

## Electro-oxidation of ethanol using PtRu/C electrocatalysts prepared by alcohol-reduction process

Estevam V. Spinacé\*, Almir Oliveira Neto, Teonas R.R. Vasconcelos, Marcelo Linardi

*Instituto de Pesquisas Energéticas e Nucleares (IPEN/CNEN), Centro de Ciência e Tecnologia de Materiais, Av. Prof. Lineu Prestes, 2242, Cidade Universitária, 05508-900 Sao Paulo SP, Brazil*

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### Abstract

PtRu/C electrocatalysts were prepared by an alcohol-reduction process using ethylene glycol as solvent and reducing agent and Vulcan Carbon XC72R as support. Two different forms of electrocatalyst preparation were used, one in which the metals were reduced together in a single step (co-reduction of mixed ions) and the other with the metals being reduced separately in two successive steps (successive reduction of metal ions). The electrocatalysts were characterized by EDAX, XRD, TEM and cyclic voltammetry and the electro-oxidation of ethanol was studied by cyclic voltammetry and chronoamperometry. The electrocatalysts prepared by co-reduction of mixed ions were the most active for ethanol oxidation and the performances increased with the increase of ruthenium content.

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### 1. Introduction

Fuel cells convert chemical energy directly into electrical energy with high efficiency and low emission of pollutants. In the proton exchange membrane fuel cell (PEMFC), the anodic oxidation of combustible and the cathodic reduction of oxygen should be catalyzed to occur at adequate rates at low temperatures [1–5]. Carbon-supported platinum or platinum-based nanoparticles are the best electrocatalysts for anodic and cathodic reaction. These electrocatalysts are produced mainly by impregnation and colloids methods [6]. Although the impregnation method is a simple procedure, the carbon-supported metal nanoparticles obtained have a large average size and a broad distribution. The colloidal methods have the advantage to produce very small and homogeneously distributed carbon-supported metal nanoparticles, however, the methodologies are very complex. Thus, the search for alternative routes to produce carbon-supported metal nanoparticles by a simple methodology is a goal in this area. Recently, alternative routes based on the “polyol method” [7] and the “alcohol-reduction process” [8] have been developed with good results. In these processes, an al-

cohol works as a solvent and a reducing agent for the metal ions.

Wang and Hsing [9] prepared Pt and PtRu/C catalysts based on an alcohol-reduction process. The surfactant-protected Pt/C and PtRu/C catalysts were prepared using  $\text{H}_2\text{PtCl}_6$ ,  $\text{RuCl}_3$ , dodecyldimethyl(3-sulfo-propyl)ammonium hydroxide (SB12), Vulcan XC-72 carbon black in a mixture of methanol–water to form a suspension, which was refluxed, filtered and washed. The surfactant SB12 was used as a stabilizer to prevent metal colloids from aggregating during the reduction process. This allowed the preparation of well-dispersed metal colloids supported on the carbon black with particle sizes in the range of 2.0–3.5 nm. In comparison to commercial E-TEK electrocatalysts of similar compositions, the Pt/C catalyst showed similar performance in oxygen reduction and PtRu/C in the oxidation of  $\text{H}_2/\text{CO}$  mixtures.

Chen et al. [10] prepared a Pt/C electrocatalyst using ethylene glycol as a reducing agent and microwave irradiation to heat the mixture. In this methodology  $\text{H}_2\text{PtCl}_6$  was added to ethylene glycol and a KOH solution was added dropwise. After this, Carbon XC-72 was dispersed in the solution by ultrasound and the mixture was heated in a microwave oven. A mole ratio of KOH/Pt of 8 was used to induce small and uniform Pt nanoparticle formation (3.5–4.0 nm). The obtained Pt/C electrocatalyst exhibited better performance than a commercial Pt/C E-TEK electrocatalyst in room

\* Corresponding author. Tel.: +55 11 3816 9440;

fax: +55 11 3816 9370.

