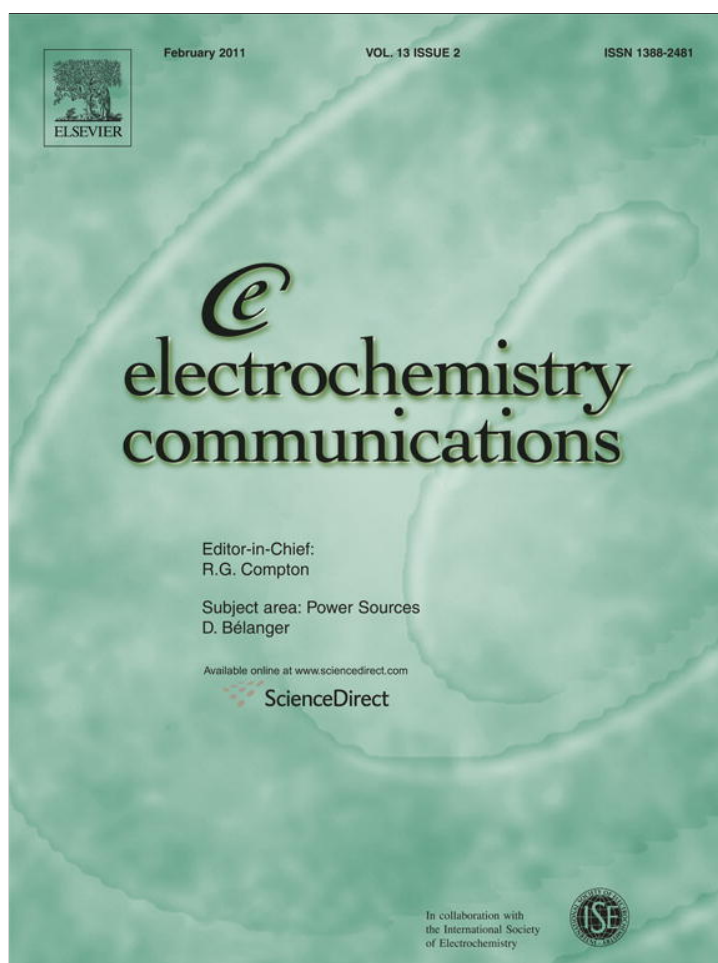


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Electrochemistry Communications

journal homepage: www.elsevier.com/locate/electrochem

The high activity of PtBi/C electrocatalysts for ethanol electro-oxidation in alkaline medium

Marcelo M. Tusi, Nataly S.O. Polanco, Sirlane G. da Silva, Estevam V. Spinacé, Almir Oliveira Neto*

Instituto de Pesquisas Energéticas e Nucleares, IPEN-CNEN/SP, Av. Prof. Lineu Prestes, 2242 – Cidade Universitária, CEP 05508-900 São Paulo-SP, Brazil

ARTICLE INFO

Article history:

Received 5 November 2010

Received in revised form 25 November 2010

Accepted 30 November 2010

Available online 8 December 2010

Keywords:

PtBi/C electrocatalysts

Ethanol electro-oxidation

Alkaline medium

Fuel cell

ABSTRACT

Pt/C, Bi/C and PtBi/C (Pt:Bi atomic ratios of 90:10, 70:30 and 50:50) electrocatalysts were prepared by borohydride reduction using $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ as metal sources and Vulcan XC72 as carbon support. The obtained electrocatalysts were characterized by energy-dispersive X-ray analysis, X-ray diffraction, transmission electron microscopy and cyclic voltammetry. The activity of the electrocatalysts for ethanol electro-oxidation was studied by chronoamperometry. PtBi/C electrocatalysts showed a significant increase of performance compared to Pt/C, while Bi/C showed no activity. Also, the performances of the PtBi/C electrocatalysts for ethanol electro-oxidation in alkaline medium were very superior to the ones obtained in acid medium.

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1. Introduction

Alkaline Direct Alcohol Fuel Cells (ADAFCs) have some advantages over proton exchange membrane fuel cells like improved kinetics at both cathode and anode and reduced alcohol crossover as the electro-osmotic drag of the hydrated hydroxide ion opposes alcohol transport [1–4]. Ethanol has been considered as an interesting fuel for DAFCs because it could be produced in large scale from renewable sources and it is less toxic than methanol [1,4]. PtSn/C electrocatalysts have been described to be more active than Pt/C and PtRu/C electrocatalysts for ethanol electro-oxidation in acid medium [5], while Pd has been described as the more active catalyst for ethanol electro-oxidation in alkaline medium [4]. On the other hand, the cleavage of the C–C bond of the ethanol molecule is difficult on the Pd catalysts in alkaline medium and acetate ions are the main product formed [4].

