

Short communication

## PtRu/C electrocatalysts prepared using $\gamma$ -irradiation

Dionísio F. Silva, Almir Oliveira Neto, Eddy S. Pino,  
Marcelo Linardi, Estevam V. Spinacé\*

*Instituto de Pesquisas Energéticas e Nucleares, IPEN/CNEN-SP, Av. Professor Lineu Prestes, 2242,  
Cidade Universitária, 05508-000 São Paulo, SP, Brazil*

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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  $\gamma$ -irradiation. The water/ethylene glycol ratio (v/v) and the total dose (kGy) were evaluated as synthesis parameters. The electrocatalysts were characterized by energy dispersive X-ray analysis (EDX), X-ray diffraction (XRD), transmission electron microscopy (TEM) and cyclic voltammetry and tested for methanol electro-oxidation aiming fuel cell application. The obtained PtRu/C electrocatalysts were more active for methanol electro-oxidation than the commercial PtRu/C electrocatalyst at ambient temperature and the electrocatalytic activity depends on the water/ethylene glycol ratio used in the preparation.

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### 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 reaction. 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].

Delcourt and co-workers [11] prepared platinum nanoparticles submitting a  $K_2PtCl_4$  salt dissolved in a CO-saturated water/2-propanol solvent to  $\gamma$ -irradiation. The reduction of platinum ions occurred by a combined effect of CO and radicals produced by radiolysis, leading to the formation of platinum nanoparticles of 2–3 nm that were further impregnated on the carbon support. These catalysts were found to be efficient for methanol or hydrogen electro-oxidation. Recently, Spinacé et al. [12] 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  $\gamma$ -irradiation. However, the obtained PtRu/C electrocatalysts showed inferior performance compared to commercial PtRu/C E-TEK, which is considered as a reference for methanol electro-oxidation [9]. This inferior performance was attributed principally due to fact that the obtained nanoparticles surfaces were enriched in Ru atoms and to a bigger nanoparticles size than the commercial catalyst [12]. In this work, PtRu/C electrocatalysts were prepared using different water/ethylene glycol ratios (v/v) as a reaction medium and tested for methanol electro-oxidation aiming fuel cell application. Ethylene glycol was

\* Corresponding author at: Instituto de Pesquisas Energéticas e Nucleares, IPEN/CNEN-SP, Programa de Células a Combustível, Av. Prof. Lineu Prestes, 2242, Cidade Universitária, 05508-900 São Paulo, SP, Brazil.

Tel.: +55 11 3816 9445; fax: +55 11 3816 9440.

E-mail address: [spinace@ipen.br](mailto:spinace@ipen.br) (E.V. Spinacé).

used because, like 2-propanol, it acts as a radical scavenger of hydroxyl radicals leading to formation of reactive radicals with reducing properties [13,14]. Also, it could act as a stabilizing agent preventing the growth of the nanoparticles [15].

## 2. Experimental

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<sup>®</sup> XC72R, used as support, was dispersed in the solution using an ultrasonic bath. Argon was bubbled through the resulting mixtures for 15 min and they were submitted to  $\gamma$ -irradiation ( $^{60}\text{Co}$  source of 800 Ci) at room temperature under stirring. The total dose varied between 1 and 30 kGy (dose rate of  $0.5 \text{ kGy h}^{-1}$ ). After irradiation the mixtures were filtered and the solids (PtRu/C electrocatalysts) were washed with water and dried [12,16].

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

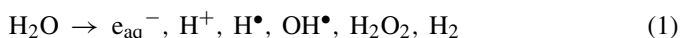
The XRD analyses were performed using a Rigaku diffractometer model Multiflex with a Cu  $\text{K}\alpha$  radiation source. The mean particle size was calculated using Scherrer equation [17].

Transmission electron microscopy (TEM) was carried out using a Carl Zeiss CEM 902 apparatus with a Proscan high-speed slow-scan CCD camera and digitalized ( $1024 \times 1024$  pixels, 8 bits) using the AnalySis software. The particle size distributions were determined by measuring the nanoparticles from micrographs using Image Tool Software.

Electrochemical studies of the electrocatalysts were carried out using the thin porous coating technique [18]. An amount of 20 mg of the electrocatalyst was added to a solution of 50 mL of water containing three 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  $0.36 \text{ cm}^2$  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 Microquimica (model MQPG01, Brazil) potentiostat/galvanostat coupled to a personal computer with a Microquimica software. Cyclic voltammetry was performed in a  $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  solution saturated with  $\text{N}_2$ . The evaluation of methanol oxidation was performed in  $1.0 \text{ mol L}^{-1}$  of methanol in  $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  at  $25^\circ\text{C}$ . For comparative purposes a commercial PtRu/C E-TEK electrocatalyst (20 wt%, Pt:Ru molar ratio 50:50, Lot # 3028401) was used.