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

temperature oxidation of methanol. Recently, PtRu nanoparticles supported on Vulcan XC-72 and carbon nanotubes were prepared by this procedure [11]. The PtRu nanoparticles were uniformly dispersed on the carbon nanotubes with 2–5 nm diameter. The PtRu/C electrocatalysts showed higher and more durable electrocatalytic activities for methanol oxidation than a comparative Pt/C electrocatalyst.

Zhou et al. [12] prepared Pt and Pt-based nanoparticles supported on carbon Vulcan XC-72R. In this procedure, the metal precursors were dissolved in ethylene glycol or its mixture solution with water. The pH of the solution was modified to 12 and the solution was heated at 130 °C for 2 h to reduce the metals. Then, the ultrasonically dispersed carbon slurry was added dropwise. After impregnation for 4 h, the mixture was filtered, washed and dried. The metal particles on the carbon support were very uniform (2.0–3.5 nm) and the addition of Ru, Sn and W enhanced the activity of Pt towards ethanol electro-oxidation.

In this work, we prepare PtRu/C electrocatalysts by the alcohol-reduction process in the absence of surfactants or modifying the pH of the medium to induce small and uniform nanoparticles formation. The obtained electrocatalysts were tested in ethanol electro-oxidation and the performances were compared to the commercial PtRu/C E-TEK electrocatalyst.

## 2. Experimental

PtRu/C electrocatalysts were prepared using  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  (Aldrich),  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  (Aldrich), ethylene glycol (Merck) as solvent and reducing agent and Vulcan XC72R as support by a methodology developed in this laboratory [13]. In the experiments where  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  and  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  were reduced together in a single step (co-reduction of mixed ions) the obtained electrocatalysts were designed as PtRu/C. When  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  was reduced alone in the first step and after that  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  was reduced in the second step (successive reduction of metal ions), the obtained electrocatalyst was designed as Pt(1)Ru(2)/C.

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 × 1024 pixels, 8 bit) using the AnalySis Software. The par-

ticle size distributions were determined by measuring the nanoparticles from micrographs using Image Tool Software.

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.

Electrochemical studies of the electrocatalysts were carried out using the thin porous coating technique [14,15]. An amount of 20 mg of the electrocatalyst was added to a solution of 50 mL of water containing three drops of a 6% 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 cm<sup>2</sup> area) of the working electrode. The quantity of the electrocatalyst in the working electrode was determined with a precision of 0.0001 g. In cyclic voltammetry and chronoamperometry 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 (Table 1). The reference electrode was a RHE and the counter electrode was a platinumized 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<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution saturated with N<sub>2</sub>. The evaluation of ethanol oxidation was performed at 25 °C in three different concentrations of ethanol: 0.1, 0.5 and 1.0 mol L<sup>-1</sup>. For chronoamperometry, the electrolyte solution was 1 mol L<sup>-1</sup> of ethanol in 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>. For comparative purposes a commercial carbon-supported PtRu catalyst from E-TEK (20 wt.%; Pt:Ru molar ratio, 1:1; Lot #3028401) was used.

## 3. Results and discussion

The carbon-supported platinum, ruthenium and platinum–ruthenium nanoparticles were prepared by co-reduction of mixed ions or by successive reduction of metal ions using ethylene glycol as solvent and reducing agent in the presence of carbon Vulcan XC72R (Table 1). The Pt:Ru atomic ratios of the obtained electrocatalysts were very similar to the

Table 1  
Pt:Ru atomic ratio (from EDAX) and particle sizes (from TEM) of the prepared electrocatalysts