Jiang et al. [6] showed that the ethanol oxidation currents of Pt/C and PtSn/C electrocatalysts in alkaline medium were higher than those obtained in acid medium, while the onset potentials in alkaline medium were less positive than those obtained in acid medium. Roychowdhury et al. [7] described the use of PtBi nanoparticles for formic acid oxidation in acid medium, which exhibited enhanced electrocatalytic activity compared to Pt and PtRu nanoparticles. Demarconnay et al. [8] showed that PtBi/C electrocatalysts promoted the catalytic activity towards ethylene glycol electro-oxidation in alkaline medium when compared to Pt/C. Recently, we described that the activity of PtBi/C electrocatalyst for ethanol electro-oxidation in

acid medium was slight superior to that of Pt/C [9,10]. In this work, PtBi/C electrocatalysts with different Pt:Bi atomic ratios were tested for ethanol electro-oxidation in alkaline medium and the obtained results were compared to the ones obtained in acid medium.

2. Experimental

Pt/C, Bi/C and PtBi/C (20 wt.% of metals loading; Pt:Bi atomic ratios of 90:10, 70:30 and 50:50) electrocatalysts were prepared using $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ 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. In this process the metal sources were dissolved in a mixture of water/2-propanol (50/50, v/v) and the carbon support was dispersed. The resulting mixture was submitted to an ultrasonic bath for 10 min. After this, a solution of sodium borohydride was added under stirring in one portion at room temperature. Finally, the mixture was filtered and the solid was washed with water and dried at 70 °C for 2 h.

Pt:Bi atomic ratios were obtained by energy-dispersive X-ray (EDX) analysis in different parts of the materials using a scanning electron microscope Phillips XL30 with a 20 keV electron beam and equipped with EDAX DX4 microanalyser.

X-ray diffraction (XRD) analyses were performed using a Rigaku diffractometer model Miniflex II with a $\text{CuK}\alpha$ radiation source. 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.

Transmission electron microscopy (TEM) was carried out using a JEOL JEM-2100 electron microscope operated at 200 kV.

Electrochemical studies were carried out using the thin porous coating technique [5]. An amount of 20 mg of the electrocatalysts was added to a solution of 50 mL of water containing 3 drops of a 6%

* Corresponding author. Tel.: +55 11 31339284; fax: +55 11 31339193.
E-mail address: aolivei@ipen.br (A.O. Neto).

polytetrafluoroethylene (PTFE) suspension. The mixture was treated in an ultrasound bath for 10 min and transferred to the cavity of the working electrode. The working electrodes have a geometric area of 0.3 cm^2 with a depth of 0.3 mm. The reference electrode was an Ag/AgCl electrode and the counter electrode was a platinized Pt plate. Cyclic voltammetry and chronoamperometry experiments were performed in 1.0 mol L^{-1} KOH solution saturated with N_2 using a Microquímica (model MQPG01, Brazil) potenciostat/galvanostat.

3. Results and discussion

The Pt:Bi atomic ratios obtained by EDX analysis for all PtBi/C electrocatalysts were similar to the nominal atomic ratios (Table 1).

The X-ray diffractograms of Pt/C, Bi/C and PtBi/C electrocatalysts are shown in Fig. 1. All diffractograms showed a broad peak at about 25° associated with the Vulcan XC72 support material. The diffractograms of Pt/C and PtBi/C electrocatalysts showed five peaks at approximately $2\theta = 40^\circ, 47^\circ, 67^\circ, 82^\circ$ and 87° , which are associated with the (111), (200), (220), (311) and (222) planes, respectively, of the face-centered cubic (fcc) structure characteristic of Pt and Pt alloys [5]. The diffractogram of Bi/C electrocatalyst showed the hexagonal structure of metallic Bi [11]. For PtBi/C electrocatalysts (Pt:Bi atomic ratio of 70:30 and 50:50) besides the Pt(fcc) phase, peaks that could be attributed to the presence of a mixture of BiPt and Bi_2Pt phases, with Bi_2Pt as the predominant phase was also observed [12].

