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The effect of acetaldehyde and acetic acid on the direct ethanol fuel cell performance using $PtSnO_2/C$ electrocatalysts

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ABSTRACT

$PtSnO_2/C$ with $Pt:SnO_2$ molar ratios of 9:1, 3:1 and 1:1 prepared by an alcohol-reduction process were evaluated as anodicelectrocatalysts for direct ethanol fuel cell (DEFC). Acetaldehyde, acetic acid and mixtures of them with ethanol were also tested as fuels. Single cell tests showed that $PtSnO_2/C$ electrocatalysts have a superior electrical performance for ethanol and acetaldehyde electro-oxidation when compared to commercial $Pt_3Sn/C_{(alloy)}$ and Pt/C electrocatalysts. For all electrocatalysts, no electrical response was observed when acetic acid was used as a fuel. For ethanol electro-oxidation, the main product was acetaldehyde when $Pt_3Sn/C_{(alloy)}$ and Pt/C electrocatalysts were employed. Besides, $PtSnO_2/C$ electrocatalysts led to the formation of acetic acid as the major product. CO_2 was formed in small quantities for all electrocatalysts studied. A sharp drop in electrical performance was observed when using a mixture of ethanol and acetaldehyde as a fuel, however, the use of a mixture of ethanol and acetic acid as a fuel did not affect the DEFC performance.

1. Introduction

An interesting alternative to H_2-fueled PEMFC (Proton Exchange Membrane Fuel Cell) for portable and mobile applications is the use of ethanol as a fuel (Direct Ethanol Fuel Cell – DEFC). Ethanol offers some advantages compared to hydrogen and other low molecular alcohols because it can be produced in large quantity from biomass, it has high energy density, it is easy handling and it is much less toxic than methanol, for instance [1,2]. However, its complete oxidation to CO_2 is difficult due to the C–C breaking bond and the formation of intermediates that poison Pt/C anode catalysts, reducing the DEFC performance. Thus, the search for new electrocatalysts, more active and selective than Pt/C, resulted in combining Pt with other elements such as Ru [3,4], Mo [3,5] and Sn [5–7]. Despite of these bimetallic electrocatalysts enhanced the DEFC electrical performance, the efficient C–C breaking bond at low temperatures (i.e., below to 100 °C) remains a big challenge and acetaldehyde and acetic acid are the major products [8,9].

Many studies have pointed PtSn/C as the best electrocatalyst for ethanol electro-oxidation [10–12]. However, some aspects such as the best Pt:Sn atomic ratio [13,14], particle size [15,16] and principally, if the material should be prepared as PtSn alloyed phase [12,17] or as Pt and SnO_2 in separated phases [10,18,19], remains a controversial

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issue. Furthermore, there are just few studies in the literature concerning the evaluation of PtSn electrocatalysts on the DEFC performance and products distribution. James et al. [20] showed the predominance of acetaldehyde as the main product formed over Pt/C electrocatalyst. Rousseau et al. [21] showed that the addition of Sn to Pt as PtSn alloy increased not only the activity of the electrocatalyst and the electrical performance of the DEFC, but also changed the product distribution, favoring the formation of acetic acid. Mann et al. [18] used a catalyst composed of Pt and SnO_2 in a DEFC operated at 130 °C and observed a CO_2 increased production. Linares et al. [22] tested different anode catalysts for high temperature polybenzimidazole-based DEFC and found for PtSn/C electrocatalyst, in which Sn was mostly in the oxide form, that the promotion of ethanol oxidation was limited due to a non-optimized distribution of the Pt and Sn and the interaction between the metals. Besides, the presence of oxides favored the partial oxidation of the ethanol molecule.

