water/2-propanol using γ -irradiation (total dose 3 kGy) [11, 12]. In this study, the influence of water/ethylene glycol ratio on the preparation of PtRu/C electrocatalysts using electron beam irradiation is shown in Table 1. In all experiments the reaction media remained colored after electron beam irradiation (total dose of 288 kGy) suggesting that the complete reduction of the metallic ions did not occurred. A dark brown color was observed using only water as reaction medium suggesting that the major part of Pt(IV) and Ru(III) ions were not reduced. This probably occurred since species exhibiting reducing power were counterbalanced by species exhibiting oxidizing power (Eq. 1). A clear brown color was observed using as reaction medium water/ethylene glycol ratios of 95/5, 75/25, 50/50 and 25/75, indicating that platinum and/or ruthenium ions could remain in the solutions. In these conditions, all samples were obtained with Pt:Ru atomic ratios of approximately 80:20, which were different from nominal Pt:Ru atomic ratios of 50:50 used in the preparations. A qualitative test with potassium iodide [18] did not detect platinum ions in reaction media, suggesting that only ruthenium ions remained in solution. These results were similar to the ones already observed for PtRu/C electrocatalysts prepared in water/ethylene glycol using γ -irradiation [11,12]. Using only ethylene glycol a green color was observed and

a Pt:Ru atomic ratio of 80:20 was also obtained. Recently, it was shown that reducing species, like e^-_{solv} and $\text{HOH}_2\text{C}\dot{\text{C}}\text{HOH}$, could be formed by the ionization and excitation of the molecules of ethylene glycol leading to the reduction of metallic ions [17]. For all samples no changes were observed if the total dose were increased to 432 kGy.

Table 1. Influence of water/ethylene glycol on Pt:Ru atomic ratio of the PtRu/C electrocatalysts prepared using electron beam irradiation (20 wt% of metals, nominal Pt:Ru atomic ratio of 50:50, dose rate 1.6 kGys^{-1} , total dose 288 kGy)

Water/ethylene glycol (v/v)	Color of reaction medium after electron beam irradiation	Pt:Ru atomic ratio (EDX)
100/0	dark brown	80:20
95/5	brown	86:14
75/25	brown	84:16
50/50	brown	86:14
25/75	brown	82:18
0/100	green	80:20

The X-ray diffractogram of the PtRu/C electrocatalyst prepared using water/ethylene glycol ratio of 25/75 is shown in Figure 1.

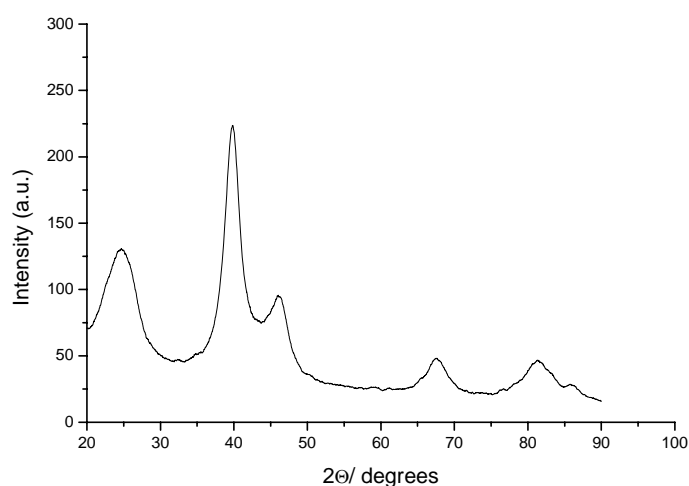


Figure 1. X-ray diffractogram of PtRu/C electrocatalyst prepared using water/ethylene glycol ratio of 25/75.

The diffratogram showed a broad peak at about 25° , which was associated to the Vulcan XC72R support material, and five diffraction peaks at about $2\theta = 40^\circ, 47^\circ, 67^\circ, 82^\circ$ e 87° that are associated to the (111), (200), (220), (311) e (222) planes, respectively, of the fcc structure of platinum and platinum alloys [19]. The particle size determined using the Scherrer equation was 2.8 nm and it was similar to the ones observed for PtRu/C electrocatalysts prepared in water/ethylene glycol using γ -irradiation [12].