The mean crystallite sizes of Pt (fcc) phase were determined using Scherrer equation [5]. For Pt/C electrocatalyst a mean crystallite size of 5 nm was obtained and with the increase of Bi content, a decrease of the crystallite sizes was observed (Table 1).

Fig. 2 presents TEM micrographs of Pt/C and PtBi/C (Pt:Bi atomic ratio of 50:50) electrocatalysts. The TEM image of Pt/C electrocatalyst (Fig. 2a) showed the Pt nanoparticles homogeneously dispersed on the carbon support with particle sizes of $4.6 \pm 1.9 \text{ nm}$. The micrograph of PtBi/C electrocatalyst (Fig. 2b) also showed the nanoparticles homogeneously dispersed on the carbon support with particle sizes of $3.3 \pm 0.8 \text{ nm}$.

The cyclic voltammograms (CV) of Pt/C and PtBi/C electrocatalysts in alkaline medium are shown in Fig. 3. The CV of PtBi/C electrocatalysts showed that the hydrogen adsorption region was greatly reduced compared to the Pt/C electrocatalyst. The anodic scan showed a main peak of Bi at about -0.1 V while the cathodic scan showed two reduction processes at about -0.3 and -0.8 V [8,13]. The electro-oxidation of ethanol (Fig. 3 inset) started at around -0.55 V for all electrocatalysts and the current values in the potential range of -0.5 V to 0.2 V increase rapidly with the increase of Bi content in the samples.

The chronoamperometry curves of the Pt/C, Bi/C and PtBi/C (Pt:Bi atomic ratios of 90:10, 70:30 and 50:50) electrocatalysts at -0.4 V (0.5 V vs RHE) in 1.0 mol L^{-1} KOH and 1.0 mol L^{-1} $\text{C}_2\text{H}_5\text{OH}$ solutions at room temperature are shown in Fig. 4. The chronoamperometry results showed that Bi/C electrocatalyst showed no activity for ethanol electro-oxidation, however, the addition of Bi increased the catalytic activity of the Pt/C catalyst. The final current values after holding the cell potential at -0.4 V vs Ag/AgCl for 30 min increase in

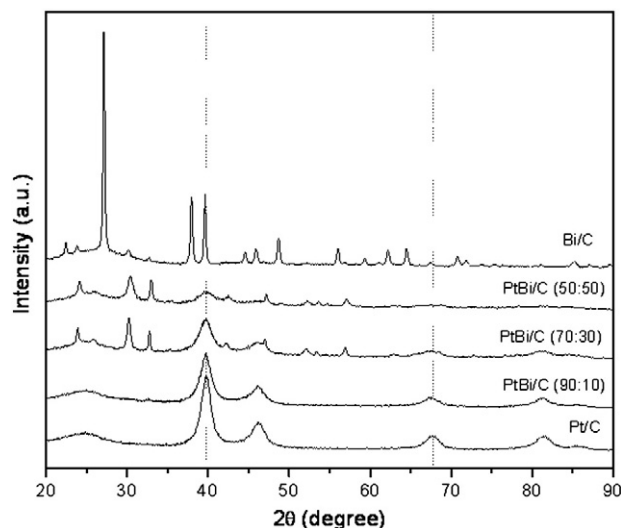


Fig. 1. X-ray diffractograms of Pt/C, Bi/C and PtBi/C electrocatalysts.

the following order: PtBi/C (50:50) > PtBi/C (70:30) > PtBi/C (90:10) > Pt/C, showing that the current values increase with the increase of Bi content in the sample, however, some influence of the particle sizes could not be discarded. Pt/C and PtBi/C (50:50) electrocatalysts were also tested for ethanol electro-oxidation in acid medium and the final current values obtained after holding the cell at -0.4 V for 30 min were compared to the ones obtained in alkaline medium (Fig. 4 inset). The final current value of the PtBi/C (50:50) electrocatalyst obtained in alkaline medium was about seven times higher than the current value of the Pt/C electrocatalyst, while in acid medium this increase was only two times. Recently, Jiang et al. [6] tested Pt/C and PtSn/C electrocatalysts for ethanol electro-oxidation in alkaline and acid media. A significant improvement of activity was observed in acid media on PtSn/C catalyst compared with Pt/C, while only negligible improvement was observed in alkaline medium. The difference of activity was attributed to the different origins of OH_{ad} species in alkaline and acid media. In acid medium ethanol molecule is first adsorbed and dehydrogenated on Pt active sites and the resulting ethoxy reacts with the OH_{ad} species (formed through H_2O decomposition) on Sn active sites to produce acetaldehyde. In alkaline medium, the OH_{ad} species are produced from the discharge of OH^- in the solution, not through water decomposition on Sn sites. Schmidt et al. [14] studied the oxidation of formic acid at Bi-modified Pt(111) electrode and proposed that the increase of the catalytic activity was due to the enhanced adsorption of OH_{ad} species on the Pt sites adjacent to Bi facilitating the oxidative removal of poisoning species. In this manner, the increase of activity of PtBi/C electrocatalysts for ethanol electro-oxidation in alkaline medium seems to be related to the enhancement of OH_{ad} species (coming from OH^- in the solution) absorption on Pt sites adjacent to Bi.