Thus, the results of PtSn/C electrocatalysts toward ethanol electro-oxidation are controversial and, in some cases, superior performances were found for electrocatalysts containing PtSn (fcc) alloy phase [11,12,17], while in others, electrocatalysts containing Pt(fcc) and SnO_2 with separated phases exhibited better results [10,18,19]. Moreover, studies showing the influence of the main products formed on ethanol electro-oxidation such as acetaldehyde and acetic acid, under fuel cell conditions are scarce. In this work, $PtSnO_2/C$ with $Pt:SnO_2$ molar ratios of 9:1, 3:1 and 1:1 prepared by an alcohol-reduction process were evaluated as anodic electrocatalysts for fuel cell using ethanol, acetaldehyde, acetic acid and mixtures of ethanol/acetaldehyde and ethanol/acetic acid as fuels. Commercial $Pt_3Sn/C_{(alloy)}$ and Pt/C electrocatalysts were also tested for comparative purposes. Based on the electrical performance and on the products distribution results some insights are proposed.

2. Experimental

2.1. Synthesis and characterization of the $PtSnO_2$ electrocatalysts

$PtSnO_2/C$ electrocatalysts with different $Pt:SnO_2$ molar ratios and 20% of metal loading were prepared by an alcohol-reduction process [23] using $H_2PtCl_6.6H_2O$ (Aldrich) and $SnCl_2.2H_2O$ (Synth) as metallic precursors and Carbon Vulcan XC72 (Cabot) as a support in the following manner: the desired quantities of metal precursors were dissolved in an ethylene glycol/water solution (75/25, v/v) followed by the addition of the carbon support. The resulting mixture was treated in an ultrasound bath for 20 min, refluxed for 3 h under open atmosphere and then filtered, washed with water and dried at 70 °C for 2 h.

The X-ray diffraction (XRD) patterns were recorded with a Rigaku diffractometer model Multiflex with a CuKα radiation source. The Pt:Sn atomic ratios were evaluated by Energy Dispersive X-ray analysis (EDX) using a JEOL 6010LA scanning electron microscope operating at 20 kV. The crystallite size was determined by Scherrer equation.

2.2. Single DEFC tests

The 5 cm^2 Membrane Electrode Assemblies (*MEA*) were 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 the following materials: Pt/C, $Pt_3Sn/C_{(alloy)}$, $Pt_9(SnO_2)/C$, $Pt_3(SnO_2)/C$ and $Pt(SnO_2)/C$ (2 mg_{Pt} cm^{-2} 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 (2 mg_{Pt} cm^{-2} catalyst loading) as electrocatalyst.

Electrical performances were determined by polarization and power density curves using a single cell at 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 $Pt_3Sn/C_{(alloy)}$ (lot# F0930209) electrocatalysts are commercial and were purchased from BASF.

2.3. Product distribution

The anodic effluent of the single fuel cell was cooled in an ice bath and an aliquot was collected (the fuel cell current was kept constant until the voltage stabilization was achieved) and analyzed in an Agilent 7890A gas chromatograph (GC). For these experiments a capillary column Plot-U (30 m) and a thermal conductivity detector (TCD) were employed. The elution was carried out using hydrogen gas at a flow rate of 45 mL min^{-1} and the oven temperature was maintained at 80 °C for 5 min and, after this, it was increased at 10 °C min^{-1} until 160 °C. Inlet and detector temperatures were set to 180 °C and 220 °C, respectively. The injections were performed manually and the elution times ranged from ca. 0.70 min for CO_2 to ca. 8.45 min for acetic acid with excellent peak separation. Ethanol and the formed products such as CO_2, acetaldehyde, ethyl acetate and acetic acid were quantified using a calibration curve.

The selectivity (S) was based on the total amount of the products reaction at the anodic effluent and was calculated by Eq. (1).

$$\%S_i = \frac{C_i}{C_{AAL} + C_{AA} + C_{CO2}} \times 100\% \qquad (1)$$

where *C* is the concentration of the product *i*; acetaldehyde, acetic acid and carbon dioxide.

