

Research Article

PtRu/C Electrocatalysts Prepared Using Gamma and Electron Beam Irradiation for Methanol Electrooxidation

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PtRu/C electrocatalysts (carbon-supported PtRu nanoparticles) were prepared in a single step submitting water/2-propanol mixtures containing Pt(IV) and Ru(III) ions and the carbon support to gamma and electron beam irradiation. 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 electrooxidation. PtRu/C electrocatalyst can be prepared in few minutes using high dose rate electron beam irradiation while using low dose rate gamma irradiation some hours were necessary to prepare it. The obtained materials showed the face-centered cubic (fcc) structure of Pt and Pt alloys with average nanoparticle sizes of around 3 nm. The material prepared using electron beam irradiation was more active for methanol electrooxidation than the material prepared using gamma irradiation.

1. Introduction

Fuel cells convert chemical energy directly into electrical energy with high efficiency. However, the use of hydrogen as a fuel presents problems, principally with storage for mobile and portable applications [1–3]. Thus, there has been an increasing interest in the use of alcohols directly as fuel (Direct Alcohol Fuel Cell—DAFC). Methanol has been considered the most promising alcohol and carbon-supported PtRu nanoparticles (PtRu/C), normally with a Pt:Ru atomic ratio of 50:50, the best electrocatalyst [4]. However, the catalytic activity of PtRu/C electrocatalysts strongly depends on the method of preparation and it is one of the major topics studied in direct methanol fuel cells (DMFC) [4, 5]. PtRu/C electrocatalysts are produced mainly by impregnation and colloids methods. Although impregnation method is a simple procedure, the major drawback is the difficulty in controlling nanoparticle size and distribution. The colloidal methods have the advantage to produce very small and homogeneously distributed carbon-supported metal nanoparticles; however, the methodologies are very complex [4].

Lately radiation-induced reduction of metal ion precursors in solution has been described to prepare carbon-supported metal nanoparticles for fuel cell applications. Despite the complexity and cost of electron beam or gamma irradiation facilities, the methodologies used to prepare the electrocatalysts are easy to perform [6–10]. Le Gratiet et al. [6] 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 diameter that were further impregnated on the carbon support. These catalysts were found to be effective for methanol or hydrogen electrooxidation. Oh et al. [7] prepared Pt-Ru alloy particles dispersed on various carbon structures in water/2-propanol using gamma irradiation, but no tests for DMFC were described using the obtained materials. Wang et al. [8] prepared Pt nanoparticles irradiating an aqueous solution of chloroplatinic acid in the presence of 2-propanol as a radical scavenger and sodium sulfonate as

a surfactant. The synthesized Pt nanoparticles (2.5–4.0 nm) were further impregnated on multiwalled carbon nanotubes. The obtained material was tested on a single proton exchange membrane fuel cell operating with H₂/O₂, and the results showed that the electrocatalysts were very promising. Silva et al. [9] prepared PtRu/C electrocatalysts in a single step submitting water/ethylene glycol solutions containing Pt(IV) and Ru(III) ions and the carbon support to gamma irradiation at room temperature under stirring. The obtained carbon-supported PtRu nanoparticles showed mean particle sizes of 2.5–3.0 nm and were very active for methanol oxidation. Recently, Chai et al. [10] prepared Pt (80 wt%) supported on a mesoporous carbon support in a single step. The Pt salt was dissolved in a solution of water/2-propanol, and the carbon support was added to the solution. The mixture was irradiated at room temperature under stirring. The obtained material exhibited enhanced catalytic activity towards the oxygen reduction reaction (ORR). In this work, PtRu/C electrocatalysts were prepared using high dose rate electron beam and low dose rate gamma irradiation and were tested for methanol electrooxidation.

2. Experimental

PtRu/C electrocatalyst (20 wt%, Pt:Ru atomic ratio of 50:50) was prepared using H₂PtCl₆·6H₂O (Aldrich) and RuCl₃·1.5H₂O (Aldrich) as metal sources, which were dissolved in water/2-propanol solution (25/75, v/v). After this, the carbon Vulcan XC72R, used as a support, was dispersed in the solution using an ultrasonic bath. The resulting mixture (dissolved metal ions and the carbon support) was submitted to gamma irradiation (⁶⁰Co source, dose rate of 0.5 kGy h⁻¹) under stirring at room temperature for 6 h (total dose of 3 kGy). After irradiation, the mixture was filtered, and the solid PtRu/C electrocatalyst was washed with water and dried. In a similar way, the resulting mixture was submitted under stirring at room temperature to an electron beam source for 3 min (Electron Accelerator's Dynamitron job 188–IPEN/CNEN–SP, dose rate 5760 kGy h⁻¹, total dose of 288 kGy) [11].