Electrocatalyst	Pt (wt.%)	Ru (wt.%)	Pt:Ru atomic ratio	Pt:Ru atomic ratio, EDAX	Particle size (nm), TEM
Pt/C	20.0	–	–	–	5.0 ± 1.5
Ru/C	–	20.0	–	–	7.5 ± 3.0
PtRu/C 1:1	13.2	6.8	1:1	1:1.1	4.0 ± 1.5
PtRu/C 1:3	7.8	12.2	1:3	1:2.5	5.5 ± 2.0
PtRu/C 3:1	17.0	3.0	3:1	3:1	5.0 ± 1.5
Pt(1)Ru(2)/C	13.2	6.8	1:1	1:1.2	7.0 ± 2.5
Ru(1)Pt(2)/C	13.2	6.8	1:1	1:1	7.5 ± 3.0
PtRu/C E-TEK	13.2	6.8	1:1	1:1.1	2.5 ± 0.7

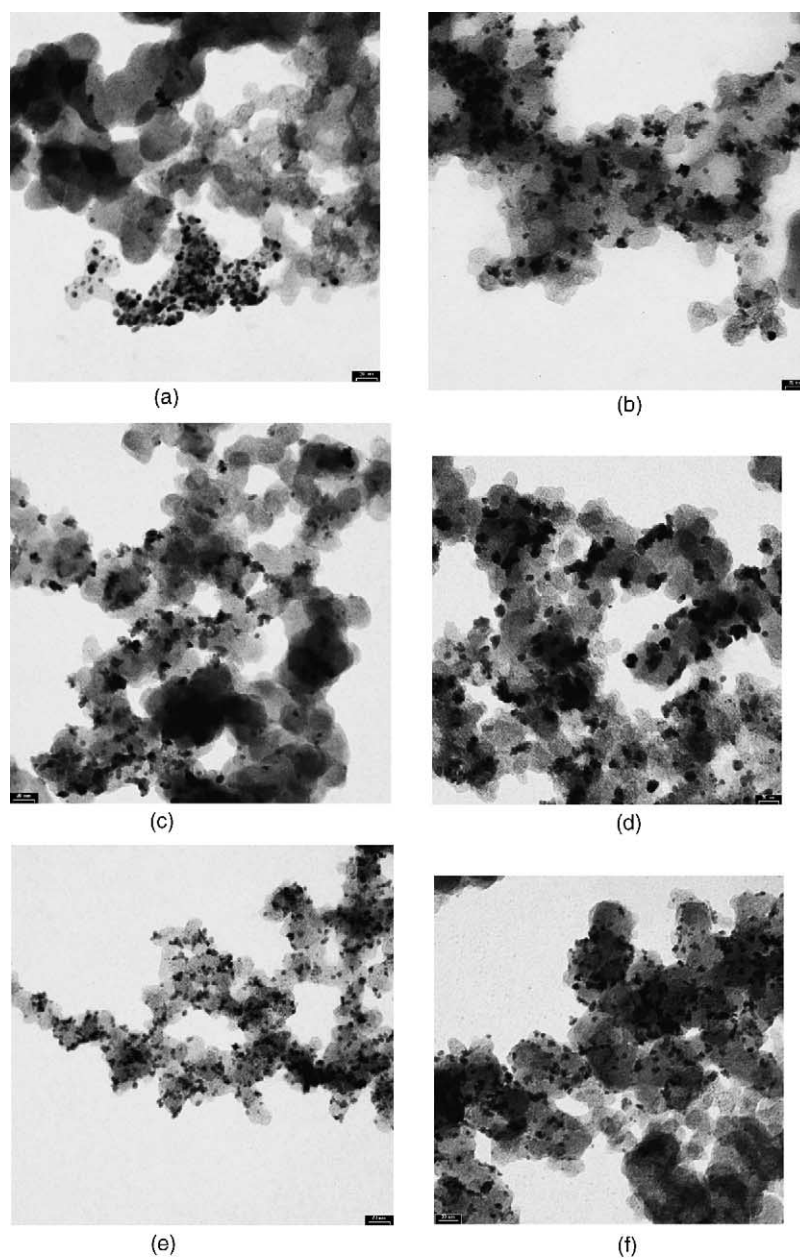


Fig. 1. TEM micrographs: (a) Pt/C; (b) Ru/C; (c) Pt(1)Ru(2)/C; (d) Ru(1)Pt(2)/C; (e) PtRu/C 1:1 and (f) PtRu/C 1:3.

atomic ratio used in the preparation, except for the electrocatalyst with a Pt:Ru atomic ratio of 1:3, where an atomic ratio of 1:2.5 was observed.

