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Acid-treated PtSn/C and PtSnCu/C electrocatalysts for ethanol electro-oxidation

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ABSTRACT

PtSn/C with Pt:Sn atomic ratio of 50:50 and PtSnCu/C electrocatalysts with different Pt:Sn:Cu atomic ratios were prepared using $NaBH_4$ as reducing agent and carbon black Vulcan XC72 as support. In a second step, the electrocatalysts were treated with nitric acid to remove the less noble metals (chemical dealloying). The obtained materials were characterized by X-ray diffraction, EDX analysis, TEM images with EDX scan-line and cyclic voltammetry. The electro-oxidation of ethanol was studied by chronoamperometry and on single direct ethanol fuel cell (DEFC). The X-ray diffractograms of the as-synthesized electrocatalysts showed the typical face-centered cubic (FCC) structure of Pt alloys. After acid treatment the FCC structure was maintained and Sn and Cu atoms were removed from the nanoparticles surface. Chronoamperometry measurements showed a strong increase of performance of PtSn/C and PtSnCu/C electrocatalysts after acid treatment; however, under DEFC conditions at 100 °C, only acid-treated PtSn/C electrocatalyst showed superior performance compared to commercial PtSn/C from BASF.

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1. Introduction

Due to environmental problems as the pollution caused by the use of fossil fuels, lately the interesting for renewable and less polluting energy sources has been increased and, in this context, fuel cells emerge as a promising alternative [1]. Direct Alcohol Fuel Cells (DAFCs) are attractive as power sources for mobile and portable applications. Compared to hydrogen-fed fuel cells, which need a reforming system or have problems of hydrogen storage, DAFCs use a liquid fuel, thus simplifying the fuel system. Methanol has been considered the most promising fuel because it is more efficiently oxidized than other alcohols; however, it is toxic and comes principally from non-renewable sources. In this sense, ethanol offers an attractive alternative as fuel because it is produced in large quantities from biomass and it is much less toxic than methanol. On the other hand, its complete oxidation to CO_2 and water is more difficult than that of methanol due to the difficulties in C–C bond breaking and to the formation of intermediates that poison the platinum anode catalysts. In this manner, its complete oxidation to CO_2 remains a great challenge and the principal products formed are acetaldehyde and/or acetic acid [2,3]. PtSn/C electrocatalysts have been shown good performance for ethanol electro-oxidation, however, their activities depends greatly on the preparation procedure, which affects the size, the morphology, the phases and the composition of the metal nanoparticles supported on the carbon [3–5].

Koh and Strasser [6] showed that a new type of electrocatalyst with high activity can be obtained by structural

modification of the Pt–Cu alloy by partial removal of Cu through electrochemical treatment (dealloying process). After Cu dealloying from carbon-supported Pt–Cu alloy nanoparticle electrocatalyst, a significant enhancement for the oxygen reduction reaction was observed when compared with pure Pt. The present work aims at preparing PtSn/C and PtSnCu/C electrocatalysts (carbon-supported PtSnCu alloy) with different Pt:Sn:Cu atomic ratios by borohydride reduction and to treat them with nitric acid to remove non-noble metals by chemical leaching. The overall procedure is anchoring PtSn and PtSnCu alloy nanoparticles on the carbon support and subsequently removing the non-noble metals from nanoparticles surface resulting in Pt-rich shells with modified surface catalytic reactivity. The obtained materials were tested for ethanol electro-oxidation.

2. Experimental

The Pt/C, PtSn/C (50:50) and PtSnCu/C electrocatalysts with different Pt:Sn:Cu atomic ratios were prepared with 20 wt% of metal loading. $H_2PtCl_6 \cdot 6H_2O$ (Aldrich), $SnCl_2 \cdot 2H_2O$ (Aldrich) and $CuCl_2 \cdot 2H_2O$ (Aldrich) as metals sources, 2-propanol (Merck) was used as solvent, carbon black Vulcan XC72 (Cabot) as support and $NaBH_4$ (Aldrich) as a reducing agent. Initially, the metal salts were dissolved in 2-propanol and carbon black was dispersed in the solution. It was subsequently added, at once, a solution of $NaBH_4$ to the mixture, which was kept under stirring for 40 min at room temperature. Finally, the mixture was filtered and the material obtained was washed with excess of water and dried at 70 °C for 2 h. In a second step, the PtSnCu/C electrocatalysts were dispersed in concentrated nitric acid (HNO_3) and the mixture was kept under stirring for 70 min at room temperature (acid-treated PtSnCu/C electrocatalysts). Then the mixture was filtered and the obtained material was washed with excess of water and dried at 70 °C for 2 h.