## 3. Results and discussion

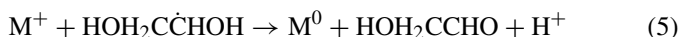
PtRu/C electrocatalysts were prepared in a single step submitting water/ethylene glycol solutions containing metallic ions and the carbon support to  $\gamma$ -irradiation at room temperature under stirring. The radiolysis of aqueous solutions leads to formation of species showed in the below equation [19]:



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



Similarly, multivalent ions, like Pt(IV) and Ru(III), are reduced by multistep reactions. On the other hand,  $\text{OH}^\bullet$  radicals could oxidize the ions or the atoms into a higher oxidation state and thus to counterbalance the reduction reactions (2) and (3). Thus, an  $\text{OH}^\bullet$  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 (Eqs. (4) and (5)) [19,20]:



In this manner, the atoms produced by the reduction of metals ions progressively coalesce, leading to the formation of carbon-supported PtRu nanoparticles. It should be noted that ethylene glycol is itself a reducing agent, however, the kinetics of reduction of metal ions by ethylene glycol at low temperatures are very slow [21] and thus, in the conditions used in this work, the reduction of metal ions proceeds principally by the mechanisms shown in Eqs. (1)–(5).

In our previous study, water/2-propanol was used as reaction medium to prepare PtRu/C electrocatalysts using  $\gamma$ -irradiation [12]. The reactional mixture was initially dark brown due the presence of Pt(IV) and Ru(III) ions. After irradiation of the reactional mixture and separation of the solid phase (PtRu/C electrocatalyst) by filtration, it was observed that the reaction medium becomes colorless due to a total reduction of Pt(IV) and Ru(III) ions. This was observed using water/2-propanol ratios of 90/10, 75/25, 50/50 and 25/75 (v/v) after 6 h of irradiation (total dose of 3 kGy) [12]. In this study, we prepared PtRu/C electrocatalyst using water/ethylene glycol as reaction medium (Table 1). It was observed in all experiments that the reaction medium remained colored after 24 h of irradiation (total dose of 12.2 kGy), suggesting that the complete reduction of the metallic ions was not occurred (Table 1). A brown and a green color were observed using only water or ethylene glycol as reaction medium, respectively, suggesting that the major part of the Pt(IV) and Ru(III) ions were not reduced. EDX analysis of the obtained samples in water or ethylene glycol did not show the presence of platinum and/or ruthenium. Thus, using only water or ethylene glycol as reaction medium no effective reduction of

Table 1

Pt:Ru atomic ratio and mean particle sizes of the PtRu/C electrocatalysts prepared with different water/ethylene glycol ratios (20 wt%, Pt:Ru atomic ratio 50:50, dose rate of  $0.5 \text{ kGy h}^{-1}$  and total dose of  $12.2 \text{ kGy}$ )

Water/ethylene glycol (v/v)	Color of reaction medium after $\gamma$ -irradiation	Pt:Ru atomic ratio, EDX	Particle size (nm)
100/0	Brown	–	–
90/10	Clear yellow	83:17	3.0
75/25	Clear yellow	81:19	2.5
50/50	Clear yellow	85:15	2.8
25/75	Clear yellow	94:6	2.7
0/100	Green	–	–

the metal ions were observed probably due to species exhibiting reducing power that were counterbalanced by species exhibiting oxidizing power (see Eq. (1)) [19,20]. Using as reaction medium water/ethylene glycol ratios of 90/10, 75/25, 50/50, 25/75 a clear yellow color was observed after 24 h of irradiation, indicating that platinum and/or ruthenium ions could remain in the solution. 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. Increasing the irradiation time to 48 h (24.4 kGy) the clear yellow color still remained in the reaction medium and Pt:Ru atomic ratios of 80:20 continues to be observed in the obtained samples. A qualitative test using potassium iodide [22] did not detect platinum ions in reaction media, suggesting that only ruthenium ions remained in solution.

The X-ray diffractograms of the PtRu/C electrocatalysts prepared using different water/ethylene glycol ratios are shown in Fig. 1. All samples showed the broad peak at about  $25^\circ$ , which was associated to the Vulcan XC72R support material. The electrocatalysts prepared with water/ethylene glycol ratios of 90/10, 75/25, 50/50 and 25/75 showed five diffraction peaks at about  $2\theta = 40^\circ, 47^\circ, 67^\circ, 82^\circ$  and  $87^\circ$  that are associated to the (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) planes, respectively, of the fcc structure of platinum and platinum alloys [23]. The XRD peaks corresponding to a metallic ruthenium or to other materials rich in ruthenium with hexagonal structure [23] were not detected for