The TEM micrograph of Pt/C electrocatalyst (Fig. 1a) showed the nearly spherical platinum nanoparticles non-uniformly distributed on the carbon support with particle sizes of  $5.0 \pm 1.5$  nm. Ru/C electrocatalyst (Fig. 1b) presented the ruthenium nanoparticles more homogeneously distributed on the carbon support than Pt/C electrocatalyst; however, the particle sizes were bigger and the distribution broader ( $7.5 \pm 3.0$  nm). For the Pt(1)Ru(2)/C electrocatalyst (Fig. 1c), where platinum was used in the first step of prepara-

tion, the metal nanoparticles were more non-uniformly distributed on the carbon support than Ru(1)Pt(2)/C electrocatalyst and the nanoparticle shape resembled the Ru/C electrocatalyst (Fig. 1b). For Ru(1)Pt(2)/C electrocatalyst (Fig. 1d), ruthenium ions were used in the first step; and in this case, the metal nanoparticles were more homogeneously distributed on the carbon support than Pt(1)Ru(2)/C electrocatalyst and the nearly spherical form of the nanoparticles looked like Pt/C electrocatalyst (Fig. 1a). These results suggest that the metal used in the second step of preparation deposits preferentially on the pre-supported nanoparticles. The electrocatalysts prepared by co-reduction of mixed ions

(Fig. 1e and f) have the advantage of being prepared in a single step and the obtained nanoparticles are smaller and more uniformly distributed on the carbon support than the electrocatalysts prepared by successive reduction of metal ions.

The cyclic voltammograms (CV) in  $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  of Pt/C, Ru/C and PtRu/C electrocatalysts with a Pt:Ru molar ratio of 1:1 obtained by successive reductions of metal ions and by co-reduction of mixed ions are shown in Fig. 2. The CV of Ru(1)Pt(2)/C electrocatalyst show a defined hydrogen oxidation region (0–0.4 V), as observed for the Pt/C electrocatalyst. The CV of Pt(1)Ru(2)/C electrocatalyst is similar to Ru/C electrocatalyst. These results also indicate that the metal used in the second step of preparation deposits preferentially on the pre-supported nanoparticles and the chemical properties of these electrocatalysts are mainly to metal deposited on the surface of the nanoparticles. Toshima and Yonezawa [8] described that successive reduction of two metal salts could be considered as one of the most suitable methods to prepare bimetallic nanoparticles having one metal element forming an inner core and the other element surrounding the core to form a shell. Hills et al. [16] studied the depositing of ruthenium and platinum precursors onto commercial samples of carbon-supported platinum and ruthenium nanoparticles followed by a reduction in hydrogen flow at elevated temperatures. They observed that the pre-supported nanoparticles also serve as nucleating sites for the growth of the resulting Pt–Ru nanoparticles; however, under these conditions, the obtained nanoparticles are fully alloyed. The CV of PtRu/C 1:1 electrocatalyst do not have a well-defined hydrogen oxidation region and the currents in the double layer (0.4–0.8 V) are larger, which are characteristic of PtRu alloy with a molar ratio of 1:1 [15,17]. This