The Pt:Sn:Cu atomic ratios were obtained by EDX analysis using a Philips XL30 scanning electron microscope with a 20 keV electron beam provided with EDAX DX-4 microanaliser.

The X-ray diffraction (XRD) analyses were carried out in a Miniflex II model Rigaku diffractometer using Cu Kα radiation ($\lambda = 0.15406$ nm). The diffractograms were recorded at 2θ in the range 20°–90° with step size of 0.05° and scan time of 2 s per step. The (220) reflections of Pt (fcc) crystalline structure were used to calculate the average crystallite sizes and lattice parameters according to reference [7].

Transmission electron microscopy (TEM) with EDX line-scan analysis was performed using a 200 kV JEOL JEM-2100 microscope.

Electrochemical studies were carried out using the thin porous coating technique. Electrochemical measurements were performed in a three-electrode cell using a platinized Pt plate as counter electrode, an RHE electrode as reference electrode and a working electrode. This electrode was prepared with amount 20 mg of the electrocatalyst, 50 mL of water and 3 drops of a 6% polytetrafluoroethylene (PTFE) suspension. The mixture was treated in an ultrasound bath for 10 min and after filtered. The solid obtained, still moist, was compressed on a cavity (0.3 mm deep and 0.36 cm^2) glassy carbon so that the surface stayed smooth. This experiment was made using a Microquimica (model MQPG01, Brazil) potentiostat/galvanostat coupled to a personal computer and using the Microquimica Software. Cyclic voltammetrys measures were performed in a 0.5 mol L^{-1} H_2SO_4 solution saturated with N_2 with a scan rate of 10 mV s^{-1}. The study of ethanol electro-oxidation was performed at room temperature by chronoamperometry at 0.5 V in solution of 1.0 mol L^{-1} of ethanol in 0.5 mol L^{-1} of H_2SO_4 for 30 min. The current values obtained were expressed in amperes (A) and normalized by amount of platinum in grams (A g$_{Pt}^{-1}$). The amount of platinum was calculated by product between mass of the electrocatalyst used in the working electrode and percentage of platinum.

DEFC tests were performed on a single cell with a 5 cm^2 Membrane Electrode Assemblies (MEA) prepared by hot pressing the anode and the cathode to a pretreated Nafion 117 membrane at 125 °C for 10 min under a pressure of 247 kgf cm^{-2}. For the anodes preparation, a catalytic ink containing PtSn/C or PtSnCu/C electrocatalyts (1 mg$_{Pt}$ cm^{-2} of catalyst loading) and Nafion solution (DE-520) were applied to a Carbon cloth (ElectroChem EC-CC1-060T). The catalytic ink was formulated in a way that Nafion comprised about 35 wt% of the total solid in the ink. In a similar way, cathodes were prepared using 20 wt% Pt/C (1 mg$_{Pt}$ cm^{-2} catalyst loading) as electrocatalyst. Electrical performances were determined by polarization and power density curves using a single cell at

Group	Electrocatalyst	Pt:Sn:Cu nominal values	As-synthesized Pt:Sn:Cu atomic ratios	Acid-treated Pt:Sn:Cu atomic ratios
Pt-50	PtSnCu/C	50:40:10	58:32:10	67:27:6
	PtSnCu/C	50:30:20	59:24:17	72:20:8
	PtSnCu/C	50:10:40	58:10:32	81:6:13
Sn-50	PtSnCu/C	40:50:10	51:41:8	55:39:6
	PtSnCu/C	30:50:20	43:37:20	56:41:3
	PtSnCu/C	10:50:40	18:37:45	29:67:4
Cu-50	PtSnCu/C	40:10:50	48:12:40	72:12:16
	PtSnCu/C	30:20:50	38:14:48	72:14:14
	PtSnCu/C	10:40:50	19:22:59	50:19:31
	PtSn/C	50:50	53:47	60:40

Table 1 – Pt:Sn:Cu and Pt:Sn atomic ratios for as-synthesized and acid-treated PtSnCu/C and PtSn/C electrocatalysts.

