

Preparation of PtSnSb/C by an alcohol reduction process for direct ethanol fuel cell (DEFC)

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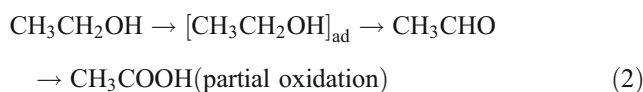
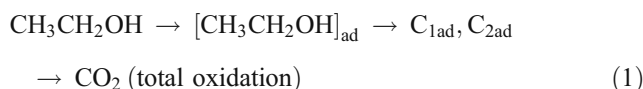
Abstract PtSn/C and PtSnSb/C electrocatalysts (20 wt.% metal loading) were prepared by an alcohol reduction process using $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, and Sb (OOCCH₃) as metal sources, ethylene glycol as solvent and reducing agent, and Vulcan XC72 as carbon support. The electrocatalysts were characterized by energy dispersive X-ray analysis, X-ray diffraction, and transmission electron microscopy, while that the performance for ethanol oxidation was investigated by cyclic voltammetry and chronoamperometry (chrono) at room temperature. The diffractograms of the PtSn/C and PtSnSb/C electrocatalysts showed four peaks associated to Pt face-centered cubic structure and two peaks that were related to a SnO_2 phase. For PtSb/C and PtSnSb/C electrocatalysts, no Sb (antimony) peaks corresponding to a metallic antimony or antimony oxide phases were observed. Transmission electron microscopy images showed that the metal particles were homogeneously distributed over the support. The PtSnSb/C (50:45:05) electrocatalyst showed an increase of performance for ethanol oxidation in relation to PtSn/C electrocatalyst at room temperature. In the tests at 100 °C on a single cell of a direct ethanol fuel cell, the maximum power density of PtSnSb/C (50:45:05) electrocatalyst was slightly higher than that of PtSn/C electrocatalyst.

Keywords PtSnSb/C · PtSn/C · Alcohol reduction process · Ethanol oxidation · Fuel cell

Introduction

Direct ethanol fuel cells (DEFCs) are an attractive option as power sources for mobile, stationary, and portable applications. Ethanol is produced in large quantities from biomass and is much less toxic than others combustibles. On the other hand, its complete oxidation to CO_2 and water is not easy due to the difficulties in C–C bond breaking and the formation of intermediates that poison the platinum anode electrocatalysts (the term electrocatalysts as used herein means a catalyst for catalyzing oxidation and reduction electrode reactions) [1].

The global oxidation mechanism of ethanol in acid solution may be summarized in the following scheme of parallel reactions [2]:



The formation of CO_2 goes through two adsorbed intermediates $\text{C}_{1\text{ad}}$ and $\text{C}_{2\text{ad}}$, which represent fragments with one and two carbon atoms, respectively. In direct ethanol fuel cell, the principal products formed are acetaldehyde and/or acetic acid [2].

The Pt/C electrocatalyst is commonly used as anode in low temperature fuel cells; however, platinum alone is not a good

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catalyst for the ethanol oxidation reaction (EOR), consequently efforts to mitigate the poisoning of Pt have been concentrated on the addition of cocatalysts to platinum [2].

In recent years, it is found that certain metal oxides, such as CeO_2 , RuO_2 , or SnO_2 , can enhance the catalytic activity for ethanol electro-oxidation through synergetic interaction with Pt in order to enhance the efficiency and reduce the catalyst price [3–5]. It was shown that an intermetallic PtSb had a significant activity for formic acid oxidation in relation to Pt/C [6]. Silva et al. [7] showed that the PtSn/C and PtSb/C supported intermetallics prepared by an alcohol reduction method were more active than the Pt/C electrocatalyst. Neto et al. [8] showed that Pt nanoparticles supported on C-Sb₂O₅.SnO₂ (C-antimony tin oxide (ATO)) were more active for ethanol oxidation compared to Pt nanoparticles supported only on ATO-(Sb₂O₅.SnO₂) or on carbon, while Lee et al. [9] showed that the activities of Pt/ATO for methanol and ethanol electro-oxidation were greater than those of Pt/C electrocatalyst. The enhancement of activity was attributed to better dispersion of Pt particles on the ATO support, as well as to the effects of SnO₂ adjacent to Pt (bifunctional effect and/or the electronic effect).