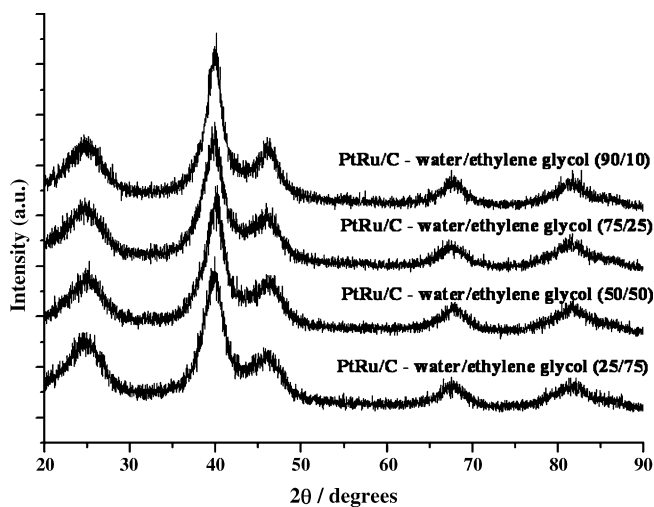


Fig. 1. X-ray diffractograms of PtRu/C electrocatalysts.

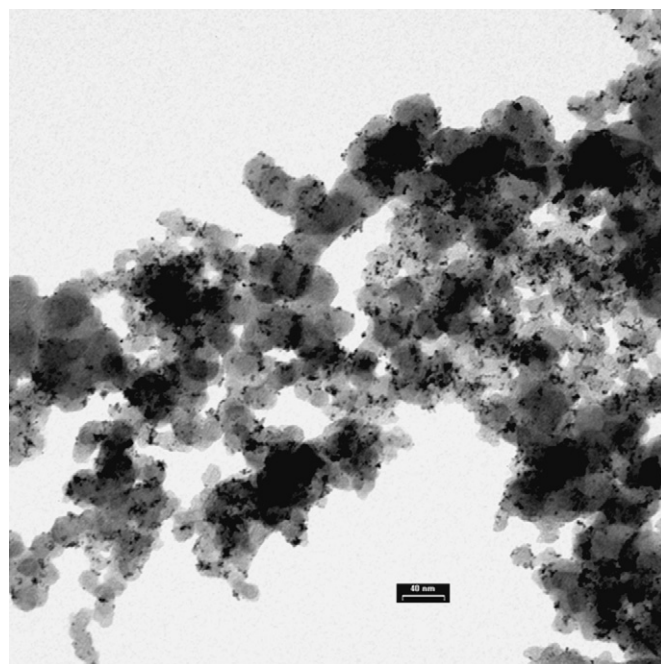


Fig. 2. TEM micrograph of PtRu/C electrocatalyst prepared with water/ethylene glycol ratio of 75/25 (v/v).

these samples, while they were observed for PtRu/C electrocatalysts prepared in water/2-propanol [12]. The mean particle sizes of the PtRu/C electrocatalysts prepared in water/ethylene glycol were in the range of 2.5–3.0 nm (Table 1) and were smaller than those obtained for PtRu/C electrocatalysts prepared in water/2-propanol (3.5–4.5 nm) [12]. This behavior could be attributed to the stabilizing effect of ethylene glycol preventing the growth of the nanoparticles during synthesis [15].

The transmission electron micrograph of the PtRu/C (Fig. 2) electrocatalyst prepared using water/ethylene glycol ratio of 75/25 showed the nanoparticles with a good distribution on the carbon support and mean particle sizes of  $3.2 \pm 0.9 \text{ nm}$ , while the commercial PtRu/C E-TEK showed mean particle sizes of  $2.5 \pm 0.7 \text{ nm}$  [23].

The cyclic voltammograms of the PtRu/C electrocatalysts prepared with different water/ethylene glycol ratios in  $0.5 \text{ mol L}^{-1}$  of  $\text{H}_2\text{SO}_4$  are shown in Fig. 3. The cyclic voltammogram of the PtRu/C electrocatalyst prepared using only ethylene glycol as reaction medium showed that no platinum and/or ruthenium were deposited. The cyclic voltammograms of the PtRu/C electrocatalysts prepared using water/ethylene glycol ratios of 90/10, 75/25, 50/50, 25/75 do not have a well-defined hydrogen adsorption–desorption region (0–0.4 V), as observed for PtRu/C electrocatalysts [23,24]. However, the hydrogen adsorption–desorption region was better defined than those observed for PtRu/C electrocatalysts prepared in water/2-propanol reaction medium, which have PtRu nanoparticles surface enriched in Ru atoms [12]. The cyclic voltammograms also showed an increase in the currents in the double layer (0.4–0.8 V) that was attributed to ruthenium oxide species [23,24]. On the other hand, this increase is less sharp compared to the ones observed for PtRu/C electrocatalysts prepared