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

XRD analysis was performed using a Rigaku diffractometer model Miniflex II using Cu K α radiation source ($\lambda = 0.15406$ nm). The diffractograms were recorded from $2\theta = 20^\circ$ to 90° with a step size of 0.05° and a scan time of 2 s per step. The average crystallite size was calculated using Scherrer equation [12].

Transmission electron microscopy (TEM) was carried out using a JEOL JEM-2100 electron microscope operated at 200 kV. The particle distribution histogram was determined by measuring 150 particles from micrograph.

Electrochemical studies of the electrocatalysts were carried out using the thin porous coating technique [13]. 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

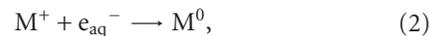
was treated in an ultrasound bath for 10 min, filtered, and transferred to the cavity (0.30 mm deep and 0.36 cm² area) of the working electrode. The quantity of electrocatalyst in the working electrode was determined with an accuracy of 0.0001 g using an analytical balance. In cyclic voltammetry experiments the current values (I) 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 Pt plate. Electrochemical measurements were made using a Microquimica (model MQPG01, Brazil) potentiostat/galvanostat coupled to a personal computer and using the Microquimica software. Cyclic voltammetry was performed in a 0.5 mol L⁻¹ H₂SO₄ solution saturated with N₂. Methanol oxidation was performed at 25°C using 1.0 mol L⁻¹ of methanol in 0.5 mol L⁻¹ H₂SO₄. For comparative purposes, a commercial PtRu/C E-TEK (20 wt%, Pt:Ru molar ratio 50:50, Lot # B0011117) was used.

3. Results and Discussion

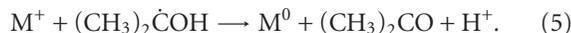
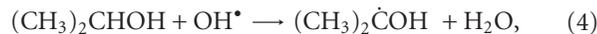
Electron beam or gamma irradiation of a water solution containing metals causes the ionization and excitation of water, forming the species shown in (1) [14].



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



Similarly, multivalent ions, like Pt(IV) and Ru(III), are reduced by multistep reactions. However, OH[•] radicals could oxidize the ions or the atoms into a higher oxidation state and thus counterbalance the reduction reactions, (2) and (3). An OH[•] radical scavenger is therefore added to the solution, in this case 2-propanol, which reacts with these radicals leading to the formation of radicals exhibiting reducing power that are able to reduce metal ions ((4) and (5)) [14].



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). The results of PtRu/C electrocatalysts preparation using electron beam and gamma irradiation are shown in Table 1.

The water/2-propanol solution containing Pt(IV) and Ru(III) ions used in the preparation of PtRu/C electrocatalysts showed a dark brown color before the addition of the carbon support and irradiation. After irradiation and separation of the solid (PtRu/C electrocatalyst) by filtration, the reaction medium becomes colorless suggesting that all of

TABLE 1: Influence of electron beam and gamma irradiation on Pt: Ru atomic ratio and average crystallite size of the PtRu/C electrocatalysts (20 wt% of metals, nominal Pt: Ru atomic ratio of 50:50, water/2-propanol volumetric ratio of 25/75).

Source	Irradiation time (h)	Dose rate (kGy h ⁻¹)	Total dose (kGy)	Pt: Ru atomic ratio (EDX)	Crystallite size (nm)
Electron beam	0.05	5760.0	288	47:53	2.9
Gamma ⁶⁰ Co	6	0.5	3	45:55	2.7