3. Results

3.1. Electrocatalysts characterization

The XRD diffraction patterns are shown in Fig. 1. All electrocatalysts exhibited a broad peak at about $2\theta = 25°$, which is associated to Vulcan XC72 carbon, used as support. Pt/C electrocatalyst showed four peaks at approximately $2\theta = 40°$, 47°, 67° and 82° related to (111), (200), (220) and (311) planes of the face-centered cubic (fcc) structure characteristics of Pt and

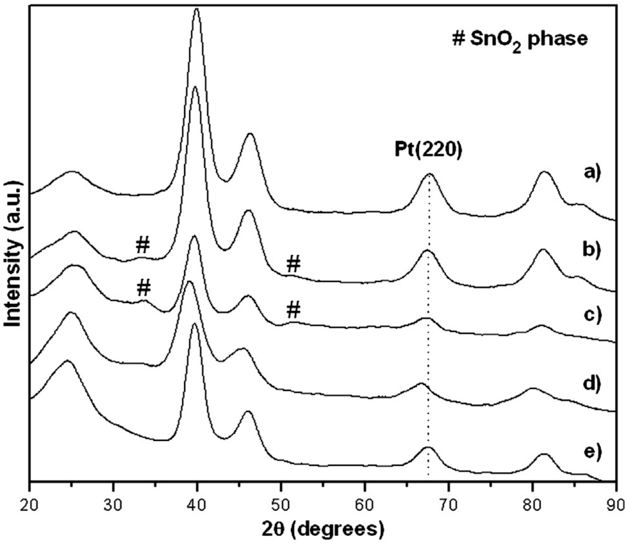

Fig. 1 – XRD patterns of a) $Pt_9(SnO_2)/C$, b) $Pt_3(SnO_2)/C$, c) $Pt(SnO_2)/C$, d) $Pt_3Sn/C_{(alloy)}$, and e) Pt/C.

Pt alloys [23]. The same peaks were observed for commercial $Pt_3Sn/C_{(alloy)}$electrocatalyst, but with a slight shift toward lower 2θ values compared to the Pt/C peaks, showing the formation of Pt–Sn alloy. $Pt_9(SnO_2)/C$, $Pt_3(SnO_2)/C$ and $Pt(SnO_2)/C$ electrocatalysts also exhibited all of these peaks but no shift was observed compared to Pt/C, indicating no alloy formation between Pt and Sn. Furthermore, it was observed for these materials two peaks at about $2\theta = 37°$ and 52° that were attributed to SnO_2 phase [24] and the intensities of these peaks increase with the increasing of Sn content. Table 1 shows that Pt:Sn atomic ratios determined by EDX analysis were close to the nominal values and the average crystallite sizes calculated from the Pt(220) diffraction peaks were in the range 2–3 nm.

3.2. *DEFC tests*

The electro-oxidation of ethanol molecule under fuel cell conditions can lead to the formation of CO_2, acetaldehyde and acetic acid as the final products (Eqs. (2)–(6)). Firstly, the ethanol molecule can be completely oxidized to CO_2, with C–C bond cleavage, releasing a total of twelve electrons for electrical work, as seen in Eq. (2). However, under PEMFC conditions ($T \leq 100\ °C$), it is very difficult to break the C–C bond and then, the ethanol dehydrogenization to acetaldehyde (Eq. (3)), yielding only two electrons, is favored.

Table 1 – Atomic Pt:Sn ratio and crystallite size of the electrocatalysts.

Electrocatalyst	Nominal Pt:Sn atomic ratio	Real Pt:Sn atomic ratio	Crystallite size (nm)
Pt/C	–	–	3.0
$Pt_3Sn/C_{(alloy)}$	75:25	77:23	2.5
$Pt(SnO_2)/C$	50:50	59:41	2.6
$Pt_3(SnO_2)/C$	75:25	80:20	2.5
$Pt_9(SnO_2)/C$	90:10	92:8	2.4

$$CH_3CH_2OH + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e^- \quad (2)$$

