

## PtRu/C and PtRuBi/C electrocatalysts prepared by two different methodologies of borohydride reduction process for ethanol electro-oxidation

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**Abstract.** PtRu/C (50:50) and PtRuBi/C (50:40:10) electrocatalysts were prepared by borohydride reduction using  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ,  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  and  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  as metals sources and Vulcan XC72 as support. The borohydride solution was added in two different ways: drop by drop and rapid addition of all the solution. The obtained electrocatalysts were characterized by EDX, XRD and cyclic voltammetry. The electro-oxidation of ethanol was studied by cyclic voltammetry and chronoamperometry at room temperature and on a single cell of a direct ethanol fuel cell (DEFC) at 100°C. PtRuBi/C electrocatalysts showed superior performance for ethanol electro-oxidation than PtRu/C electrocatalysts prepared in a similar way. However, PtRuBi/C electrocatalyst prepared by rapid addition of the borohydride solution showed superior performance for ethanol electro-oxidation at room temperature, while PtRuBi/C electrocatalyst prepared by addition drop by drop of borohydride solution showed superior performance on DEFC at 100°C.

### Introduction

Direct Alcohol Fuel Cells (DAFCs) are attractive as power sources for mobile and portable applications [1-2]. The methanol has been considered the most promising fuel because it is more efficiently oxidized than other alcohols. On the other hand, slow anode kinetics has been observed and it is considered a toxic product [3-4]. Consequently, ethanol has been considered as an alternative fuel because it could be produced in large scale from renewable sources and showed lower toxicity than methanol. However, the complete ethanol oxidation to  $\text{CO}_2$  is more difficult than that of methanol due to the difficulty in C—C bond breaking and the formation of intermediates that poison the platinum anode catalysts.

Platinum is commonly used as anode catalyst in low temperature fuel cells; however, pure Pt is not an efficient anodic catalyst for the direct alcohol fuel cell. Platinum itself is known to be rapidly poisoned on its surface by strongly adsorbed species coming from the dissociative adsorption of alcohols. Thus, the addition of co-catalysts to platinum is essential to improve the oxidation. It has been shown that ruthenium oxides can enhance the catalytic activity for ethanol and methanol electro-oxidation through synergetic interaction with Pt. The Pt sites act as adsorption and dehydrogenation centers for ethanol, while the ruthenium oxides sites provide oxygen-containing species at lower potentials than those on a pure Pt surface [5-6].

Recently, Disalvo [7-9] related the use of intermetallic PtBi as alternative materials for fuel cells applications. The catalytic action of Bi was interpreted in terms of electronic effect and enhanced adsorption of OH species on adjacent Pt sites. Thus, the addition of Bi element to PtRu/C electrocatalyst could increase its activity for ethanol oxidation. So, in this work PtRu/C (50:50) and PtRuBi/C (50:40:10) electrocatalysts were prepared by borohydride reduction process in two

different ways: addition drop by drop of the borohydride solution and rapid addition of all the borohydride solution.

## Experimental

PtRu/C (Pt:Ru atomic ratio of 50:50) and PtRuBi/C (Pt:Ru:Bi atomic ratio of 50:40:10) electrocatalysts (20 wt.% metal loading) were prepared in a single step using  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ,  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ , and  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  as metal sources, sodium borohydride as reducing agent, and carbon Vulcan XC72 as support. The metal sources were dissolved in a mixture of water/2-propanol (50/50, v/v) and the carbon support was dispersed in the solution [10]. A solution of sodium borohydride was added in two different ways: addition drop by drop of the borohydride solution and rapid addition of all the borohydride solution. The final mixture was kept under stirring for 30 min. Finally, the mixture was filtered and the solid was washed with water and dried at 70 °C for 2 h.

The X-ray diffraction (XRD) analyses were performed using a Rigaku diffractometer model Miniflex II using Cu  $K\alpha$  radiation source ( $\lambda=0.15406$  nm). The diffractograms were recorded from  $2\theta = 20^\circ$  to  $90^\circ$  with a step size of  $0.05^\circ$  and a scan time of 2 s per step.

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 microanalyser.

Electrochemical studies of electrocatalysts were carried out using the thin porous coating technique [11]. 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  $0.47 \text{ cm}^2$  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 ( $\text{A g}_{\text{Pt}}^{-1}$ ). 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 MQPG 01, Brazil) potentiostat/galvanostat coupled to a PC and using the Microquimica software. Cyclic voltammetry and Chronoamperometry were performed in a  $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  and  $1.0 \text{ mol L}^{-1}$  ethanol solutions saturated with  $\text{N}_2$ .