Neto et al. [10] showed that PtSn/C is a good electrocatalysts for ethanol electro-oxidation reaction. Nevertheless, it is still necessary to improve further the performance with PtSn/C anodic catalysts because the principal products formed are acetaldehyde and/or acetic acid; consequently, the development of new electrocatalysts and new preparation methods are necessary. An alternative to the PtSn/C electrocatalysts for the ethanol oxidation reaction could be a ternary electrocatalyst. Lee et al. [11] showed that the incorporation of Mo to PtSn/C enhances further the catalytic activity for EOR. Ribeiro et al. [12] showed that PtRuNi/C prepared by an alcohol reduction process had superior performance for methanol oxidation at room temperature compared to commercial PtRu/C electrocatalyst. Spinacé et al. [13] showed that in a single cell at 100 °C, the PtSnRh/C electrocatalyst had superior performance compared to PtSn/C and PtRh/C electrocatalyst.

In this context, the aim of this work is to present a preliminary electrochemical study and direct ethanol fuel cell tests with PtSnSb/C prepared in a single step by an alcohol reduction process (coreduction of mixed ions) using ethylene glycol as solvent and reducing agent in the presence of carbon Vulcan XC72.

Experimental

The atomic composition of the electrocatalysts prepared by an alcohol reduction process was chosen to be close to

PtSn/C (50:50), the most active composition for the ethanol electro-oxidation [10], so PtSn/C electrocatalysts (Pt/Sn atomic ratio 50:50) and PtSnSb/C electrocatalysts (Pt:Sn:Sb atomic ratios of 50:45:05, 50:40:10 and 50:10:40) were prepared with metal loading of 20 wt.% using H₂PtCl₆·H₂O (chloroplatinic acid, Aldrich), Sb(OOCCH₃)₃ (antimony triacetate, Aldrich), and SnCl₂·2H₂O (stannous chloride, Aldrich) as metal sources, ethylene glycol (Merck) as the solvent and reducing agent and carbon Vulcan XC72 as the carbon support. In the alcohol reduction process procedure, the metal sources were dissolved in ethylene glycol/water (75/25, v/v) and carbon Vulcan XC72 support was added. The resulting mixtures were sonicated and were refluxed for 3 h under open atmosphere. The mixtures were filtered and the solids washed with water and dried at 70 °C for 2 h.

The atomic ratios were obtained by energy-dispersive X-ray analysis using a scanning electron microscope Phillips XL30 working at 20 kV and equipped with EDAX DX4 microanalyzer.

The synthesized materials were characterized by X-ray diffraction (XRD), with a Rigaku diffractometer model Miniflex II using Cu K α radiation source ($\lambda=0.15406$ nm). The diffractograms were recorded in the range of $2\theta=20$ – 90° with a step size of 0.05° and a scan time of 2 s per step.

The morphology, distribution, and size of the nanoparticles were observed with a JEOL electron microscope model JEM-2100 operated at 200 kV.

The electrochemical activity of the electrocatalysts for ethanol oxidation were tested by cyclic voltammetry and chronoamperometry experiments (performed at 25 °C with 1.0 mol L⁻¹ of ethanol in 0.5 mol L⁻¹ H₂SO₄ solutions saturated with N₂) using a Microquimica (model MQPG01, Brazil) potenciostat/galvanostat and the thin porous coating technique [14]. The reversible hydrogen electrode was employed as reference system and the counter electrode was a Pt plate.