$$CH_3CH_2OH \rightarrow Pt - CH_3CHO + 2H^+ + 2e^- \quad (3)$$

$$CH_3CHO + H_2O \rightarrow CH_3COOH + 2H^+ + 2e^- \quad (4)$$

$$CH_3CH_2OH + H_2O \rightarrow CH_3COOH + 4H^+ + 4e^- \quad (5)$$

$$CH_3CHO + 3H_2O \rightarrow 2CO_2 + 10H^+ + 10e^- \quad (6)$$

Acetic acid was one of the detected fuel cell products and its formation can proceed both via acetaldehyde electro-oxidation with two electrons (Eq. (4)) or directly from ethanol electro-oxidation, in this case, releasing four electrons (Eq. (5)). Additionally, acetaldehyde can be further oxidized leading to the CO_2 formation, and then releasing more ten electrons, as seen in Eq. (6).

The polarization and power density curves in single DEFC with different electrocatalysts as anodes, are shown in Fig. 2. Pt/C electrocatalyst showed a poor electrical performance with an open circuit voltage (OCV) of about 610 mV and the

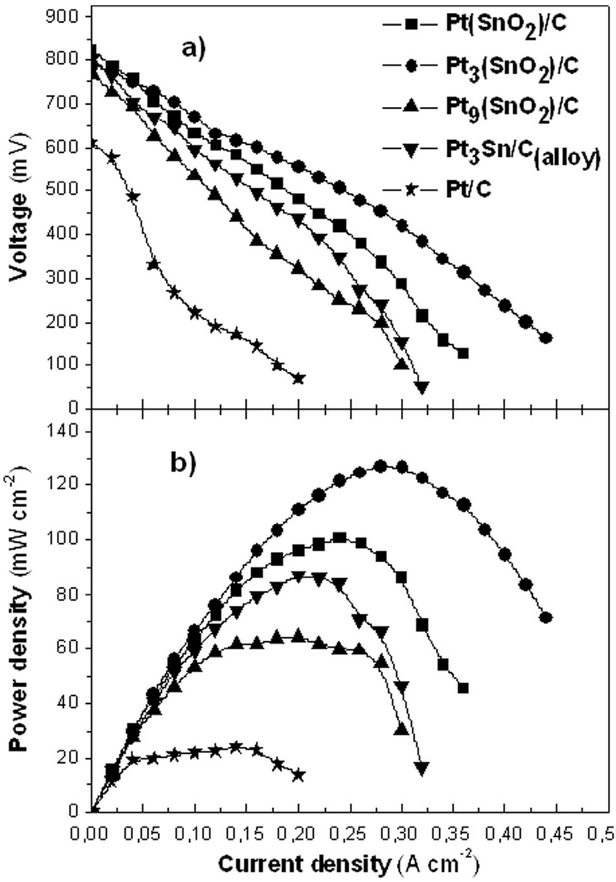

Fig. 2 – Performance comparison employing Pt/C, $Pt_3Sn/C_{(alloy)}$, $Pt_9(SnO_2)/C$, $Pt_3(SnO_2)/C$, and $Pt(SnO_2)/C$ as anodic catalysts (2 $mg_{Pt}\ cm^{-2}$) and Pt/C as cathode (2 $mg_{Pt}\ cm^{-2}$). a) Polarization curves; b) power density. $T_{cell} = 100\ °C$; $P_{O2} = 2$ bar; [EtOH] = 2 mol L^{-1}; Nafion 117 membrane.