4. Conclusions

PtBi/C electrocatalysts exhibited high performance for ethanol oxidation in alkaline medium. The X-ray diffractograms of PtBi/C electrocatalysts showed the typical fcc structure of Pt and Pt alloys and the presence of BiPt and Bi_2Pt phases, which increase with Bi content. The activity of PtBi/C electrocatalysts increases with Bi content and it could be related to enhancement of OH_{ad} species absorption on Pt sites adjacent to Bi, which facilitates the oxidative removal of intermediates formed. Further work is now necessary to investigate the PtBi/C electrocatalysts surface by different techniques and to elucidate the mechanism of ethanol electro-oxidation in alkaline medium.

Table 1
Atomic ratios and crystallite sizes of the Pt/C and PtBi/C electrocatalysts.

Electrocatalysts	Pt:Bi–nominal atomic ratio	Pt:Bi–atomic ratio (EDX)	Crystallite size (nm)
Pt/C	–	–	5
PtBi/C	90:10	83:17	5
PtBi/C	70:30	71:29	3
PtBi/C	50:50	47:53	2

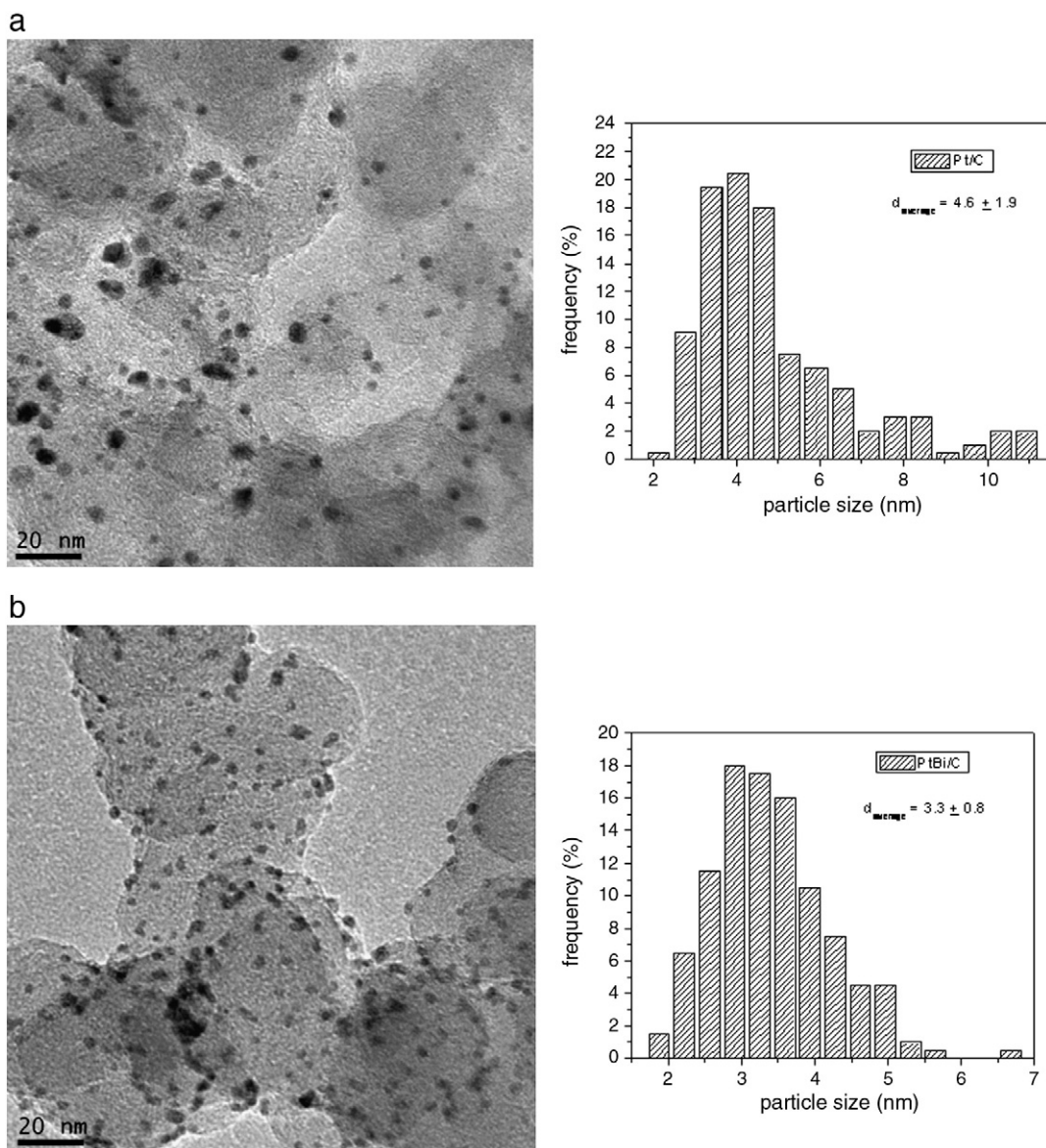


Fig. 2. TEM micrographs of a) Pt/C and b) PtBi/C (50:50) electrocatalysts.

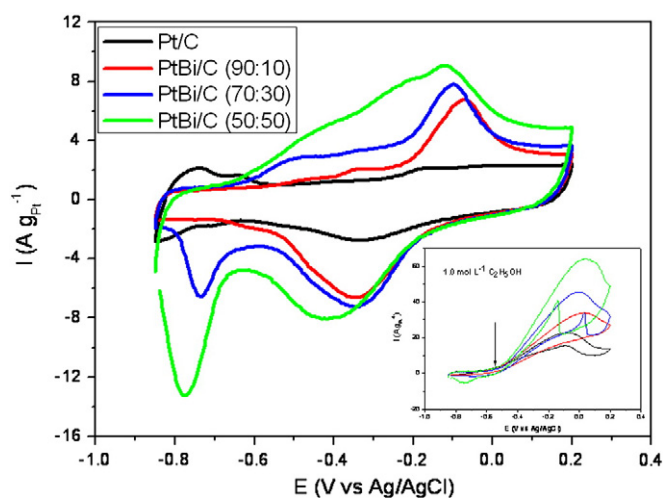


Fig. 3. Cyclic voltammograms (CV) of Pt/C and PtBi/C electrocatalysts in 1.0 mol L^{-1} KOH with a sweep rate of 10 mV s^{-1} . (Inset) CVs in 1.0 mol L^{-1} KOH containing 1.0 mol L^{-1} of ethanol.

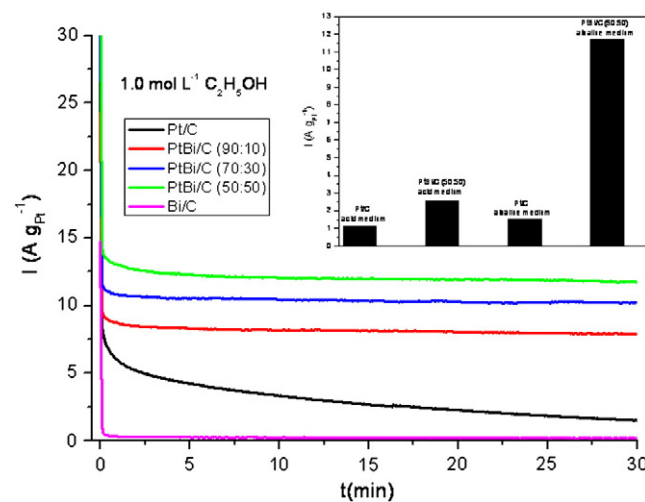


Fig. 4. Current-time curves at -0.4 V in 1 mol L^{-1} ethanol solution in 1.0 mol L^{-1} KOH for Pt/C, Bi/C and PtBi/C electrocatalysts. (Inset) Current values at -0.4 V after 30 min for Pt/C and PtBi/C electrocatalysts in alkaline and acid media.

Acknowledgments

The authors thank FINEP-ProH₂, FAPESP and CNPq for the financial support.

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