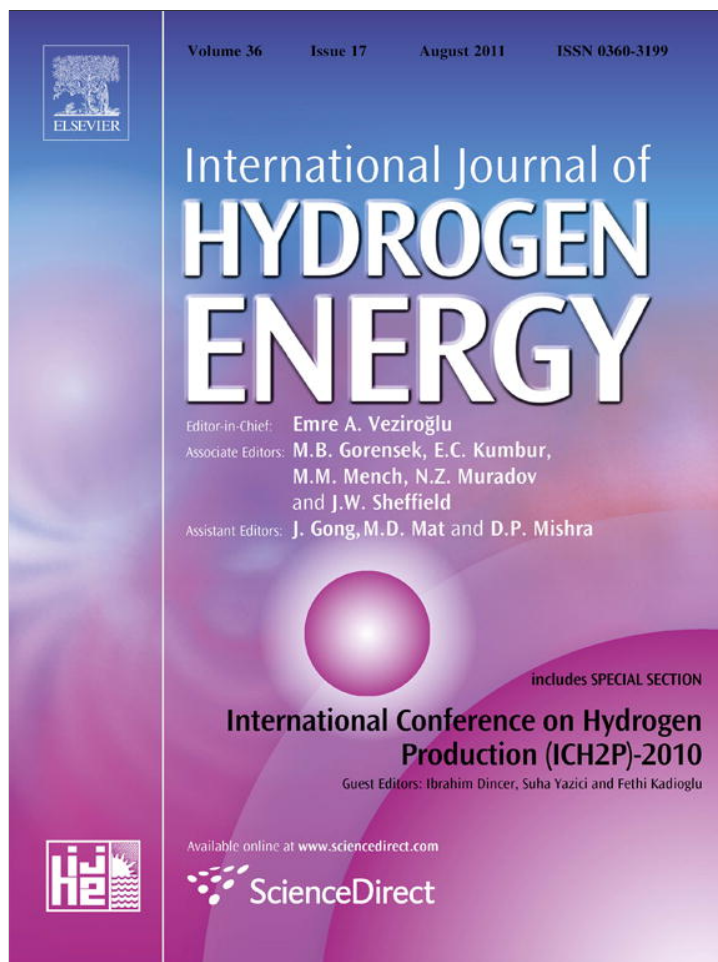


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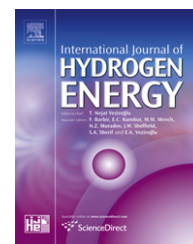


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Technical Communication

PdBi/C electrocatalysts for ethanol electro-oxidation in alkaline medium

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ABSTRACT

PdBi/C electrocatalysts (Pd:Bi atomic ratios of 95:05, 90:10, 80:20 and 70:30) were prepared by borohydride reduction using $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ as metal sources and Vulcan XC72 as support. The electrocatalysts were characterized by energy-dispersive X-ray analysis, X-ray diffraction, transmission electron microscopy and cyclic voltammetry. The activity for the ethanol electro-oxidation in alkaline medium was investigated at room temperature by chronoamperometry and the results were compared with Pt/C and PtBi/C electrocatalysts. PdBi/C (95:05) electrocatalyst showed a significant increase of performance for ethanol electro-oxidation compared to Pd/C and others PdBi/C electrocatalysts. The final current value after holding the cell at -0.4 V versus Ag/AgCl electrode for 30 min in alkaline medium for PdBi/C (95:05) electrocatalyst was about eleven times higher than the current value of the Pt/C electrocatalyst and 1.5 times higher than PtBi/C (50:50).

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1. Introduction

Ethanol is considered one of the most promising candidates for DAFCs, because it could be produced in large scale from renewable sources and it is less toxic than methanol [1,2]. Most of research on DEFC has been done in acidic media and in these studies PtSn/C electrocatalysts showed to be more active than Pt/C and PtRu/C electrocatalysts, however, the Pt-based electrocatalysts shows a high cost and the use of platinum is limited, consequently the development of new Pt-free electrocatalysts is necessary [3,4].

Recently, the development of alkaline anion-exchange membranes (AEMs) evokes increasing interest on electrocatalysis in alkaline media and the use of Pd/C has been an alternative to Pt/C electrocatalysts, because the Pd/C showed an electrocatalytic activity higher than that of Pt/C, the onset potential for ethanol oxidation on Pd/C also was shifted to lower potentials compared to that of Pt in alkaline medium and the Pd/C electrocatalysts also shown high stability for alcohol electro-oxidation in alkaline medium [5,6].