maximum current density reaches to 0.2 A cm^{-2}, leading to only 24 mW cm^{-2} of maximum power density. The cell performance improves when Sn is added to Pt, even in low amounts. For $Pt_9(SnO_2)/C$ electrocatalyst, the OCV increased to 750 mV and the maximum current density reached 50% more than Pt/C, leading the maximum power density to 65 mW cm^{-2}; however, it seems to exist an optimum of Sn content for $PtSnO_2/C$ electrocatalysts. The maximum power density obtained for $Pt(SnO_2)/C$ electrocatalyst was 101 mW cm^{-2}, whereas $Pt_3(SnO_2)/C$ reached to 127 mW cm^{-2}. It is noteworthy that $Pt_3(SnO_2)/C$ and $Pt_3Sn/C_{(alloy)}$, although having the same Pt:Sn atomic ratios, showed different electrical performances. $Pt_3(SnO_2)/C$ electrocatalyst achieved almost 70% more power density than $Pt_3Sn/C_{(alloy)}$. The difference in the electrical performances could be explained in terms of the quantity and the selectivity of the formed products (Eqs. (2)–(6)). In order to identify and quantify the products reaction and the unreacted ethanol for the different electrocatalysts, the anodic effluent was collected at the maximum power and current densities and analyzed by GC. Acetaldehyde, acetic acid, CO_2 and ethyl acetate were identified as formed products. Ethyl acetate, which is not commonly related in literature, comes from esterification reaction between ethanol and acetic acid, which may occur on the acid sites ($-SO_3H$ groups) of Nafion contained in the catalytic ink. Thus, the detected amount of ethyl acetate was added to unreacted ethanol and acetic acid formed. The mass balance values (unreacted ethanol plus formed products/initial ethanol concentration × 100%) obtained for the different electrocatalyts were in the range of 95–99%, which are good values considering the possibility of the crossover of the ethanol and the products through the Nafion membrane from anode to the cathode [25]. As can be seen in Table 2, where the anodic effluent samples were collected at maximum current densities, the products formed are only a few percent (ca. 5–7%) of the ethanol used as a fuel. In Fig. 3, the products formed using the different electrocatalysts are showed in terms of selectivity. In this case, all the anodic effluent samples were collected at a maximum power density. Although the quantities (mmol L^{-1}) of the products had increased with the current increasing, the selectivity values obtained at maximum current density (Table 1) and the selectivity values obtained at a maximum power density (Fig. 3) did not vary significantly, especially for the production of acetaldehyde and acetic acid. For Pt/C electrocatalyst, acetaldehyde was the main product formed with 86% of selectivity while acetic acid and CO_2 were both formed with 7% of selectivity. $Pt_3Sn/C_{(alloy)}$ also exhibited acetaldehyde as the main product formed with 76% of selectivity, but in this case, an increase of acetic acid production (21% of selectivity) was observed. For $PtSnO_2/C$ electrocatalysts the product distribution changed with the Sn content. $Pt_9(SnO_2)/C$, with high Pt content, was very selective for acetaldehyde production (82%), however it was found an increase for acetic acid production (13% of selectivity) compared to Pt/C electrocatalyst. $Pt(SnO_2)/C$ electrocatalyst showed a selectivity decrease for acetaldehyde production to 65% and an increase of acetic acid production to 35%, while $Pt_3(SnO_2)/C$ electrocatalyst showed practically an acetic acid/acetaldehyde molar ratio of 1. With a similar Pt:Sn atomic ratio, $Pt_3Sn/C_{(alloy)}$ electrocatalyst showed an acetic acid/acetaldehyde molar ratio of only 0.3, indicating that SnO_2 contributed to the formation of acetic acid. Pt/C was the most selective electrocatalyst for CO_2 production (7%), however, for all electrocatalysts the CO_2 selectivity was very low.

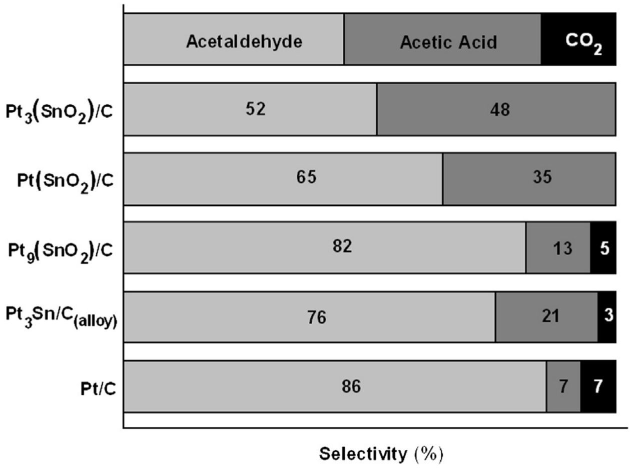

Fig. 3 – Selectivity of products collected from ethanol electro-oxidation using different catalysts operating at maximum power density.