The DEFC performances were determined in a single cell with an area of 5 cm². The temperature was set to 100 °C for the fuel cell and 80 °C for the oxygen humidifier. The fuel was 2 mol L⁻¹ ethanol solution feed at approximately 2 mL min⁻¹, the oxygen flow was regulated at 500 mL min⁻¹ and pressure of 2 bar. Polarization curves were obtained using a TDI RBL 488 electronic load. The membrane electrode assemblies were prepared by hot pressing of a pretreated Nafion[®] 117 membrane placed between either PtSn/C, PtSb/C, or PtSnSb/C electrocatalysts prepared in this work as anode (1 mg_{Pt} cm⁻² catalyst loading) and a 20 wt.% Pt/C E-TEK as cathodic catalyst (1 mg_{Pt} cm⁻² catalyst loading) at 125 °C for 2 min under pressure of 225 Kgf cm⁻².

Results and discussion

PtSn/C, PtSb/C, and PtSnSb/C were prepared in a single step by an alcohol reduction process (coreduction of mixed ions) using ethylene glycol as solvent and reducing agent in the presence of carbon Vulcan XC72. The Pt/Sn, Pt/Sb, and Pt/Sn/Sb atomic ratios of the obtained electrocatalysts were similar to the nominal atomic ratios and the mean crystallite sizes determined using Scherrer equation [10] were in the range of 2–4 nm (Table 1).

The X-ray diffractograms with all synthesized electrocatalysts are shown in Fig. 1. In all diffractograms, a broad peak at about $2\theta=25^\circ$ can be clearly seen associated with the Vulcan XC72 support and four peaks at approximately $2\theta=40^\circ$, 47° , 67° , and 82° , which are associated with the (111), (200), (220), and (311) planes, respectively, of the face-centered cubic (fcc) structure characteristic of platinum and platinum alloys [10]. In the diffractograms of PtSn/C, PtSb/C, and PtSnSb/C, electrocatalysts two very broad peaks were also observed at approximately $2\theta=34^\circ$ and 52° that could be identified as a SnO_2 (cassiterite) [10] and/or $\text{Sb}_2\text{O}_5\cdot\text{SnO}_2$ phases. For all PtSnSb/C electrocatalysts, the diffraction peaks of Pt (fcc) phase are shifted to small angles compared to Pt/C electrocatalyst, which indicates some lattice expansion and that part of Sb and/or Sn atoms could be incorporated into the fcc lattice.

Figure 2 shows transmission electron microscopy (TEM) images with all synthesized electrocatalysts. All electrocatalysts showed a good distribution of the nanoparticles on the carbon support. The TEM image of PtSnSb/C (50:45:05) electrocatalyst (Fig. 2c) showed nanoparticles on the carbon support with particle sizes of 3.5 ± 2.0 nm, while that PtSnSb/C (50:40:10), PtSnSb/C (50:10:40), PtSn/C (50:50), and PtSb/C (50:50) showed particles sizes of 2.8 ± 2.0 , 3.0 ± 2.0 , 2.0 ± 1.0 , and 2.5 ± 2.0 nm, respectively. The particles sizes of the PtSn/C were smaller than those of PtSnSb/C and PtSb/C; however, the morphologies were not significantly changed. TEM micrographs of PtSn/C, PtSnSb/C, and PtSb/C are in agreement with XRD result.