Pd/C electrocatalyst also has been considered promising for the ethanol oxidation in alkaline medium as well as for

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formic acid oxidation in acidic medium, because its electrocatalytic activity is higher than that of Pt/C [7,8]. However, the activity of Pd for ethanol oxidation in alkaline media needs to be enhanced.

Demarconnay et al. [9] showed that PtBi/C electrocatalysts increased the catalytic activity towards ethylene glycol electro-oxidation in alkaline medium when compared to Pt/C.

Shen et al. [10,11] showed that PdCeO₂, PdNiO, or PdCo₃O₄ were more active and stable compared to platinum for ethanol oxidation in alkaline medium. In another studies Pd₂Ni₃/C catalyst also exhibited higher activity and stability for the ethanol oxidation reaction in alkaline medium than does Pd/C catalyst [5]. Bambagioni et al. [12] also showed that Pd-(Ni-Zn)/C and Pd-(Ni-Zn-P)/C are much more stable and active than Pd/C for ethanol oxidation in alkaline medium.

Recently Tusi et al. [13] showed that PtBi/C electrocatalysts had a significant increase of performance for ethanol oxidation in alkaline medium compared to Pt/C, while Bi/C electrocatalyst showed no activity. Moreover, the performances of the PtBi/C electrocatalysts for ethanol electro-oxidation in alkaline medium were very superior to the ones obtained in acid medium.

In this work, PdBi/C electrocatalysts with different Pd:Bi atomic ratios were prepared by borohydride reduction and tested for ethanol electro-oxidation in alkaline medium. The performance results were compared to the ones obtained with Pt/C and PtBi/C electrocatalysts [13].

2. Experimental

PdBi/C (20 wt.% of metals loading; Pd:Bi atomic ratios of 95:05, 90:10, 80:20 and 70:30) electrocatalysts were prepared using Pd(NO₃)₂·2H₂O and Bi(NO₃)₃·5H₂O 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. The resulting mixture was submitted to an ultrasonic bath for 5 min. After this a solution of sodium borohydride was added under stirring in one portion at room temperature. Finally, the obtained solid was filtered, washed with water and dried at 70 °C for 2 h.

The Pd:Bi atomic ratios were obtained by energy-dispersive X-ray (EDX) analysis using a scanning electron microscope Philips XL30 with a 20 keV electron beam and equipped with EDAX DX-4 microanaliser.

X-ray diffraction (XRD) analyses were performed using a Rigaku diffractometer model Miniflex II using Cu K α radiation source ($\lambda = 0.15406$ nm). The diffractograms were recorded from $2\theta = 20^\circ$ – 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. The particle size distributions were determined by measuring of 200 nanoparticles in the micrographs using Image Tool Software.

Electrochemical studies were carried out using the thin porous coating technique [14]. In this process an amount of 20 mg of the electrocatalysts was added to a solution of 50 mL of water containing 3 drops of a 6% 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 Pt plate. Cyclic voltammetry and chronoamperometry experiments were performed in 1.0 mol L^{-1} KOH solution saturated with N₂ using a Microquímica (model MQPG01, Brazil) potentiostat in presence or absence of 1.0 mol L^{-1} of ethanol.

3. Results and discussion

The Pd:Bi atomic ratios of the obtained electrocatalysts were similar to the nominal atomic ratios.

The X-ray diffractograms of the electrocatalysts were shown in Fig. 1. All diffractograms showed a broad peak at about $2\theta = 25^\circ$ associated with the Vulcan XC72 support material. The diffractograms of Pd/C, PdBi/C (95:05), PdBi/C (90:10), PdBi/C (80:20) and PdBi/C (70:30) electrocatalysts showed four peaks around the 2θ values of 40° , 47° , 68° and 82° which are characteristic of the face-centered cubic (fcc) structure of metallic Pd or Pd alloys [5]. For all PdBi/C electrocatalyst it was also observed that the diffraction peaks of Pd (fcc) phase are shifted to small angles compared to Pd/C electrocatalyst, which indicates a lattice expansion and that Bi atoms were incorporated into a fcc Pd lattice. For PdBi/C (70:30) electrocatalyst besides the Pd (fcc) phase, it was also observed the presence of some peaks that could be attributed to the presence of Bi and/or PdBi phases [13]. The (220) reflections of Pd(fcc) crystalline structure were used to calculate the average crystallite sizes using Scherrer equation [14] and the calculated values were around 3 nm for all electrocatalysts.