The membrane electrode assemblies (MEA) were prepared by hot pressing a pretreated Nafion® 117 membrane placed between either a PtRu/C or PtRuBi/C anode ( $1 \text{ mg Pt cm}^2$  catalyst loading) and a 20 wt.% Pt/C E-TEK cathode ( $1 \text{ mg Pt cm}^2$  catalyst loading) at 125 °C for 2 min under a pressure of  $225 \text{ kgf cm}^2$ . The direct ethanol fuel cell performances were determined in a single cell with an area of  $5 \text{ cm}^2$ . The temperature was set to 100 °C for the fuel cell and 80 °C for the oxygen humidifier. The fuel was  $2 \text{ mol L}^{-1}$  ethanol solution delivered at approximately  $2 \text{ mL min}^{-1}$  and the oxygen flow was regulated at  $500 \text{ mL min}^{-1}$  and pressure of 2 bar. Polarization curves were obtained by using a TDI RBL 488 electronic load.

## Results and Discussion

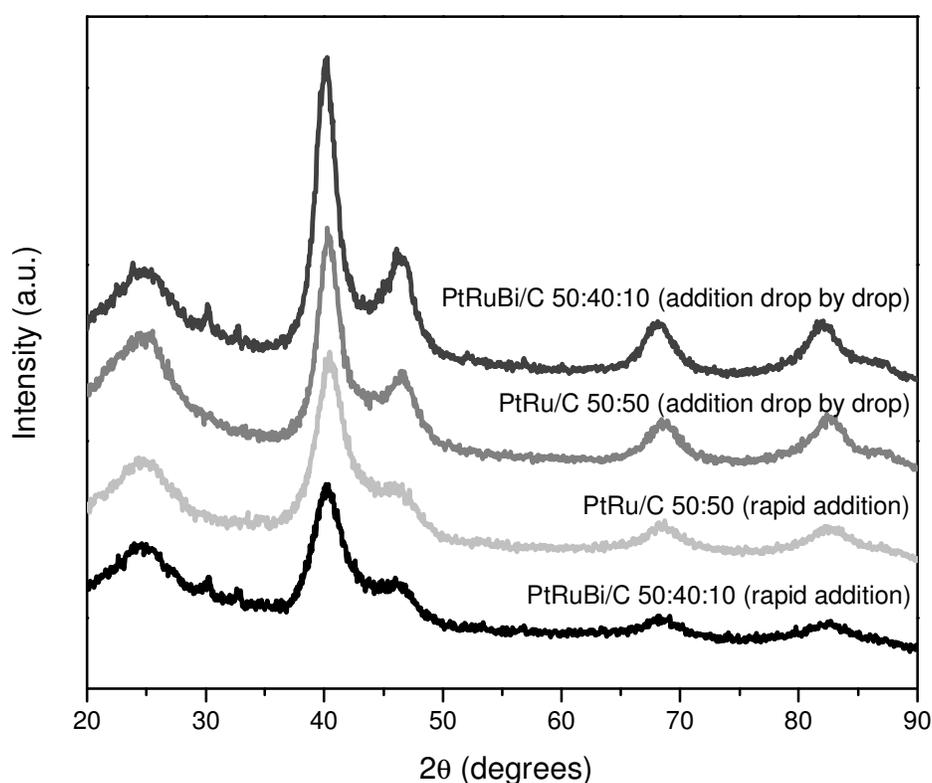
The Pt:Ru and Pt:Ru:Bi atomic ratios of the prepared electrocatalysts determined by EDX were similar to the nominal ones and the mean crystallite sizes determined using Scherrer equation [11] were in the range of 2–3 nm (Table 1).

**Table 1** - Atomic ratios and crystallite size of the PtRu/C and PtRuBi/C electrocatalysts.

Electrocatalyst	Addition of borohydride	Nominal atomic ratio	Atomic ratio EDX	Average crystallite size (nm) <sup>#</sup>
PtRu/C	drop by drop	50:50	57:43	3.0
PtRuBi/C	drop by drop	50:40:10	42:43:15	3.0
PtRu/C	rapid addition	50:50	45:55	2.0
PtRuBi/C	rapid addition	50:40:10	50:40:10	2.0

<sup>#</sup>Calculated from X-ray diffractograms using Scherrer equation.