The quantities of products formed (Table 2) for $Pt_3(SnO_2)/C$ (84 mmol L^{-1}) and $Pt_3Sn/C_{(alloy)}$ (79 mmol L^{-1}) electrocatalysts were very similar; however, $Pt_3(SnO_2)/C$ electrocatalyst showed superior electrical performance for ethanol electro-oxidation, which could be attributed to the major selectivity for acetic acid production (release of 4 electrons)

Table 2 – Products distribution, mass balance and selectivity of ethanol electro-oxidation at 50 mV.

Electrocatalyst	Products (mmol L^{-1})				Mass balance (%)	Selectivity (%)		
	AAL[a]	AA[a]	CO_2	EtOH[a]		AAL[a]	AA[a]	CO_2
Pt/C	65	5	6	1870	97	86	7	7
$Pt_3Sn/C_{(alloy)}$	56	20	3	1910	99	71	25	4
$Pt_9(SnO_2)/C$	62	13	5	1883	98	77	16	7
$Pt(SnO_2)/C$	55	25	2	1867	97	67	30	3
$Pt_3(SnO_2)/C$	44	37	3	1826	95	52	44	4

[a] AAL: acetaldehyde, AA: acetic acid, EtOH: unreacted ethanol.

while $Pt_3Sn/C_{(alloy)}$ lead mainly to acetaldehyde production (release of 2 electrons).

3.3. *Direct acetaldehyde fuel cell tests*

Fig. 4 shows the performance of the different electrocatalysts toward acetaldehyde electro-oxidation. The OCV for PtSn/C electrocatalysts were in the range of 800–850 mV while for Pt/C was 620 mV, indicating again the positive effect of Sn addition. Compared to the results obtained for a DEFC, a similar order in electrical performance was observed using acetaldehyde as a fuel: $Pt_3(SnO_2)/C > Pt(SnO_2)/C \approx Pt_3Sn/C_{(alloy)} > Pt_9(SnO_2)/C > Pt/C$; however, the maximum power densities were lower than the ones observed for the DEFC. Using $Pt(SnO_2)/C$ as electrocatalyst and acetaldehyde as a fuel, the quantity of the products formed (29 mmol L^{-1}) was half of that observed for ethanol (60 mmol L^{-1} using 1 mol L^{-1} of ethanol as a fuel) showing that the reaction proceeds with a slow rate for acetaldehyde. Only acetic acid and CO_2 were identified as the formed products (Fig. 5) and, for all cases, acetic acid was produced with 80–90% of selectivity being the main formed product. However, compared to ethanol as a fuel, it should be noted an increase in CO_2 selectivity (Fig. 3) indicating that C–C breaking bond is favored for acetaldehyde molecule. Similar results were also described by Koper and co-works [26] showing that the C–C breaking bond was easier in acetaldehyde than in ethanol. Again, Pt/C electrocatalyst showed to be the most selective for CO_2 production, proving to be the most efficient for C–C breaking bond; on the other hand, the quantities of CO_2 produced were very low and it presented the poorest electrical performance.

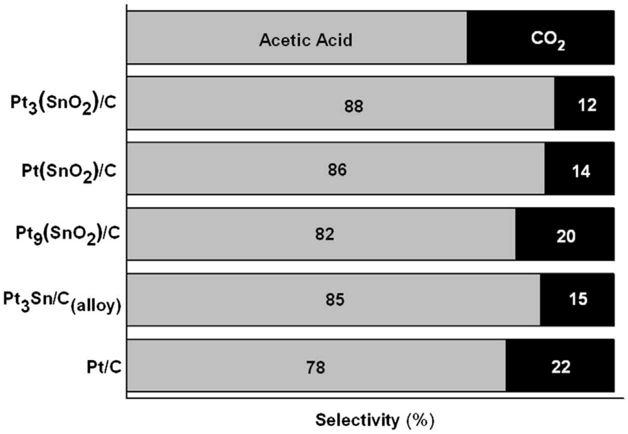

Fig. 5 – Selectivity of products collected from acetaldehyde electro-oxidation using different catalysts operating at maximum power density.