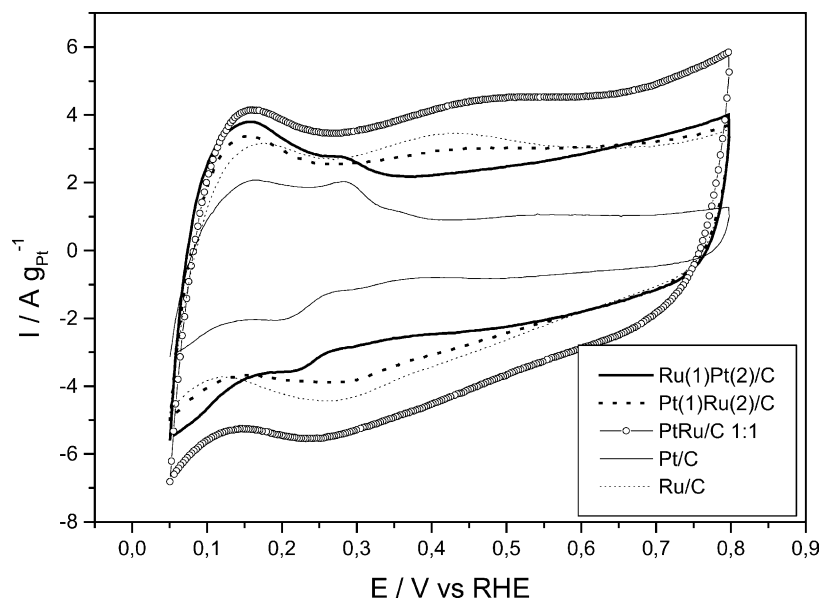


Fig. 2. Cyclic voltammetry of Pt/C; Ru/C; Pt(1)Ru(2)/C; Ru(1)Pt(2)/C and PtRu/C 1:1 electrocatalysts in  $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  with a sweep rate of  $10 \text{ mV s}^{-1}$ .

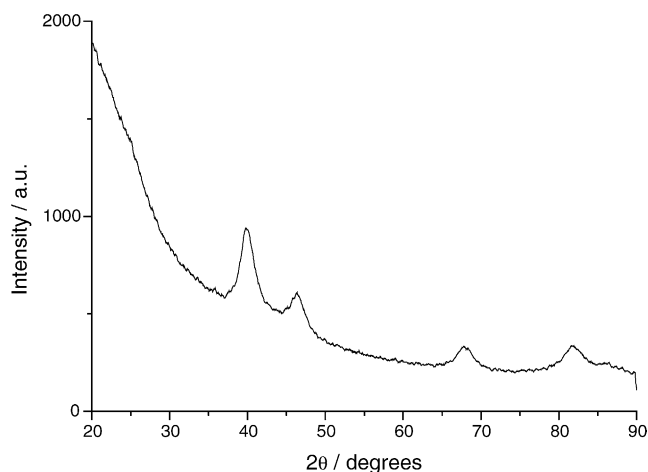


Fig. 3. X-ray diffractogram of PtRu/C 1:1 electrocatalyst prepared by co-reduction of mixed ions.

is confirmed by the X-ray diffractogram (Fig. 3) that shows peaks at approximately  $2\theta = 40, 47, 67$  and  $82$  that are associated to the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes, respectively, of the fcc structure of platinum and characteristic of PtRu alloys with up to 50 at.% of ruthenium [14,15].

The CV of the electrocatalysts prepared by co-reduction of mixed ions with different Pt:Ru atomic ratios are shown in Fig. 4. In this case, all the electrocatalysts do not have a well-defined hydrogen oxidation region and the currents in the double layer increase with the increase of ruthenium content. This could be attributed to the presence of more ruthenium oxide species that are very important to methanol and ethanol oxidation at low potentials [15,17].

The electro-oxidation of ethanol was studied varying the concentration from  $0.1$  to  $1.0 \text{ mol L}^{-1}$  (Fig. 5) and in a