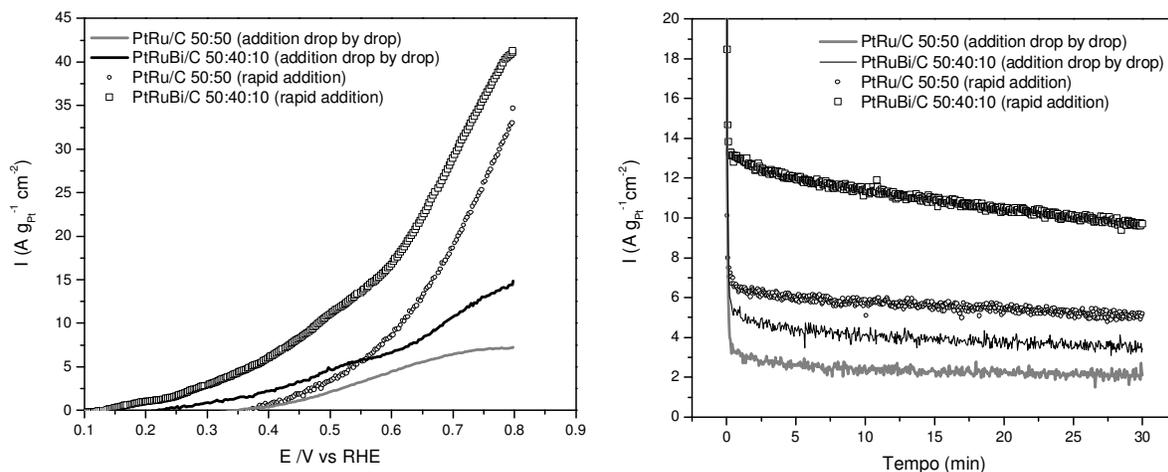
The X-ray diffractograms of the prepared electrocatalysts were shown in Fig. 1.



**Figure 1** - X-ray diffractograms of the PtRu/C and PtRuBi/C electrocatalysts prepared by borohydride reduction process.

All diffractograms showed a broad peak at about  $2\theta = 25^\circ$  that was associated with the carbon support and five diffraction peaks at about  $2\theta = 40^\circ, 47^\circ, 67^\circ, 82^\circ,$  and  $87^\circ$  characteristic of the face-centered cubic (fcc) structure of platinum and platinum alloys. No peaks corresponding to a metallic ruthenium, materials rich in ruthenium with a hexagonal structure, or the ruthenium oxide phase were observed [1]. The diffractograms of the PtRuBi/C electrocatalysts also showed peaks at about  $2\theta = 29^\circ, 33^\circ, 53^\circ,$  and  $57^\circ$  that were attributed to  $\text{Bi}_2\text{O}_3$  phases [10].

The anodic cyclic voltammetry and the current–time curves of PtRu/C and PtRuBi/C electro-catalysts in 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> and 1.0 mol L<sup>-1</sup> ethanol are shown in Fig. 2a and 2b, respectively.