Fig. 2 shows TEM micrographs and histograms of size distribution of Pd/C and PdBi/C (Pd:Bi atomic ratios of 95:05 and 90:10) electrocatalysts. The TEM micrographs of all electrocatalysts showed a good distribution of the nanoparticles on the carbon support with average particle sizes around

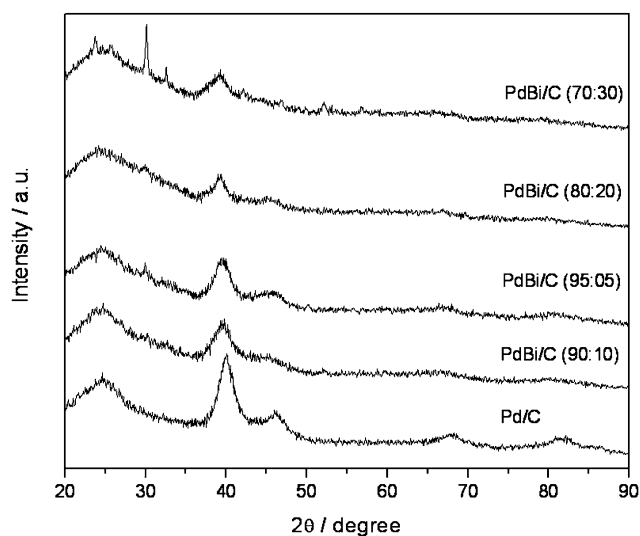


Fig. 1 – X-ray diffractograms of Pd/C and PdBi/C electrocatalysts.