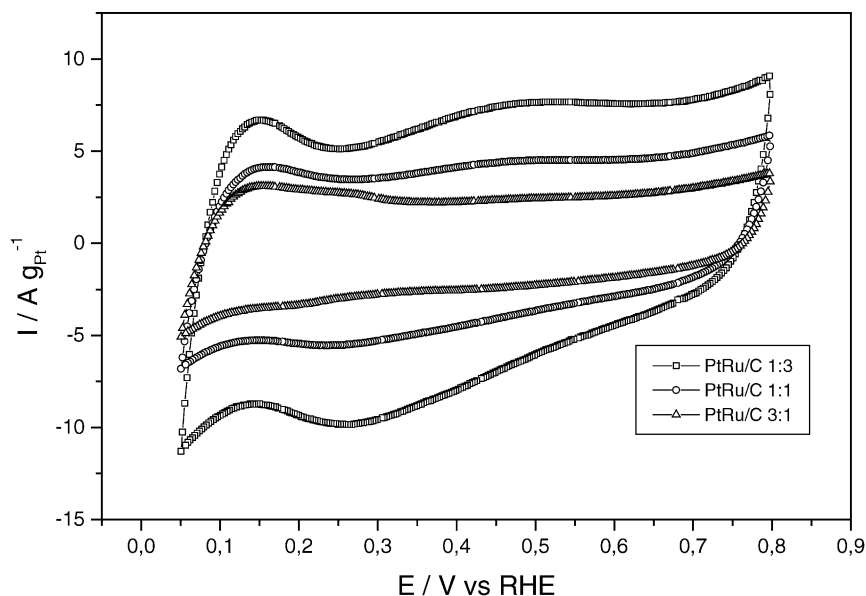


Fig. 4. Cyclic voltammetry of PtRu/C electrocatalysts with different Pt:Ru atomic ratios prepared by co-reduction of mixed ions in  $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  with a sweep rate of  $10 \text{ mV s}^{-1}$ .

general manner for all electrocatalysts, the current values in the hydrogen region (0–0.4 V) decrease with the increase of ethanol concentration most likely due to the increase of ethanol adsorption on the surface [17]. For potentials more positive than 0.4 V, the current values increase with ethanol concentration even for  $1.0 \text{ mol L}^{-1}$ . The electrocatalysts' performances in ethanol oxidation are shown in Figs. 6 and 7. In these figures, the current values were normalized per gram of platinum and corrected for the current in the absence of ethanol. Ru/C electrocatalyst showed low activ-

ity in the region of interest for direct ethanol fuel cell applications (0.3–0.6 V). For Pt/C electrocatalyst, the ethanol oxidation only starts at 0.55 V and the currents values are low. The performances of the electrocatalysts prepared by successive reduction of metal ions are lower than the electrocatalysts prepared by co-reduction of mixed ions. The performance outlines of the Pt(1)Ru(2)/C and Ru(1)Pt(2)/C electrocatalysts are similar to Ru/C and Pt/C electrocatalysts, respectively, which indicates that the activity of these electrocatalysts are mainly due to the metal deposited on

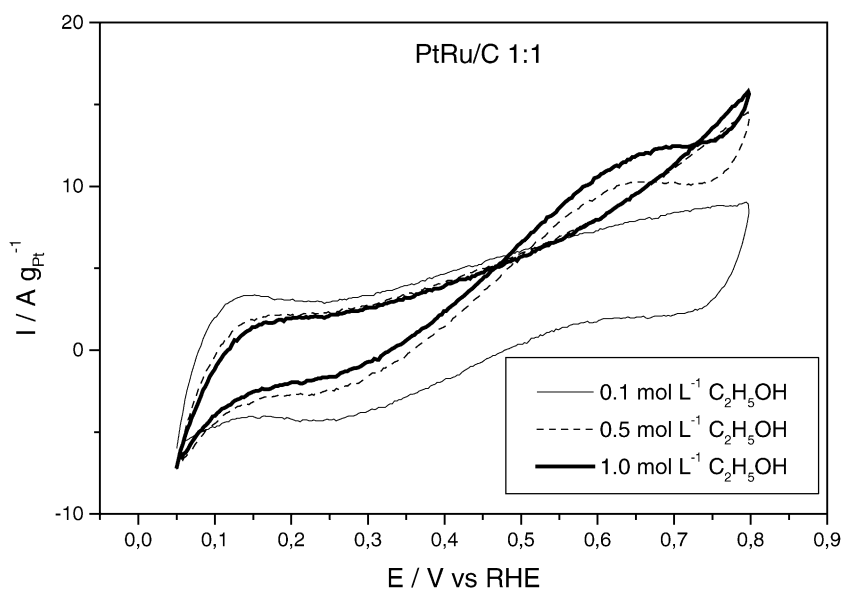


Fig. 5. Cyclic voltammetry of PtRu/C 1:1 electrocatalyst in  $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  with a sweep rate of  $10 \text{ mV s}^{-1}$  with different concentrations of ethanol.