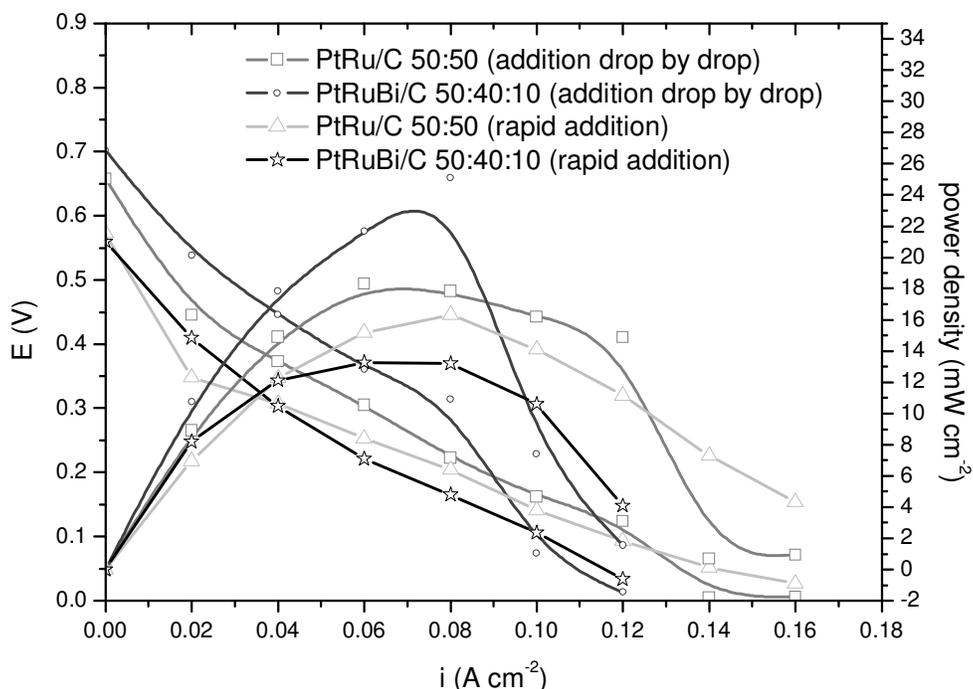


**Figure 2** – (a) Cyclic voltammograms of PtRu/Carbon materials in 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> containing 1.0 mol L<sup>-1</sup> of ethanol with a sweep rate of 10 mV s<sup>-1</sup>, considering only the anodic sweep. (b) Current–time curves at 0.5 V in 1 mol L<sup>-1</sup> ethanol solution in 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> for PtRu/C and PtRuBi/C electrocatalysts.

The PtRu/C (50:50) and PtRuBi/C (50:40:10) electrocatalysts performances in 1.0 mol L<sup>-1</sup> of ethanol are shown in Fig. 2a. The anodic cyclic voltammetry responses were plotted after subtracting the background currents and the current values were normalized per gram of platinum, considering that ethanol adsorption and dehydrogenation occur only on platinum sites at ambient temperature [11]. Independent of the way of preparation, it was observed that the ethanol electro-oxidation started at approximately 0.35 V for PtRu/C electrocatalysts while the onset potential was shifted negatively by about 150 mV for PtRuBi/C electrocatalysts. In both cases, PtRuBi/C electrocatalysts showed superior performance compared to PtRu/C prepared in a similar way. The PtRuBi/C prepared by rapid addition showed superior performance in all range of potential compared to the other electrocatalysts.

The chronoamperometry experiments were carried out to examine the electrochemical activity and stability of the electrocatalysts (Fig. 3b). The results were obtained in 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> and 1.0 mol L<sup>-1</sup> C<sub>2</sub>H<sub>5</sub>OH at an anodic potential of 0.5 V versus RHE. In all chronoamperometric curves, there is a sharp initial current drop in the first 2 min and then the current values practically remain constant until 30 min. The final current values after holding the cell potential at 0.5 V versus RHE for 30 min also showed that PtRuBi/C prepared by rapid addition was more active for ethanol electro-oxidation compared to the other electrocatalysts. The superior activity of PtRuBi/C electrocatalysts compared to PtRu/C electrocatalysts probably could be attributed to the bifunctional mechanism, where Pt acts on ethanol adsorption and dissociation, while ruthenium and bismuth provides oxygenated species at lower potentials for oxidative removal of the adsorbed intermediates formed during ethanol oxidation.

The performances of single cell and the power density of PtRu/C and PtRuBi/C as anode catalysts are shown in Fig. 3.



**Figure 3** - I-V curves of a 5 cm<sup>2</sup> DEFC and the power density at 100 °C using PtRu/C or PtRuBi/C electrocatalyst anodes (1 mg Pt cm<sup>2</sup> catalyst loading) and Pt/C E-TEK electrocatalysts cathode (1 mg Pt cm<sup>2</sup> catalyst loading, 20 wt.% catalyst on carbon), Nafion® 117 membrane, ethanol (2.0 mol L<sup>-1</sup>), oxygen pressure (2 bar).

The open circuit voltage of the PtRu/C electrocatalyst prepared by addition drop by drop was 0.65 V, while for PtRuBi/C prepared by addition drop by drop it increased to 0.71 V. Also, the maximum power density of PtRuBi/C electrocatalyst (25 mW cm<sup>-2</sup>) was greater than that of PtRu/C electrocatalyst (20 mW cm<sup>-2</sup>). Contrary to the observed for the electrochemical experiments at room temperature, under DEFC operating conditions, PtRu/C and PtRuBi/C electrocatalysts prepared by the addition drop by drop of borohydride solution showed superior performance compared to the electrocatalysts prepared by the rapid addition of all the borohydride solution.

## Conclusions

Active PtRu/C and PtRuBi/C electrocatalysts for ethanol oxidation could be prepared in two different ways by borohydride reduction. On the other hand, the activity of the obtained electrocatalysts depending on the conditions they were used. A more detailed characterization of the electrocatalysts by other techniques like transmission electron microscopy (TEM) and X-Ray Photoelectron Spectroscopy (XPS) should be done in order to explain these results.

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