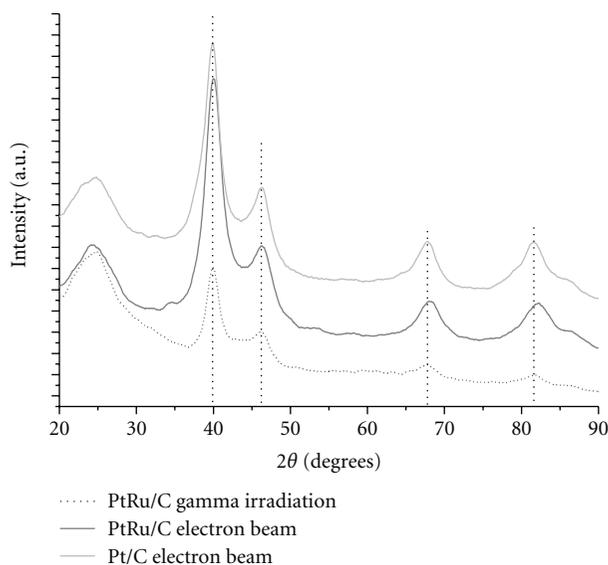


FIGURE 1: X-ray diffractograms of Pt/C and PtRu/C electrocatalysts prepared using electron beam and gamma irradiation.

the Pt(IV) and Ru(III) ions were reduced. To confirm this assumption, a qualitative test using potassium iodide [15] did not detect Pt ions in the filtrates, which suggest that all Pt(IV) ions were reduced to metallic Pt. As no Pt ions were not detected in the filtrates, and the obtained Pt: Ru atomic ratios were similar to the nominal ones (Table 1), it was considered that both electrocatalysts were obtained with 20 wt% of metal loading. Using low dose rate gamma irradiation the total reduction of metal ions was observed only after 6 h of irradiation. On the other hand, only 3 min were necessary to observe the total reduction of the metal ions using high dose rate electron beam irradiation.

The X-ray diffractograms of Pt/C and PtRu/C electrocatalysts are prepared using electron beam, and gamma irradiation are shown in Figure 1.

The X ray diffractograms showed a broad peak at about 25°, which was associated to the Vulcan XC72R support material and five diffraction peaks at about $2\theta = 40^\circ, 47^\circ, 67^\circ, 82^\circ,$ and 87° that were associated to the (111), (200), (220), (311), and (222) planes, respectively, which are characteristic of the face-centered cubic (fcc) structure of platinum and platinum alloys [16]. No peaks, which could be attributed to metallic ruthenium or to materials rich in ruthenium with a hexagonal structure, were observed in the XRD patterns. On

the other hand, the presence of these species as amorphous materials cannot be discarded. The X-ray diffractogram of PtRu/C electrocatalyst prepared using electron beam irradiation showed the diffraction peaks of fcc phase shifted to higher angles with respect to those of Pt/C electrocatalyst, indicating a lattice contraction and some alloy formation. This was not observed for the PtRu/C electrocatalyst prepared using gamma irradiation. The (220) reflection of Pt fcc structure was used to calculate the average crystallite sizes according to Scherrer equation and for both electrocatalysts the calculated values were about 3 nm.

TEM micrographs and the corresponding particle size distribution histograms of the PtRu/C electrocatalysts are prepared using gamma and electron beam irradiations are shown in Figures 2(a) and 2(b), respectively. It can be seen for both electrocatalysts that the nanoparticles were homogeneously distributed on the carbon support, and the mean particle sizes were around 3 and 2.5 nm for the materials obtained using gamma and electron beam irradiation, respectively.

The cyclic voltammograms in acid medium of the PtRu/C electrocatalysts are shown in Figure 3.

The cyclic voltammograms (CV) of both PtRu/C electrocatalysts do not have a well-defined hydrogen adsorption-desorption region (0–0.4 V) and show an increase of the current values in the double-layer region (0.4–0.8 V) when compared to the CV of Pt/C electrocatalyst [17]. The increase of current values in the double region was attributed to the capacitive currents and redox process of ruthenium oxides [17, 18]. However, comparing the CVs of both PtRu/C electrocatalysts, it is observed for the material prepared using electron beam irradiation a more defined hydrogen region when compared to the material prepared using gamma irradiation. On the other hand, the material prepared using gamma irradiation showed the double layer region more pronounced. This could suggest that the material prepared using electron beam irradiation has a surface more enriched in Pt while the material prepared using gamma irradiation has a surface more enriched in Ru.

The electrooxidation of methanol was studied by cyclic voltammetry in 1 mol L⁻¹ methanol in 0.5 mol L⁻¹ H₂SO₄ (Figure 4).