100 °C. The fuel was delivered at 2 mL min^{-1} through the anode and pure oxygen flow was regulated at 500 mL min^{-1} over a cathodic pressure of 2 bar. Pt/C (lot# F0381022) and Pt$_3$Sn/C$_{(alloy)}$ (lot# F0930209) electrocatalysts are commercial and were purchased from BASF. The products distribution were determined by gas chromatography (GC) as described elsewhere [3].

3. Results and discussion

Three groups of PtSnCu/C electrocatalysts were prepared: in the first group PtSnCu/C electrocatalysts with Pt:Sn:Cu atomic ratios 50:x:y (**Pt-50**), in the second group with Pt:Sn:Cu atomic ratios x:50:y (**Sn-50**) and in the third group with Pt:Sn:Cu atomic ratios x:y:50 (**Cu-50**). The EDX analysis (Table 1) of as-synthesized PtSnCu/C electrocatalysts showed that the obtained Pt:Sn:Cu atomic ratios were similar to the nominal values. In a general manner, after acid treatment it was observed for all PtSnCu/C electrocatalysts that the Pt:Sn:Cu atomic ratios change showing an increase of Pt values and a decrease of Cu values; whereas the variations of Sn values were normally smaller than the ones observed for Cu and Pt values. This suggests that Cu atoms were preferentially removed by chemical leaching with nitric acid. As-synthesized PtSn/C electrocatalyst also showed Pt:Sn atomic ratio similar to the nomimal value and after acid treatment a decrease of Sn value with an increase of Pt value was also observed.

The X-ray diffractograms of as-synthesized Pt/C, PtSn/C (50:50) and PtSnCu/C (50:40:10 and 50:10:40) electrocatalysts are shown in Fig. 1. The XRD diffractogram of the Pt/C electrocatalyst showed a broad peak at about 25°, which was associated to the Vulcan XC72 support material, and five diffraction peaks at about $2\theta = 40°, 47°, 67°, 82°$ e $87°$, which are characteristic of the face-centered cubic (FCC) structure of Pt [8]. For PtSn/C (50:50) electrocatalyst, it was observed a shift of the peaks relative to Pt (FCC) phase to lower angles compared to those of Pt/C electrocatalyst indicating a PtSn alloy formation [8]. PtSnCu/C electrocatalysts showed a shift of the peaks
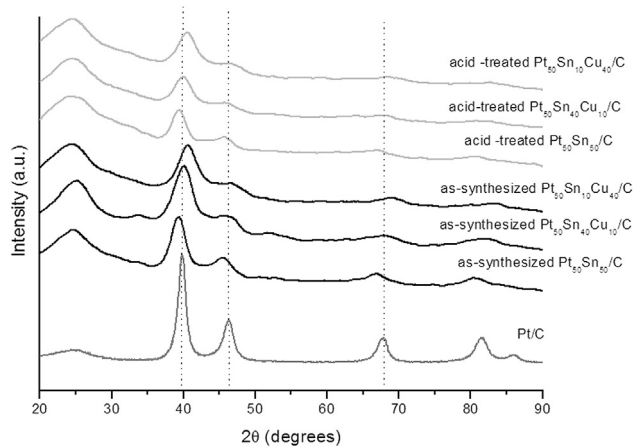

Fig. 1 – X-ray diffractograms as-synthesized and acid-treated Pt/C, PtSn/C(50:50) and PtSnCu/C 50:40:10 and 50:10:40 electrocatalysts.