The performances of PtRu/C electrocatalysts prepared with different water/ethylene glycol ratios are shown in Figure 2.

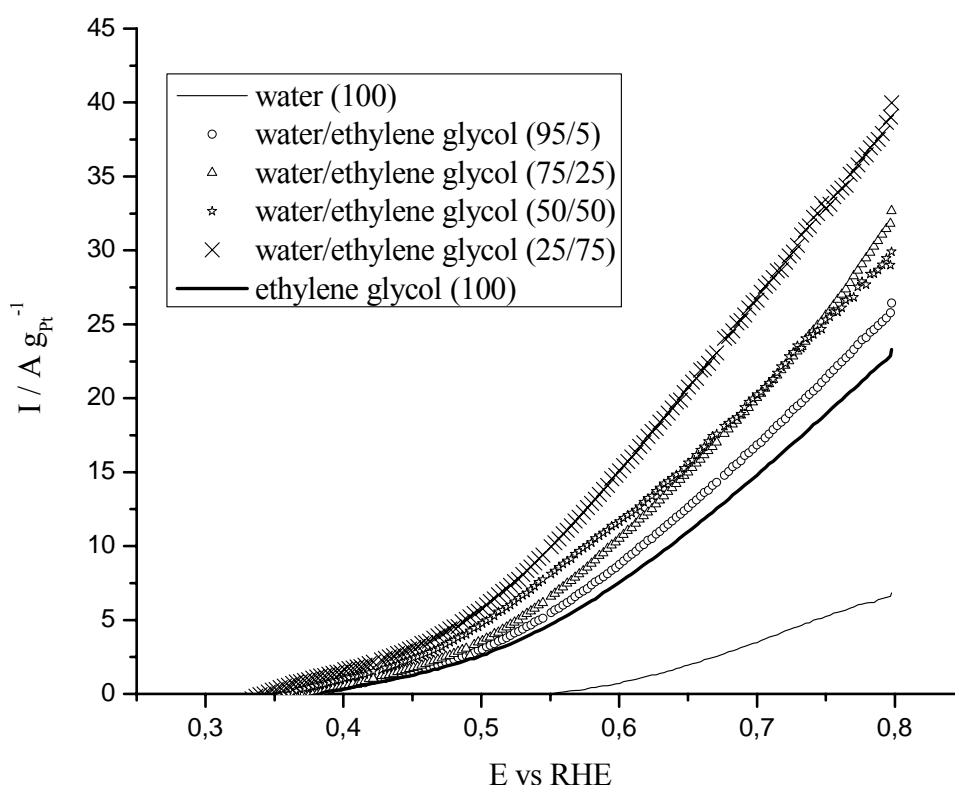


Figure 2. Cyclic voltammograms of PtRu/C electrocatalysts in H_2SO_4 0.5 mol L^{-1} containing 1.0 mol L^{-1} of methanol with a sweep rate of 10 mV s^{-1} , considering only the anodic sweep.

The anodic cyclic voltammetry responses were plotted after subtracting the background currents [15,20] and the currents values were normalized per gram of platinum, considering that methanol adsorption and dehydrogenation occur only on platinum sites at ambient temperature [21,22]. The performance of the electrocatalyst prepared using only water as reaction medium was very poor probably due the small quantities of metals present in this material. Using only ethylene glycol as reaction medium an increase of performance was

observed. However, better performances were observed using water/ethylene glycol solutions and the performances increase with the increase of ethylene glycol content.

The electrocatalysts performances were also studied by chronoamperometry at an anodic potential of 0.5 V versus RHE (Figure 3).