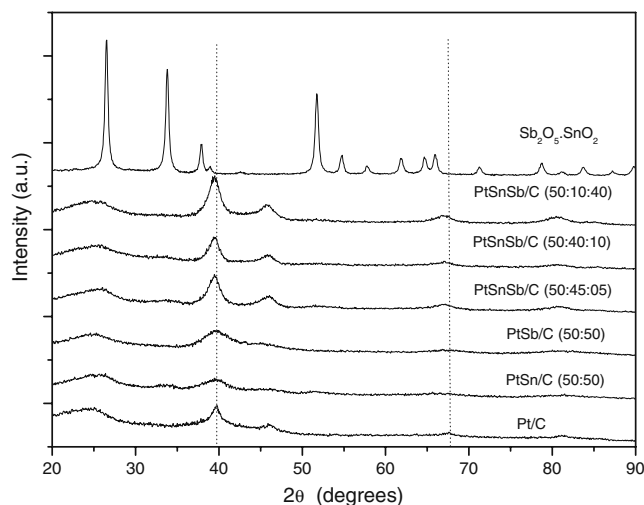


Fig. 1 X-ray diffractograms of the Pt/C, PtSn/C (50:50), PtSb/C (50:50)/C, PtSnSb/C (50:45:05), PtSnSb/C (50:40:10), PtSnSb/C (50:10:40), and $\text{Sb}_2\text{O}_5\cdot\text{SnO}_2$

Figure 3a shows the cyclic voltammetry with all synthesized electrocatalysts obtained in a half cell at a scan rate of 10 mVs^{-1} in a potential range of 0.05–0.8 V in absence of ethanol, while that the Fig. 3b shows the cyclic voltammetry results in the presence of 1.0 mol L^{-1} of ethanol and 0.5 mol L^{-1} of H_2SO_4 . The current values for cyclic voltammetry and chronoamperometry studies were normalized per gram of platinum considering that ethanol adsorption and dehydrogenation occur only on platinum sites at room temperature [10].

PtSb/C and all PtSnSb/C electrocatalysts showed that the hydrogen adsorption region is greatly reduced by the presence of Sb in comparison with PtSn/C (Fig. 3a). PtSb/C (50:50) and PtSnSb/C (50:10:40) electrocatalysts also showed an increase in the current values in the double layer (0.4–0.8 V) in relation to PtSn/C (50:50), which may be attributed to the formation of antimony or tin oxide species. The ethanol electro-oxidation started at approximately 0.25 V for PtSnSb/C (50:45:05) and PtSn/C (50:50) electrocatalysts (Fig. 3b), while that for PtSnSb/C (50:40:10), PtSnSb/C (50:10:40), and PtSb/C (50:50) the ethanol electro-oxidation started at approxi-

Table 1 Pt/Sn, Pt/Sb, and PtSn/Sb atomic ratios and mean particle size of the prepared electrocatalysts

Electrocatalysts	Atomic ratio (nominal)	Atomic ratio (EDX)	Average crystallite size (nm)
PtSn/C	50:50	52:48	2.0
PtSnSb/C	50:45:05	54:38:08	3.7
PtSnSb/C	50:40:10	51 :37:12	3.5
PtSnSb/C	50:10:40	50:07:43	3.2
PtSb/C	50:50	47:53	2.2