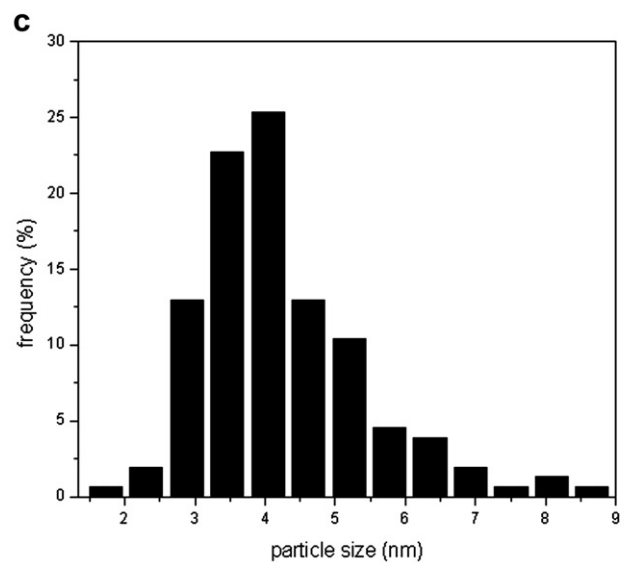
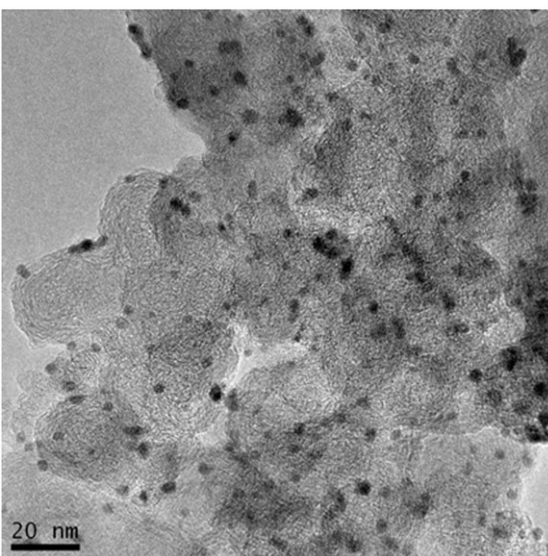
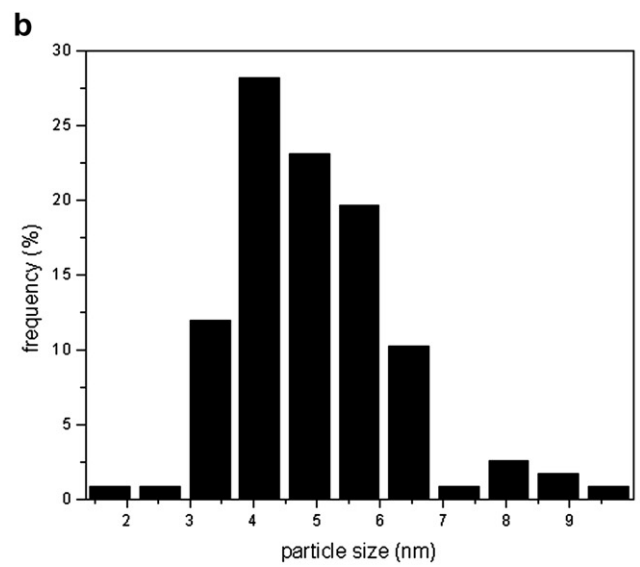
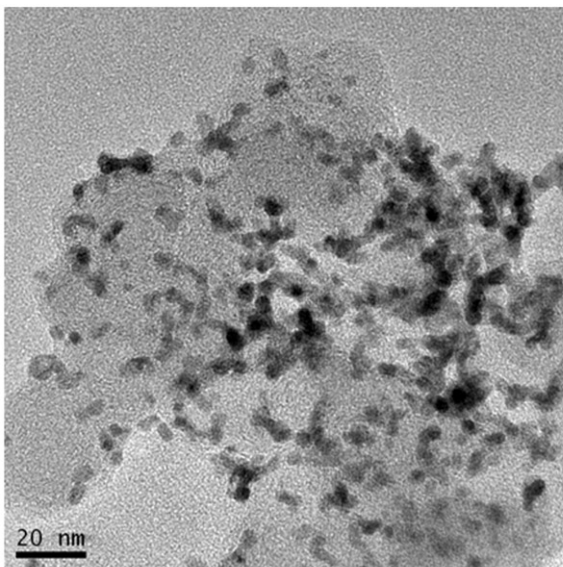
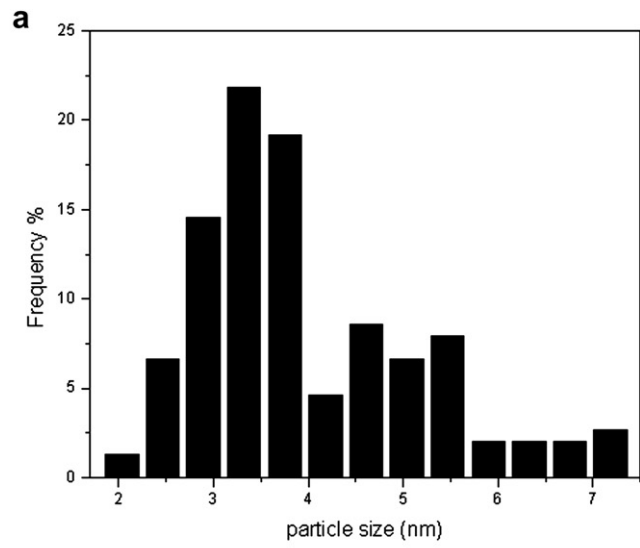
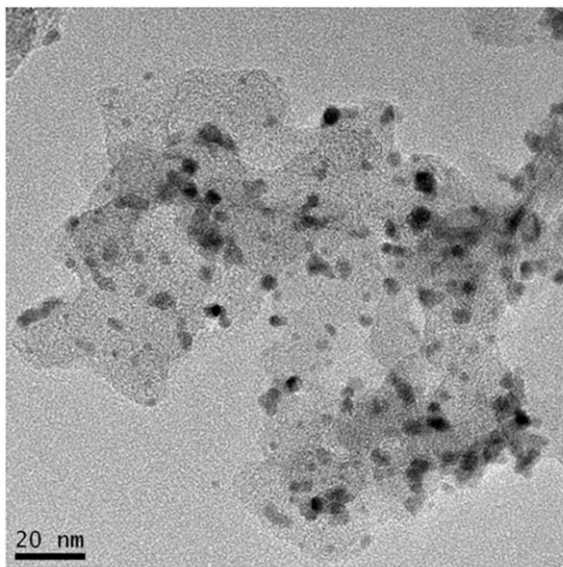


Fig. 2 – TEM micrographs and histograms of the particle size distribution of (a) Pd/C, (b) PdBi/C (95:05) and (c) PdBi/C (90:10) electrocatalysts.