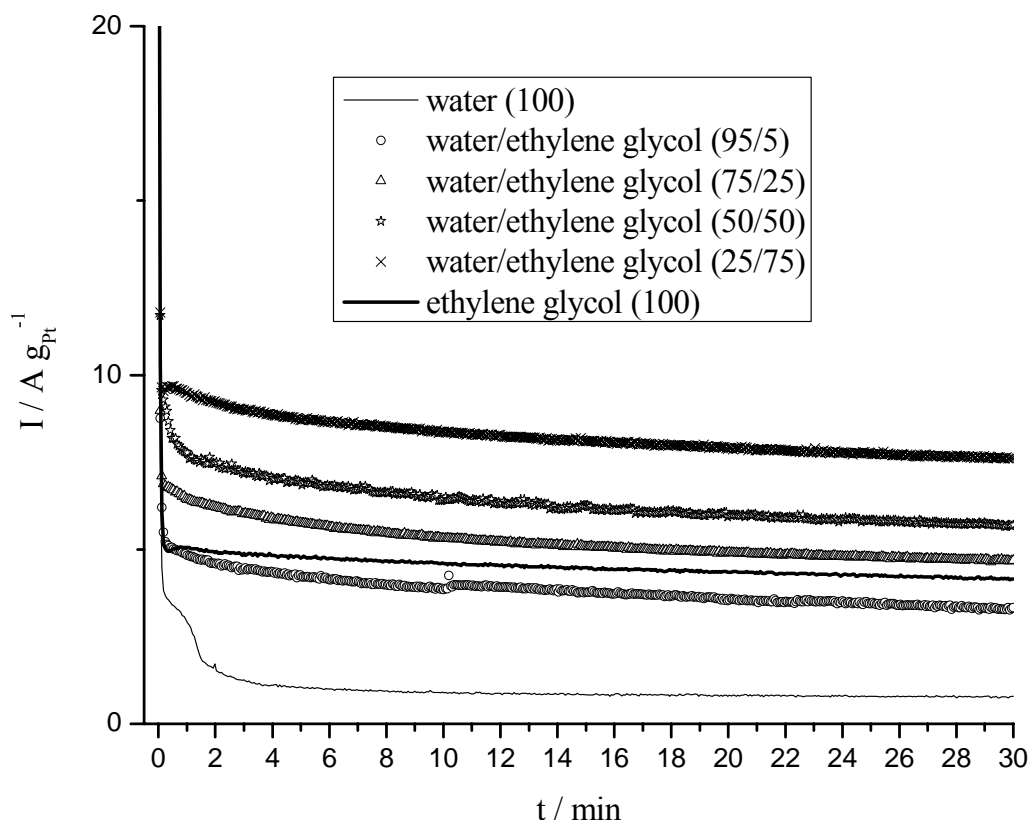


Figure 3. Current-time curves at 0.5 V of PtRu/C electrocatalysts in H_2SO_4 0.5 mol L^{-1} containing 1.0 mol L^{-1} of methanol with a sweep rate of 10 mV s^{-1} .

In all current-time curves there was an initial drop in the first 5 min followed by a slower decay. The current values obtained for PtRu/C electrocatalyst prepared with water/ethylene glycol ratio of 25/75 were always higher than those obtained for the other electrocatalyst. These results are in concordance with the ones obtained by cyclic voltammetry.

4. CONCLUSIONS

Active PtRu/C electrocatalysts for methanol oxidation were prepared within few minutes of electron beam irradiation. The obtained Pt:Ru atomic ratios were approximately 80:20, showing that not all of the Ru(III) ions were reduced even if a total dose of 432 kGy was applied. The obtained PtRu/C electrocatalysts showed the typical fcc structure of platinum-ruthenium alloys with mean particles size of approximately 3.0 nm. The electrocatalyst prepared using only water as reaction medium showed a very poor performance probably due the small quantities of metals present in this material. Using only ethylene glycol as reaction medium an increase of performance was observed, however, better performances were observed using electrocatalysts prepared in water/ethylene glycol solutions and the performances increase with the increase of ethylene glycol content. Modifications of experimental procedure in order to prepare PtRu/C electrocatalysts with more ruthenium content and experiments using these electrocatalysts in gas diffusion electrodes for tests in single direct methanol fuel cell are currently in progress.

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