The electrooxidation of methanol started only at about 0.45 V for the PtRu/C electrocatalyst was prepared using gamma irradiation, and the current values were lower than those observed for the PtRu/C electrocatalyst prepared using an electron beam. For the latter electrooxidation started at about 0.35 V, and the performance of this catalyst was very

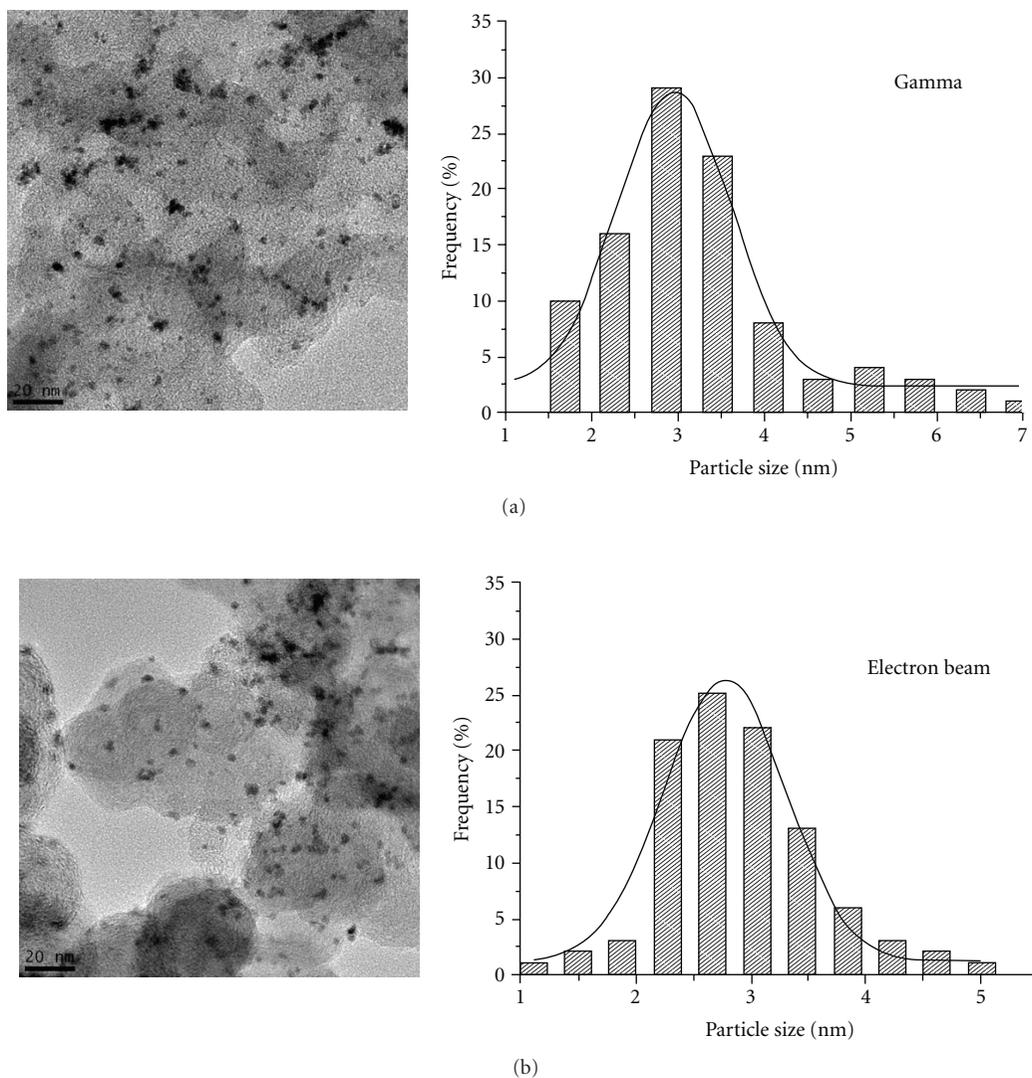


FIGURE 2: TEM micrographs and particle size distributions of PtRu/C electrocatalysts prepared using (a) gamma and (b) electron beam irradiation.