relative to Pt (FCC) structure to higher angles compared to those of Pt/C and PtSn/C electrocatalysts and this shift was more pronounced for the material with more Cu content, showing an incorporation of Cu atoms into the PtSn (FCC) lattice [8]. After the acid treatment, the X-ray diffractograms (Fig. 1) of PtSn/C and PtSnCu/C electrocatalysts showed that the Pt (FCC) structure was maintained; however, the peaks of the FCC structure of the acid-treated PtSnCu/C electrocatalysts become slightly broader than the ones of the as-synthesized materials. Table 2 shows the average crystallite sizes and the lattice parameters calculated from the X-ray diffraction for as-synthesized and acid-treated Pt/C, PtSn/C (50:50) and PtSnCu/C (group Pt-50) electrocatalysts. A decrease of the average crystallite sizes was observed with the incorporation of Sn and Cu into the Pt FCC structure. After the acid treatment there were small variations in the average crystallite sizes. As-synthesized PtSn/C 50:50 electrocatalyst showed a lattice parameter value of 0.396 nm that was higher than the value observed for Pt/C electrocatalyst (0.390 nm), indicating a crystal lattice expansion by incorporation of Sn atoms into the Pt FCC structure and the formation of a PtSn alloy. After acid treatment, there was a slight decrease in the value of the lattice parameter of the PtSn/C 50:50 electrocatalyst, a fact that can be attributed to a slight contraction of the crystal lattice by removing Sn atoms; however, the average crystallite size did not change. As-synthesized PtSnCu/C electrocatalyst (50:40:10) showed the same value of the lattice parameter observed for Pt/C electrocatalyst. The incorporation of Sn and Cu atoms into the Pt FCC structure leads to expansive and contractive effects of Sn and Cu atoms, respectively, and in this case, a similar value of Pt/C electrocatalyts was observed. After acid treatment, it was not observed changes in the lattice parameter despite of the Pt:Sn:Cu atomic ratio (Table 1) was changed. For the as-synthesized materials with more Cu content (PtSnCu/C electrocatalysts 50:30:20 and 50:10:40) it was observed a pronounced decrease of the lattice parameters compared to Pt/C and PtSn/C electrocatalysts and, after acid treatment, for both cases, it was observed an increase of the lattice parameters due the removal of Cu atoms. The increase of the lattice parameter values, as well, the broadening of the FCC peaks were also observed by Yang et al. [9] investigating the structure and composition of dealloyed PtCu$_3$ thin films. Both the as-deposited PtCu$_3$ and Pt films showed single FCC phase and average lattice parameters of 0.371 and 0.392 nm, respectively. After dealloying, the diffraction peaks of the PtCu$_3$ shifted toward lower angles and became broader when compared to the as-deposited materials, showing that Cu was leached from PtCu$_3$ alloy and that the microstructure found more disordered and had a smaller grain size. Due to the low crystallinity of the samples of groups Sn-50 and Cu-50 it was not possible to calculate the average crystallite sizes and lattice parameters.

TEM micrographs with the corresponding EDX line-scan analysis of the as-synthesized and acid-treated PtSnCu/C electrocatalyst 50:10:40 are shown in Fig. 2. The Cu elemental intensity of the as-synthesized material (Fig. 2a) was somewhat higher than that of Pt and after acid treatment (Fig. 2b) it was observed an inversion of the Pt and Cu intensities. This also confirms the effectiveness of acid treatment to remove Cu from nanoparticles surface. Oezaslan et al. [10] studied the

Table 2 – Average crystallite sizes and lattice parameters for Pt/C, PtSn/C and PtSnCu/C electrocatalysts.

Electrocatalyst	Crystallite size (nm)		Lattice parameter (nm)	
	As-synthesized	Acid-treated	As-synthesized	Acid-treated
Pt/C	5	–	0.390	–
$Pt_{50}Sn_{50}/C$	3	3	0.396	0.395
$Pt_{50}Sn_{40}Cu_{10}/C$	2	≤2	0.390	0.390
$Pt_{50}Sn_{30}Cu_{20}/C$	≤2	≤2	0.386	0.388
$Pt_{50}Sn_{10}Cu_{40}/C$	2	≤2	0.384	0.387

chemical dealloying of Pt–Cu nanoparticles with different particle sizes. For Pt–Cu with particle sizes smaller than 10–15 nm it was observed that single core–shell structures (the arrangement of Pt shell surrounding a single alloy core) were formed; while particle sizes between 15 and 30 nm leads to the formation of multiple cores–shell nanoparticles. Increasing particle size above 30 nm, the formation of pores becomes prevalent and the particles exhibited surface pits (nanopores) and multiple cores inside the pores. Thus, based on this study [10] and the results of XRD and TEM images with EDX scan-line measurements, we could infer that after acid treatment the nanoparticles surface of the PtSn/C and PtSnCu/C electrocatalysts became more rich in Pt resulting in an arrangement of a Pt-rich shell surrounding a single alloy core (core–shell like structures).