EDX energy dispersive X-ray analysis

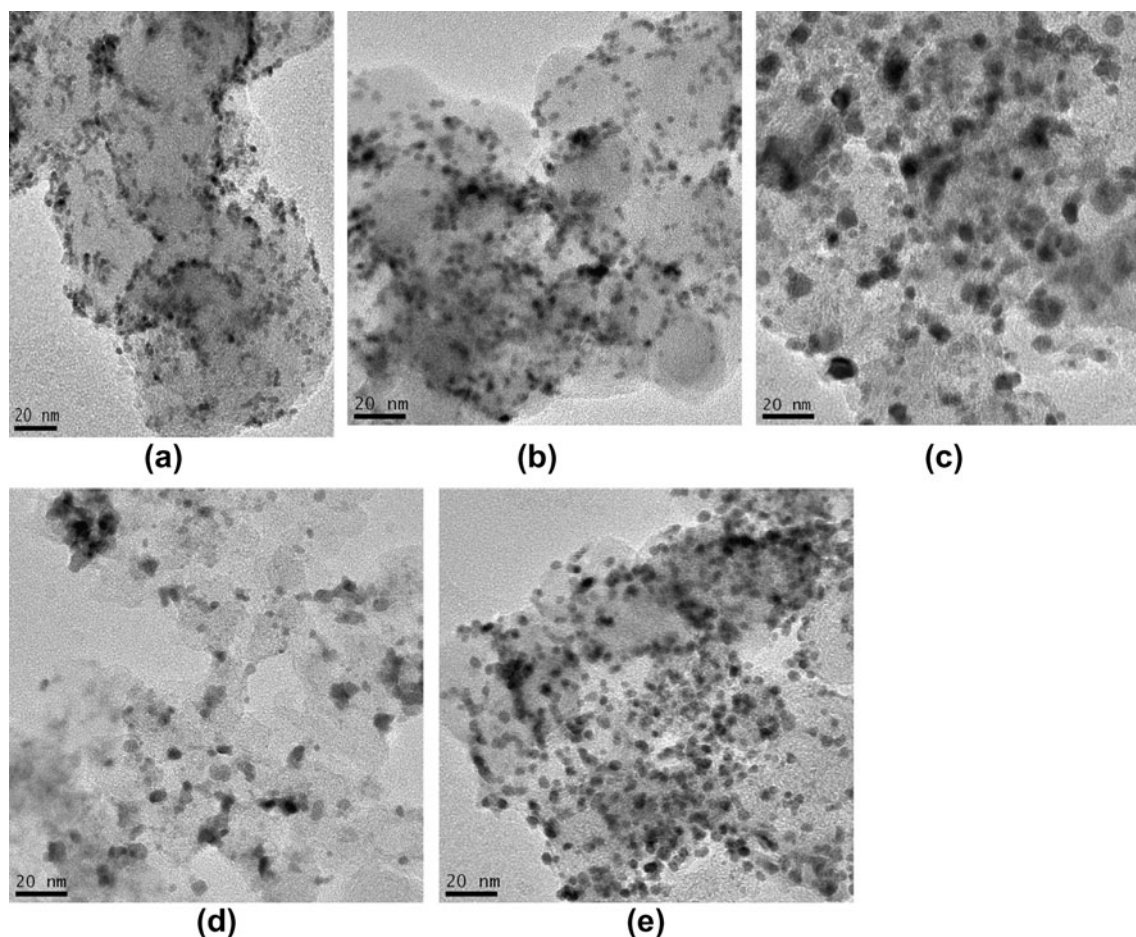


Fig. 2 TEM images of the electrocatalysts (a) PtSn/C (50:50), (b) PtSb/C (50:50), (c) PtSnSb/C (50:45:05), (d) PtSnSb/C (50:40:10), and (e) PtSnSb/C(50:10:40)

mately 0.40 V. In the potential range of interest for a direct ethanol fuel cell (0.2–0.5 V), the current values of the PtSnSb/C (50:45:05) and PtSn/C (50:50) electrocatalysts were higher than of the others electrocatalysts prepared; however, PtSnSb/C (50:45:05) electrocatalyst showing the best performance for ethanol oxidation. The better performance of PtSnSb/C (50:45:05) for ethanol electro-oxidation is due to the bifunctional effects. The presence of the tin oxides and antimony oxides in the electrocatalysts promotes the formation of oxygenated species in a potential region less positive than the pure platinum and these species play a crucial role in the oxidation of adsorbed intermediates releasing the active sites of Pt [8].

The chronoamperometry curves of all synthesized electrocatalysts (at 0.5 V) are shown in Fig. 4. PtSnSb/C (50:10:40) and PtSb/C (50:50) electrocatalysts showed a great initial current drop and a very low performance for ethanol oxidation at room temperature in relation to the others electrocatalysts. The current values obtained for PtSnSb/C (50:45:05) electrocatalysts were higher than those

obtained for PtSn/C (50:50) and PtSnSb/C (50:40:10) in agreement with cyclic voltammetry experiments.

Figure 5 shows the performances of single fuel cell with all synthesized electrocatalysts. The open circuit voltage of the fuel cell containing PtSnSb/C (50:45:05) and PtSn/C (50:50) electrocatalyst were 0.81 and 0.76 V, respectively, while the corresponding value for PtSb/C (50:50) was approximately 0.50 V. PtSnSb/C (50:45:05) electrocatalysts showed higher the open circuit voltage with relation to others electrocatalysts prepared indicating an increased cell performance.