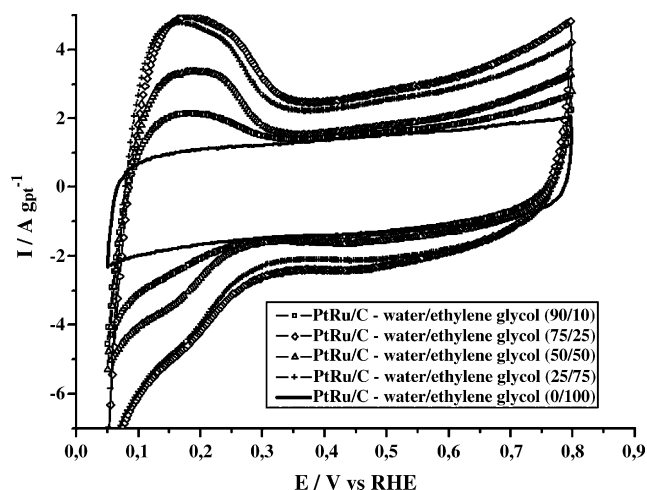


Fig. 3. Cyclic voltammograms of PtRu/C electrocatalysts in  $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  with a sweep rate of  $10 \text{ mV s}^{-1}$ .

in water/2-propanol reaction medium [12]. Thus, compared to the PtRu/C electrocatalysts prepared in water/2-propanol, which contain PtRu nanoparticles with surfaces that are enriched in ruthenium [12], these results suggest that PtRu/C electrocatalysts prepared in water/ethylene glycol contain PtRu nanoparticles with surfaces that are enriched in platinum.

The performance of the PtRu/C electrocatalysts prepared using different water/ethylene glycol ratios are shown in Fig. 4. The anodic cyclic voltammetry responses were plotted after subtracting the background currents [18,25] and the current values were normalized per gram of platinum, considering that methanol adsorption and dehydrogenation occur only on platinum sites at ambient temperature [26,27]. The electrocatalysts prepared using only water or ethylene glycol as reaction medium do not show electrocatalytic activity probably due to the small quantities of metals present in these materials. The PtRu/C electrocatalysts prepared with water/ethylene glycol ratio of 90/10 showed a performance inferior to the commercial PtRu/C E-TEK electrocatalyst in the region of interest for direct methanol

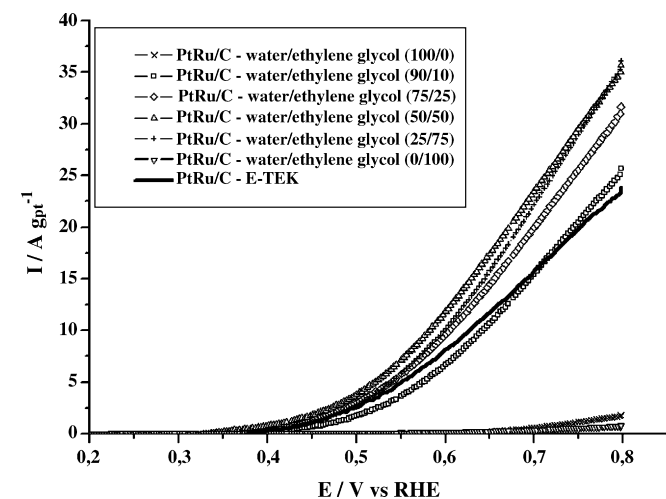


Fig. 4. Cyclic voltammograms of PtRu/C electrocatalysts in  $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  containing  $1.0 \text{ mol L}^{-1}$  of methanol with a sweep rate of  $10 \text{ mV s}^{-1}$ , considering only the anodic sweep.

fuel cell (0.3–0.6 V), while PtRu/C electrocatalysts prepared using water/ethylene glycol ratios of 75/25, 50/50 and 25/75 showed a superior performance. It has been shown that PtRu/C electrocatalysts with more platinum content showed a superior performance for methanol electro-oxidation at ambient temperature [28,29].

#### 4. Conclusions

Active PtRu/C electrocatalysts were prepared in a single step using  $\gamma$ -irradiation. Using only water or ethylene glycol as a reaction medium the reduction of metal ions was not observed. For PtRu/C electrocatalysts prepared with water/ethylene glycol ratios of 90/10, 75/25, 50/50 and 25/75, the Pt:Ru atomic ratios obtained were approximately 80:20, showing that not all of the Ru(III) ions were reduced, even if the irradiation time was increased. The obtained PtRu/C electrocatalysts showed the typical fcc structure of platinum and platinum alloys, mean particle sizes of 2.5–3.0 nm and were more active for methanol electro-oxidation than the commercial PtRu/C electrocatalyst at ambient temperature. Further work is necessary to modify our catalyst preparation methodology in order to obtain PtRu/C electrocatalyst with more ruthenium content. It is also necessary to test these electrocatalysts in gas diffusion electrodes in single direct methanol fuel cell.

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