The cyclic voltammograms (CVs) in acid medium of some as-synthesized and acid-treated PtSn/C and PtSnCu/C electrocatalysts are shown in Fig. 3. The CV of the as-synthesized PtSnCu/C (50:10:40) did not show the hydrogen oxidation region (0–0.4 V) well-defined, while PtSnCu/C (50:40:10) and PtSn/C (50:50) showed this region more defined when compared to Pt/C electrocatalyst. After acid treatment PtSnCu/C 50:10:40 showed the hydrogen oxidation region more defined suggesting that Cu atoms were removed from the surface which is consistent with the changes of Pt:Sn:Cu atomic ratios, XRD and TEM images with EDX scan-line results. After acid treatment PtSnCu/C (50:40:10) and PtSn/C (50:50) practically showed no changes on the hydrogen oxidation region, however, the tin oxidation region around 0.78 V suffered a decrease for both catalysts suggesting that some Sn atoms were removed from the nanoparticles surface.

The performances of PtSn/C and PtSnCu/C electrocatalysts for ethanol electro-oxidation were studied by chronoamperometry in 1.0 mol L^{-1} of ethanol in 0.5 mol L^{-1} H$_2$SO$_4$
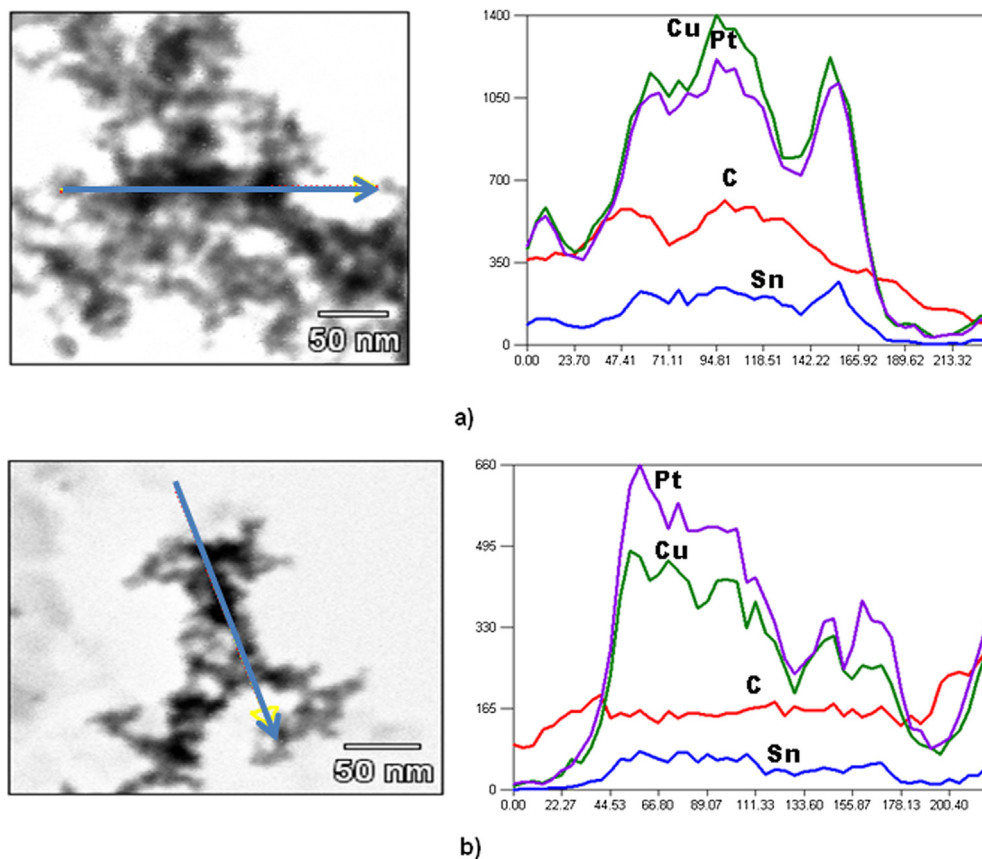