4 nm, however, the histograms showed a broad distribution of the particle sizes for all catalysts.

The cyclic voltammograms (CV) of Pd/C and PdBi/C electrocatalysts in alkaline medium and in absence of ethanol are shown in Fig. 3a. Compared to Pd/C electrocatalyst the CV of PdBi/C electrocatalysts showed that the hydrogen adsorption region is greatly reduced by the presence of Bi. The anodic scan of all PdBi/C electrocatalysts showed the formation of a main peak at around 0.0 V, while for PdBi/C (80:20 and 70:30) it was also observed another peak at around -0.3 V. The presence of these peaks could be attributed to the formation of bismuth and/or palladium oxide species [9,13]. The cathodic scans showed a reduction processes between -0.3 and -0.8 V.

The CV of Pd/C and PdBi/C electrocatalysts in 1.0 mol L^{-1} KOH and 1.0 mol L^{-1} ethanol are shown in Fig. 3b. For PdBi/C (80:20 and 70:30) electrocatalysts the ethanol electro-oxidation started only at approximately -0.4 V while for Pd/C the onset potential was shifted negatively by about -100 mV (around -0.5 V). For PdBi/C (95:05 and 90:10) the onset potential shifted to small values (around -0.6 V) and the PdBi/C (95:05) electrocatalyst showed higher current values in the potential range of -0.6 to -0.2 V than the others catalyst. This shows that the

addition of small quantities of Bi greatly enhances the kinetics of ethanol electro-oxidation in alkaline medium.

The chronoamperometry experiments were carried out to examine the electrochemical stability of the electrocatalysts (Fig. 4a). The final current values after holding the cell potential at -0.4 V vs Ag/AgCl for 30 min increase in the following order: PdBi/C (95:05) > PdBi/C (90:10) > Pd/C > PdBi/C (80:20) \approx PdBi/C (70:30) confirming the results obtained by cyclic voltammetry. The final current values of Pd/C and PdBi/C electrocatalysts were compared to the ones obtained for Pt/C and PtBi/C electrocatalysts [13] in alkaline medium (Fig. 4b). The results showed that the final current value of the Pd/C electrocatalyst was higher than the obtained for Pt/C electrocatalyst. Also, the addition of Bi to Pt/C and Pd/C electrocatalysts greatly enhanced the performances of these electrocatalysts, however, for Pt/C the addition of great quantities of Bi (50 at.%) was necessary to obtain good performances [13] while for Pd/C only a small quantity was sufficient (5 at.% Bi). The increase of the activity of PtBi/C electrocatalysts with the increase of Bi content was attributed to the enhancement of OH species adsorption on Pt sites