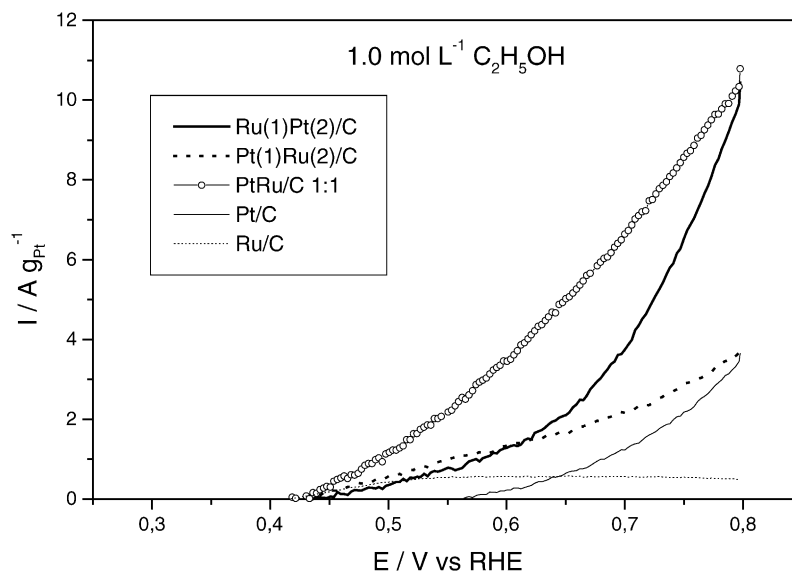


Fig. 6. Cyclic voltammetry of Pt/C; Ru/C; Pt(1)Ru(2)/C; Ru(1)Pt(2)/C and PtRu/C 1:1 electrocatalysts in  $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  containing  $1.0 \text{ mol L}^{-1}$  of methanol with a sweep rate of  $10 \text{ mV s}^{-1}$ , considering only the anodic sweep.

the surface of the pre-supported nanoparticles. The performance of the electrocatalysts prepared with different Pt:Ru atomic ratios by co-reduction of mixed ions is shown in Fig. 7. The performance of the PtRu/C 1:1 electrocatalyst is similar to the commercial PtRu/C E-TEK electrocatalyst with the ethanol oxidation starting at approximately 0.4 V. The best performance was observed for PtRu/C 1:3 electrocatalyst with the oxidation starting at a lower potential (0.35 V). This could be attributed to the presence of more ruthenium oxide species on the nanoparticles surface as ob-

served in the cyclic voltammogram (Fig. 4). The increase of activity for ethanol oxidation with the increase of ruthenium content and/or ruthenium oxide species on the nanoparticles surface was also observed for PtRu/C electrocatalysts prepared by reduction with formic acid [14], using single molecular precursor [18] and by spontaneous deposition [19].

The current–time curves for PtRu/C 1:1 and commercial PtRu/C E-TEK electrocatalysts in ethanol oxidation (Fig. 8) showed that the electrocatalysts have similar currents and behavior in the studied conditions.