Fig. 2 – Transmission electron micrographs with the corresponding line-scan location and plots showing elemental intensities with line position: PtSnCu/C 50:10:40 a) as-synthesized and b) acid-treated.
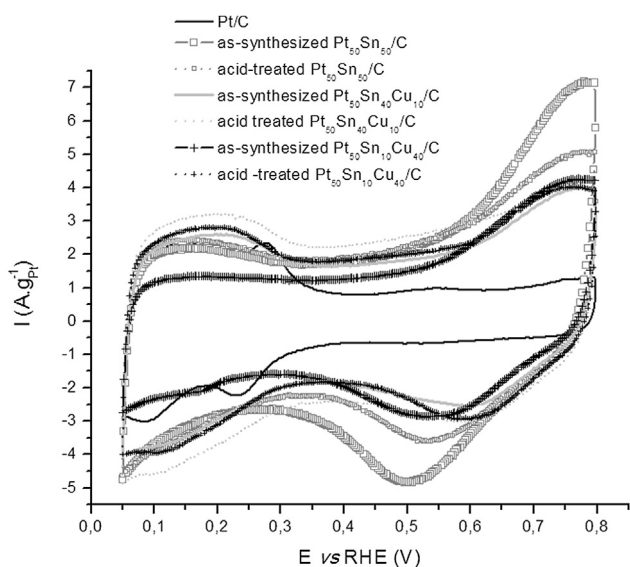
Fig. 3 – Cyclic voltammetry of as-synthesized and acid-treated PtSn/C 50:50 and PtSnCu/C 50:40:10 and 50:10:40 electrocatalysts in 0.5 mol L^{-1} H_2SO_4 with a sweep rate of 10 mV s^{-1}.

at an anodic potential of 0.5 V versus RHE and some results are shown in Fig. 4. A comparative analysis (Table 3) between the final current values obtained for as-synthesized and acid-treated electrocatalysts after 30 min at 0.5 V showed, for most cases, an increase of the electrocatalytic activity after acid treatment. Besides, this increase was principally observed for materials with high Pt content (group **Pt-50**), while, for the materials prepared with low Pt content (groups **Sn-50 and Cu-50**) a decrease of activity was observed suggesting that the core–shell like structures with a Pt-rich shell were not formed for these materials. The most actives acid-
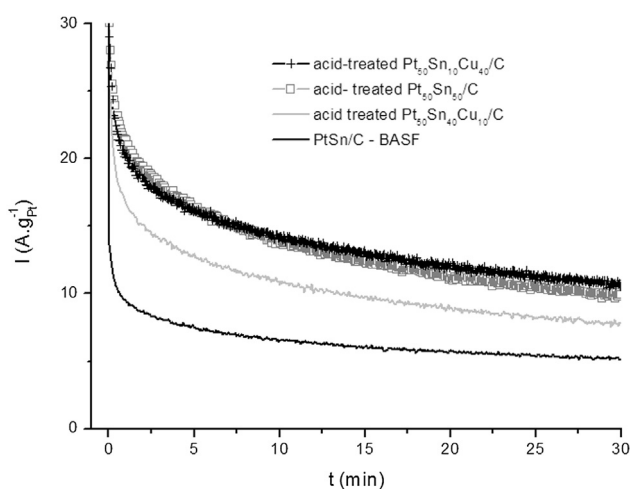

Fig. 4 – Current–time curves at 0.5 V in 1.0 mol L^{-1} of ethanol solution in 0.5 mol L^{-1} H_2SO_4 for commercial PtSn/C (BASF), acid-treated PtSn/C (50:50) and PtSnCu/C 50:40:10 and 50:10:40 electrocatalysts.

treated PtSn/C (50:50) and PtSnCu/C (50:40:10) electrocatalysts showed final current values for ethanol electrooxidation greater than the commercial PtSn/C from BASF. This increase of activity could be attributed to the acid treatment which removes the non-noble metals from nanoparticles creating new structural arrangements of the Pt atoms on their surfaces. Strasser et al. [11] studied the enhanced of electrocatalytic activity for Oxygen Reduction Reaction of dealloyed Pt–Cu nanoparticles and concluded that after dealloying a core–shell structure was formed and the Pt-rich shell exhibited a strain that modify the d-band structure of Pt atoms and weakens the adsorption energy of reactive intermediates compared to unstrained Pt resulting in an increase of catalytic reactivity.