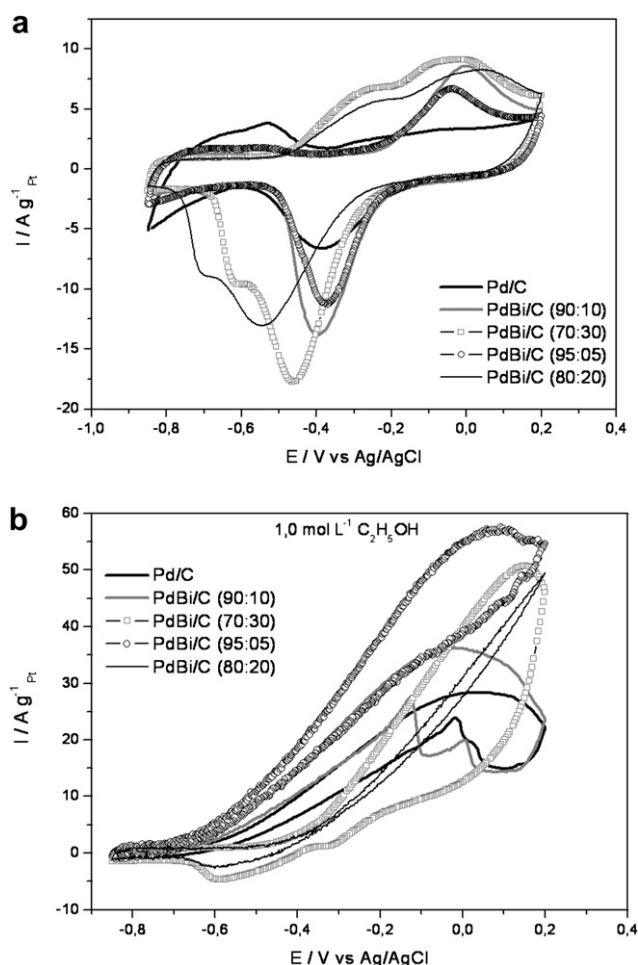


Fig. 3 – (a) Cyclic voltammograms (CV) of Pd/C and PdBi/C electrocatalysts in 1.0 mol L^{-1} KOH with a sweep rate of 10 mV s^{-1} (b) CVs in 1.0 mol L^{-1} KOH containing 1.0 mol L^{-1} of ethanol.

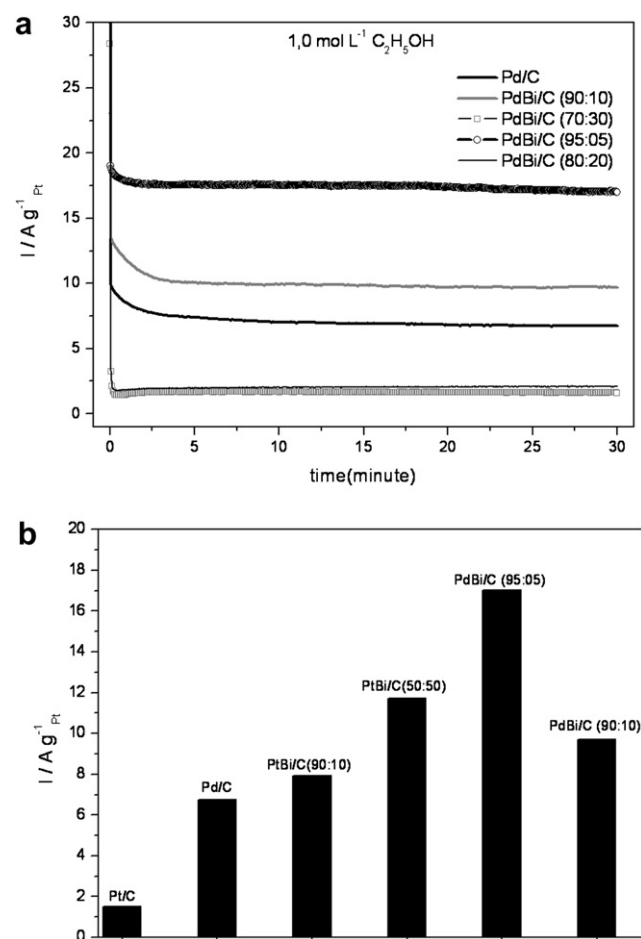


Fig. 4 – (a) Current–time curves at -0.4 V vs Ag/AgCl in 1.0 mol L^{-1} KOH solution containing 1 mol L^{-1} of ethanol for Pd/C and PdBi/C electrocatalysts. (b) Current values at -0.4 V vs Ag/AgCl after 30 min for Pt/C, Pd/C, PdBi/C (95:05), PdBi/C (90:10), PtBi/C (90:10) and PtBi/C (50:50) electrocatalysts in alkaline medium.

adjacent to Bi, which facilitates the oxidative removal of intermediates formed on ethanol electro-oxidation [13,15]. In a similar way, it was described for ethanol electro-oxidation on a Pd electrode in alkaline media that the dissociative adsorption of ethanol proceed quickly and the rate-determining step was the removal of the adsorbed ethoxi intermediates by the OH_{ad} species on the Pd electrode [16]. In this manner, the mechanism of ethanol electro-oxidation seems occurs in a similar way on PtBi/C and PdBi/C electrocatalysts, however, different quantities of Bi are required to obtain a better performance. Similar results were described by Simões et al. [17]. They prepared PdBi/C and PtBi/C electrocatalysts with different compositions by a microemulsion method and evaluated the performance for sodium borohydride electro-oxidation in alkaline media. It was observed that the bismuth atomic ratio needed to achieve better performances were different for Pd and Pt catalysts.