similar to the commercial PtRu/C electrocatalyst from E-TEK. Studies have shown that the maximum activity for methanol oxidation at room temperature could be obtained using PtRu/C electrocatalysts with low Ru coverage [19–21]. The obtained results could be explained by the different dose rates of electron beam and gamma radiation and to different reduction potentials of Pt(IV) and Ru(III) ions. Using electron beam irradiation (high dose rate), the reduction of Pt(IV) and Ru(III) ions proceeds very quickly and enhances the probability of alloying, as confirmed by XRD measurements. Thus, the carbon-supported PtRu nanoparticles obtained using electron beam seem to have a more homogeneous distribution of Pt and Ru atoms on the nanoparticles surface. On the other hand, at low dose rate (gamma source) it seems that the Pt(IV) ions were reduced before the Ru(III) ions. In this case, Ru atoms deposit preferentially on the presupported Pt nanoparticles and

the resulting carbon-supported PtRu nanoparticles have a Ru-rich surface. Another possibility is that Pt(IV) and Ru(III) ions were reduced with equal probabilities by radiolytic radicals, but a further electron transfer from the less noble metal atom, Ru, to the more noble metal ion, Pt(IV), could also result in the formation of carbon-supported PtRu nanoparticles with the surface enriched by Ru atoms, which could explain the low activity of this sample for methanol electrooxidation.

4. Conclusions

An active PtRu/C electrocatalyst for methanol oxidation was easily obtained in a single step within a few minutes using electron beam irradiation. The PtRu/C electrocatalysts showed the typical fcc structure of platinum and platinum

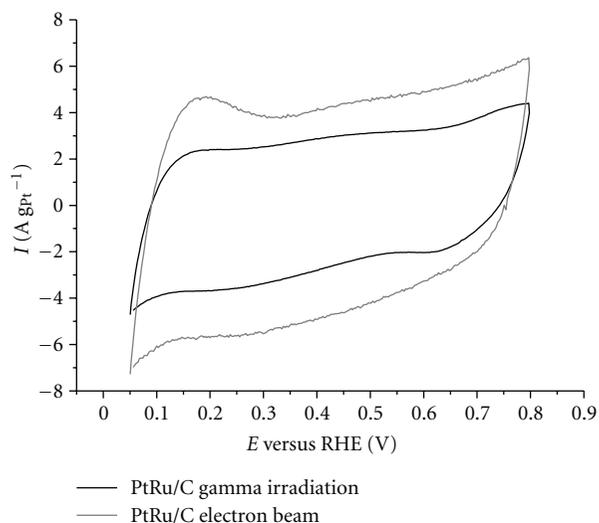


FIGURE 3: Cyclic voltammograms of PtRu/C electrocatalysts prepared using electron beam and gamma irradiation in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ with a scan rate of 10 mV s^{-1} .

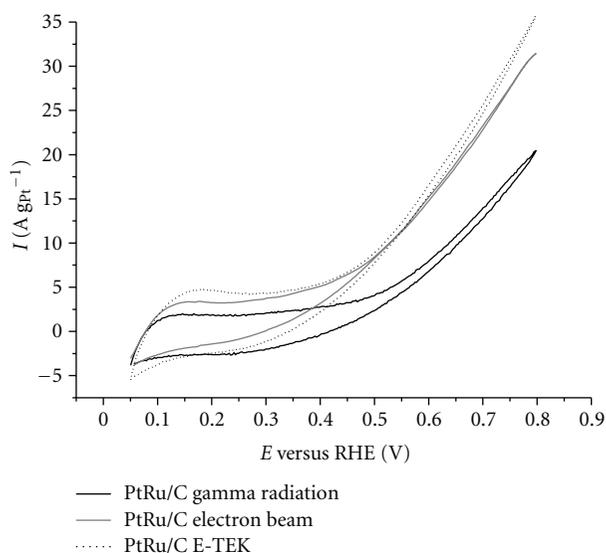


FIGURE 4: Cyclic voltammograms of PtRu/C electrocatalyst prepared using electron beam and gamma irradiation and commercial PtRu/C E-TEK in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ and 1.0 mol L^{-1} methanol with a scan rate of 10 mV s^{-1} .

alloys with average particle sizes of 2.5 nm. At room temperature, the material prepared using electron beam irradiation has a similar methanol oxidation performance as that of a commercial PtRu/C electrocatalyst.

Acknowledgments

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