The maximum power density of PtSnSb/C electrocatalyst (40 mW cm^{-2}) is slightly higher than that with PtSn/C electrocatalyst (37 mW cm^{-2}). The maximum power density of PtSnSb/C and PtSn/C electrocatalyst also were greater than that of PtSb/C electrocatalyst (12 mW cm^{-2}). Curiously, similar results were observed for PtSnSb/C (50:45:05) prepared in this work by an alcohol reduction process using Pt, Sn, and Sb metals salts as precursors (40 mW cm^{-2}) and for Pt/C-Sb₂O₅.SnO₂/ (38 mW cm^{-2}) [8] where Pt nanoparticles were deposited

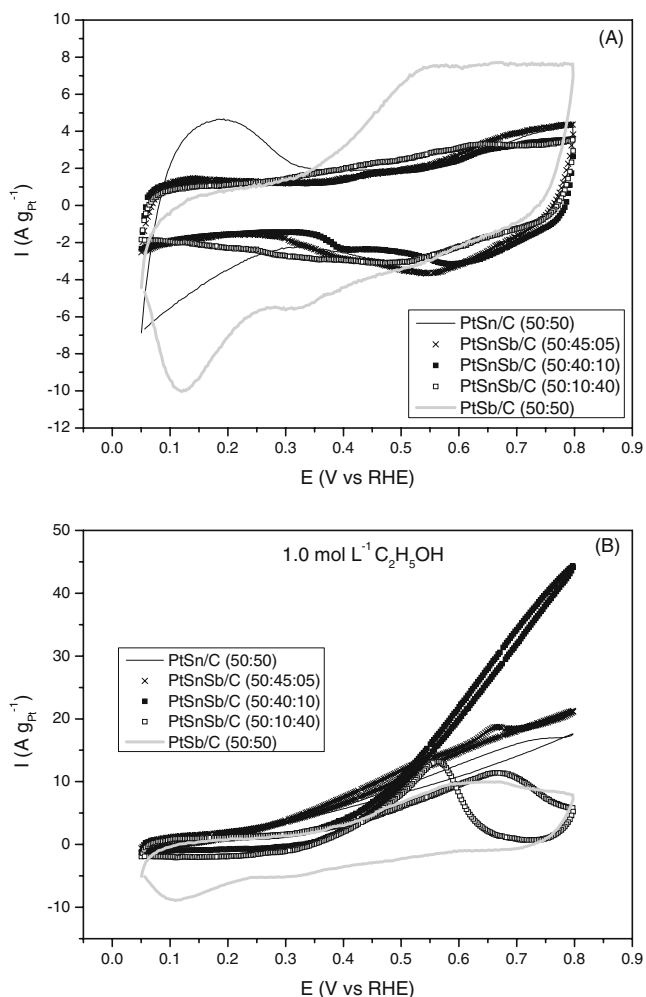


Fig. 3 (a) Cyclic voltammetry of PtSn/C (50:50), PtSb/C (50:50) and PtSnSb/C (50:45:05), PtSnSb/C (50:40:10), and PtSnSb/C (50:10:40) electrocatalysts obtained in absence of ethanol. (b) Cyclic voltammetry results in presence of 1.0 mol L⁻¹ of ethanol and 0.5 mol L⁻¹ of H₂SO₄