4. Conclusions

The addition of small quantities of Bi (5 at.%) to Pd/C electrocatalyst greatly enhanced the performance for ethanol electro-oxidation in alkaline medium. The X-ray diffractograms revealed the formation of PdBi alloys in the obtained materials. The high activity of PdBi/C electrocatalysts could be related to the removal of the intermediates by the OH_{ad} species. Further work is now necessary to characterize the electrocatalyst surface by different techniques and to elucidate the mechanism of ethanol electro-oxidation in alkaline medium using PdBi/C electrocatalysts.

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REFERENCES

- [1] Wendt H, Spinacé EV, Neto AO, Linardi M. Electrocatalysis and electrocatalysts for low temperature fuel cells: fundamentals, state of the art, research and development. *Quím Nova* 2005;28:1066–75.
- [2] Antolini E, Gonzalez ER. Alkaline direct alcohol fuel cells. *J Power Sources* 2010;195:3431–50.
- [3] Nguyen ST, Law HM, Nguyen HT, Kristian N, Wang S, Chan SH, et al. Enhancement effect of Ag for Pd/C towards the ethanol electro-oxidation in alkaline media. *Appl Catal B Environ* 2009;91:507–15.
- [4] Neto AO, Dias RR, Tusi MM, Linardi M, Spinacé EV. Electro-oxidation of methanol and ethanol using PtRu/C, PtSn/C and PtSnRu/C electrocatalysts prepared by an alcohol-reduction process. *J Power Sources* 2007;166:87–91.
- [5] Shen SY, Zhao TS, Xu JB, Li YS. Synthesis of PdNi catalysts for the oxidation of ethanol in alkaline direct ethanol fuel cells. *J Power Sources* 2010;195:1001–6.
- [6] Bianchini C, Shen PK. Palladium-based electrocatalysts for alcohol oxidation in half cells and in direct alcohol fuel cells. *Chem Rev* 2009;109:4183–206.
- [7] Uhm S, Yi Y, Lee J. Electrocatalytic activity of Pd–CeO₂ nanobundle in an alkaline ethanol oxidation. *Catal Lett* 2010; 138:46–9.
- [8] Xu C, Cheng L, Shen PK, Liu Y. Methanol and ethanol electrooxidation on Pt and Pd supported on carbon microspheres in alkaline media. *Electrochem Commun* 2007;9:997–1001.
- [9] Demarconnay L, Brimaud S, Coutanceau C, Léger JM. Ethylene glycol electrooxidation in alkaline medium at multi-metallic Pt based catalysts. *J Electroanal Chem* 2007; 601:169–80.
- [10] Shen PK, Xu C. Alcohol oxidation on nanocrystalline oxide Pd/C promoted electrocatalysts. *Electrochem Commun* 2006; 8:184–8.
- [11] Xu C, Shen PK, Liu Y. Ethanol electrooxidation on Pt/C and Pd/C catalysts promoted with oxide. *J Power Sources* 2007; 164:527–31.
- [12] Bambagioni V, Bianchini C, Filippi J, Oberhauser W, Marchionni A, Vizza F, et al. Ethanol oxidation on electrocatalysts obtained by spontaneous deposition of palladium onto nickel-zinc materials. *ChemSusChem* 2009;2: 99–112.
- [13] Tusi MM, Polanco NSO, da Silva SG, Spinacé EV, Neto AO. The high activity of PtBi/C electrocatalysts for ethanol electro-oxidation in alkaline medium. *Electrochem Commun* 2011; 13:143–6.
- [14] Neto AO, Farias LA, Dias RR, Brandalise M, Linardi M, Spinacé EV. Enhanced electro-oxidation of ethanol using PtSn/CeO-C electrocatalyst prepared by an alcohol-reduction process. *Electrochem Commun* 2008;10:1315–7.
- [15] Schmidt TJ, Behm RJ, Grgur BN, Markovic NM, Ross Jr PN. Formic acid oxidation on pure and bi-modified Pt(111): temperature effects. *Langmuir* 2000;16:8159–66.
- [16] Liang ZX, Zhao TS, Xu JB, Zhu LD. Mechanism study of the ethanol oxidation reaction on palladium in alkaline media. *Electrochim Acta* 2009;54:2203–8.
- [17] Simões M, Baranton S, Coutanceau C. Influence of bismuth on the structure and activity of Pt and Pd nanocatalysts for the direct electrooxidation of NaBH₄. *Electrochim Acta* 2010;56:580–91.