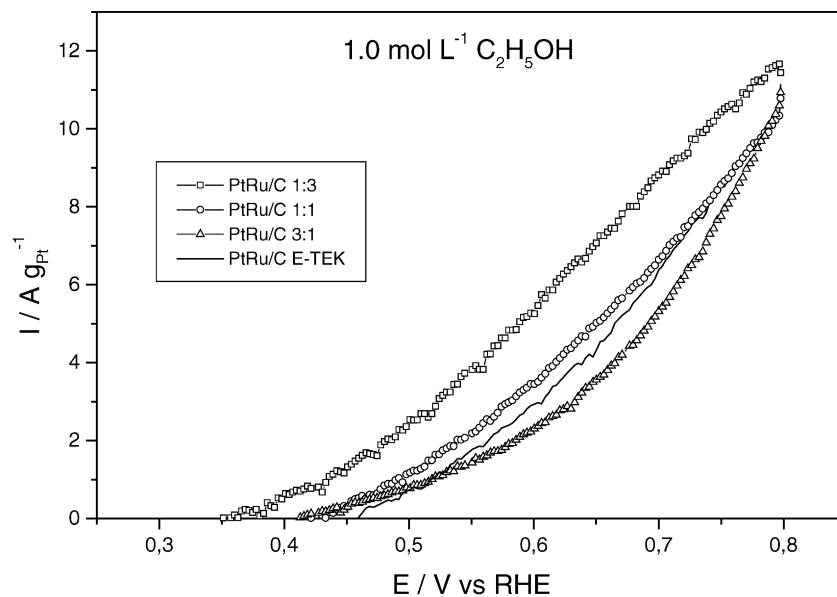


Fig. 7. Cyclic voltammetry of PtRu/C electrocatalysts with different Pt:Ru atomic ratios prepared by co-reduction of mixed ions in  $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  containing  $1.0 \text{ mol L}^{-1}$  of ethanol with a sweep rate of  $10 \text{ mV s}^{-1}$ , considering only the anodic sweep.

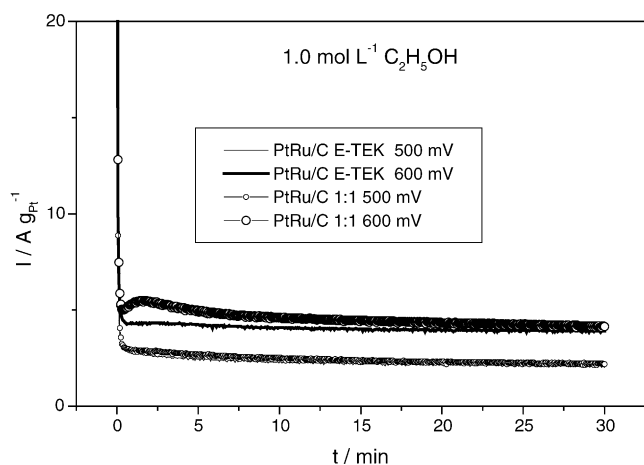


Fig. 8. Current–time curves at 0.5 and 0.6 V in  $1.0 \text{ mol L}^{-1}$  ethanol solution (in  $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ ) for PtRu/C 1:1 and commercial PtRu/C E-TEK electrocatalysts.

#### 4. Conclusions

Active PtRu/C electrocatalysts for ethanol oxidation can be obtained by an alcohol-reduction process in the absence of stabilizers and without modifying the pH of the medium. Using only platinum as a metal source, the obtained nanoparticles were smaller than using ruthenium. On the other hand, the platinum nanoparticles were non-uniformly distributed on the carbon support while a good distribution was obtained using ruthenium alone. The electrocatalysts prepared by successive reduction of metal ions have chemical and morphological properties and performances that resemble the ones of the metal used in the second step of preparation. The metal used in the second step most likely deposited preferentially on the surface of the pre-supported nanoparticles. The PtRu/C electrocatalysts prepared by co-reduction of mixed ions have the advantage of being prepared in a single step and a “synergistic effect” seems to occur because the obtained carbon-supported nanoparticles have particle sizes similar to those obtained for pure platinum and a good distribution on the carbon support as observed for pure ruthenium.

For ethanol oxidation, good performance was obtained with the electrocatalysts prepared by co-reduction of mixed ions. The performances increase with the increase of ruthenium content.

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