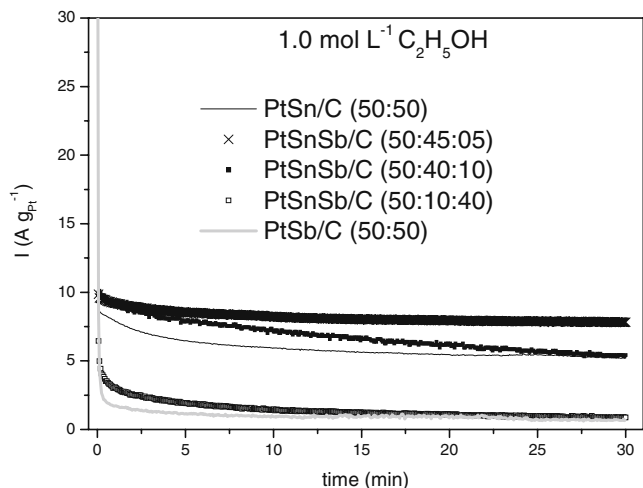


Fig. 4 Current–time curves at 0.5 V in 1 mol L⁻¹ ethanol solution in 0.5 mol L⁻¹ H₂SO₄ for PtSn/C (50:50), PtSb/C (50:50), PtSnSb/C (50:45:05), PtSnSb/C (50:40:10), and PtSnSb/C (50:10:40)

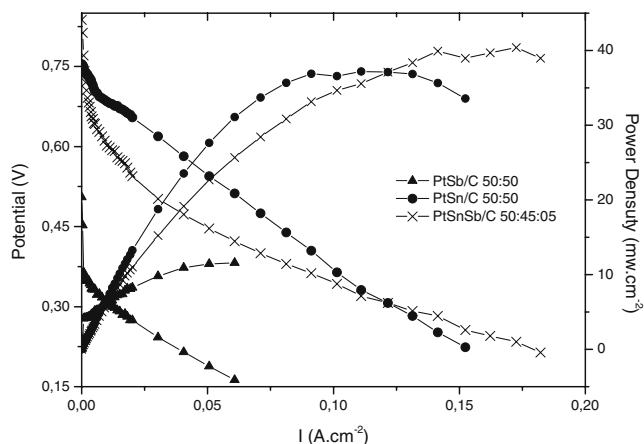


Fig. 5 I–V curves and the power density at 100 °C of a 5 cm² DEFC using PtSb/C (50:50), PtSn/C (50:50), and PtSnSb/C (50:45:05) electrocatalysts anodes (1 mg_{Pt} cm⁻² catalyst loading) and Pt/C E-TEK electrocatalyst cathode (1 mg_{Pt} cm⁻² catalyst loading, 20 wt.% Pt loading on carbon), Nafion[®] 117 membrane, ethanol (2.0 mol L⁻¹), and oxygen pressure (2 bars)

by the same methodology on a physical mixture of carbon and Sb₂O₅.SnO₂ (~10% Sb₂O₅ and ~90% SnO₂). Thus, these catalysts have similar compositions and probably structures (Pt fcc phase and Sn and Sb oxides).

The single-cell tests demonstrate that the addition of Sb into PtSn catalyst can promote its activity for EOR in agreement with cyclic voltammetry and chronoamperometry experiments. The enhanced performance of PtSnSb/C (50:45:05) catalyst could be associated to the presence of Sn and Sb oxides that favors the oxidation of adsorbed intermediates by the bifunctional mechanism. Also, the incorporation of Sb into the SnO₂ lattice (Sb₂O₅.SnO₂) could increase of its electrical conductivity [8, 9].

Conclusions

The alcohol reduction process showed to be an effective method for producing in a single step of PtSnSb/C electrocatalyst for ethanol oxidation. The X-ray diffractograms of PtSn/C and PtSnSb/C electrocatalysts showed the presence of Pt (fcc) and SnO₂ or Sb₂O₅.SnO₂ phases. The results of TEM for all electrocatalysts showed a good distribution of the nanoparticles on the carbon support. The electrochemical experiments showed that PtSnSb/C(50:45:05) electrocatalyst was more active than PtSn/C (50:50) and PtSb/C (50:50) electrocatalysts for ethanol oxidation at room temperature and the tests in a single DEFC at 100 °C also confirm these results. The increase of performance of PtSnSb/C electrocatalyst could be attributed to the effect of tin and antimony oxides adjacent to Pt sites, which favors the oxidation of adsorbed intermediates by the

bifunctional mechanism. The presence of Sb_2O_5 could also increase of electrical conductivity of to SnO_2 phase.

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