The polarization and power density curves in single DEFC operating at 100 °C using commercial Pt/C BASF; acid-treated PtSn/C (50:50), acid-treated PtSnCu/C (50:10:40) and commercial PtSn/C BASF electrocatalysts as anodes, are shown in Fig. 5. Pt/C electrocatalyst showed an open circuit voltage (OCV) of 580 mV and a maximum power of 18 mW cm^{-2}. For acid-treated PtSnCu/C (50:10:40) electrocatalyst the OCV increase to 700 mV and the maximum power density increased to 40 mW cm^{-2}, however, both the OCV (about 750 mV) and the maximum power (42.5 mW cm^{-2}) were smaller than the ones observed for the commercial PtSn/C BASF electrocatalyst. The best performance was observed for acid-treated PtSn/C (50:50) electrocatalyst with an OCV of about 750 mV and a maximum power density of 60 mW cm^{-2}. The anodic effluents were collected at a maximum current density and analyzed by GC in order to identify and quantify the products formed (Fig. 6). For all electrocatalyst the main products formed were acetaldehyde (AAL) and acetic acid (AA). Only commercial Pt/C BASF electrocatalyst led to the formation of a small quantity of CO_2 (2% of selectivity); however, acetaldehyde and acetic acid were formed with 86% and 12% of selectivity, respectively. Commercial PtSn/C BASF produced acetaldehyde and acetic acid with 75% and 25% of selectivity, respectively. Acid-treated PtSn/C (50:50) electrocatalyst showed the best performance under DEFC conditions and presented the biggest AA/AAL ratio among the catalysts tested producing acetaldehyde and acetic acid with 70% and 30% of selectivity, respectively. Thus, the increase of activity observed for acid-treated PtSn/C electrocatalyst could be related to an increase of acetic acid production (release of four electrons) instead of acetaldehyde (release of two electrons) [3]. Unfortunately, under DEFC conditions, acid-treated PtSnCu/C (50:10:40) electrocatalyst did not show the good performance observed in the chronoamperometry experiments (under half-cell conditions) leading to the formation of acetaldehyde as the principal product with 85% of selectivity and acetic acid with only 15% of selectivity. This showed the importance of investigating the electrocatalysts under real DEFC conditions. The formation of dealloyed surface layers on acid-treated PtSnCu/C (50:10:40) electrocatalyst, due to the removal of Cu and Sn, leads to the formation of a Pt-rich shell surrounding a PtSnCu core (Pt:Sn:Cu atomic ratio of 81:6:13 after chemical dealloying). Thus, in this case, the low performance of acid-treated PtSnCu/C (50:10:40) under DEFC conditions, could be due the fact that the ethanol molecules react preferentially on the active sites of the first shells of the

Table 3 — Final current values obtained after 30 min at 0.5 V for as-synthesized and acid-treated PtSn/C and PtSnCu/C electrocatalysts.

Group	Electrocatalyst	As-synthesized electrocatalysts (A g_{Pt}^{-1})	Acid-treated electrocatalysts (A g_{Pt}^{-1})	Rate of change (%)
Pt-50	PtSnCu/C 50:40:10	5.1	7.9	55
	PtSnCu/C 50:30:20	3.8	7.0	84
	PtSnCu/C 50:10:40	4.5	**11.0**	140
Sn-50	PtSnCu/C 40:50:10	4.1	7.5	83
	PtSnCu/C 30:50:20	1.6	2.5	56
	PtSnCu/C 10:50:40	1.1	0.4	−63
Cu-50	PtSnCu/C 40:10:50	5.3	6.7	26
	PtSnCu/C 30:20:50	2.0	3.9	95
	PtSnCu/C 10:40:50	1.7	0.9	−47
	PtSn/C 50:50	5.4	**9.9**	83

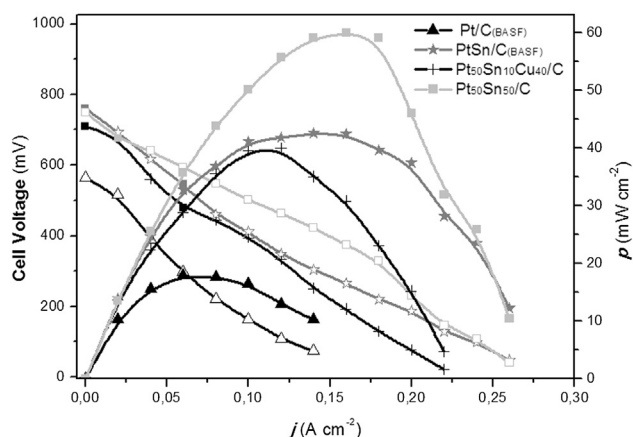Bold values emphasize the highest values of current obtained.

Fig. 5 — Polarization curves and power density of commercial Pt/C and PtSn/C from BASF, acid-treated PtSn/C 50:50 and PtSnCu/C 50:10:40 as anode (1 mg$_{Pt}$ cm^{-2}) and commercial Pt/C as cathode (1 mg$_{Pt}$ cm^{-2}) at 100 °C, P$_{O_2}$ 2 bar, 2 mol L^{-1} ethanol and Nafion 117 membrane.

nanoparticle surface (Pt-rich shell) and acetaldehyde and acid acetic were obtained with a similar selectivity observed for Pt/C electrocatalyst. On the other hand, when this electrocatalyst was tested under half-cell conditions (chronoamperometry experiments), the ethanol accessibility to all active sites was
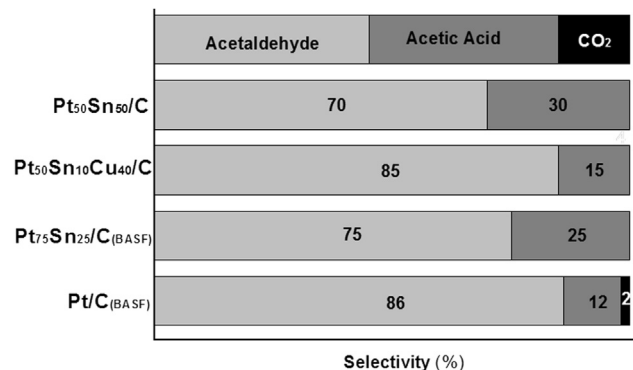

Fig. 6 — Selectivity of the products collected from anodic effluent of the DEFC operating at maximum current density with different electrocatalysts.

facilitated and an enhancement of electroactivity was observed in these conditions. The best performance for acid-treated PtSn/C electrocatalyst under DEFC conditions could be explained by a small amount of Sn removed after chemical dealloying (Pt:Sn atomic ratio of 60:40 after dealloying). In this case, the ethanol molecules have accesses to Pt and Sn sites on the first shells, which are essential for ethanol electro-oxidation [3].

4. Conclusions

Active acid-treated PtSn/C and PtSnCu/C electrocatalysts could be prepared for ethanol electro-oxidation. The XRD of the as-synthesized materials showed the FCC structure of Pt alloys. After treatment with nitric acid the EDX analysis showed that Sn and Cu were partially removed and the FCC structure was maintained; however, the diffraction peaks became broader and the lattice parameters increased. TEM micrograph with EDS line-scan analysis showed an increase of Pt intensity signal with a decrease of Cu intensity signal after acid treatment. Also, CV in acid medium also showed a more defined hydrogen oxidation region after acid treatment suggesting an enrichment of Pt on the nanoparticles surface. In the electrochemical experiments (half-cell conditions), acid-treated PtSnCu/C electrocatalyst with Pt:Sn:Cu atomic ratio of 50:10:40 showed the best performance for ethanol showing an increase of activity of 140% compared to the as-synthesized material. Acid-treated PtSn/C with Pt:Sn atomic ratio of 50:50 also showed an increase of performance (83%) compared to the as-synthesized material. On the other hand, under DEFC conditions, only acid-treated PtSn/C electrocatalyst showed a superior performance compared to commercial PtSn/C BASF.

Acknowledgments

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