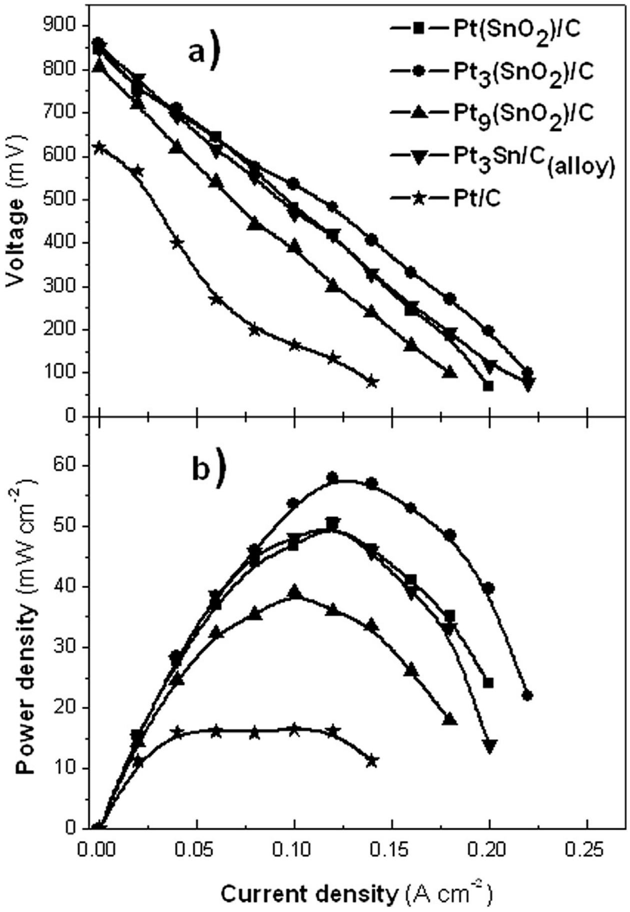

Fig. 4 – Performance comparison employing Pt/C, $Pt_3Sn/C_{(alloy)}$, $Pt_9(SnO_2)/C$, $Pt_3(SnO_2)/C$, and $Pt(SnO_2)/C$ as anodic catalysts (2 mg Pt cm^{-2}) and Pt/C as cathode (2 mg Pt cm^{-2}). a) Polarization curves and b) power density. $T_{cell} = 100\ ^{\circ}C$; $P_{O2} = 2$ bar; [AAL] = 1 mol L^{-1}; Nafion 117 membrane.

3.4. *Direct acetic acid fuel cell tests*

Tests using acetic acid as a fuel were also made using the different electrocatalysts but no electrical response was observed in all cases and no products were detected in the anodic effluent. This suggests that acetic acid cannot be oxidized using Pt/C and PtSn/C materials under the fuel cell conditions or its adsorption leads to the formation of species that are capable to poison the catalytic sites.

3.5. *DEFC performance employing fuel mixtures*

In order to know if acetaldehyde or acetic acid affect the DEFC performance, experiments were performed adding these compounds into the ethanol solution. The studies of the influence of acetaldehyde and acetic acid in the electro-oxidation of ethanol under real DEFC conditions are scarce. Prieto and Tremiliosi-Filho [27] studied the effect of acetic acid on the electro-oxidation of ethanol using Pt/C electrocatalyst by cyclic voltammetry (half cells) and FTIR *in situ*. They concluded that the acetate derived from 0.1 μmol L^{-1} of acetic acid added to ethanol solution inhibits Pt active sites resulting in a drop of acetaldehyde and CO_2 formation. Fig. 6 shows the polarization and power density curves relative to fuel mixtures over Pt/C (Fig. 6a and b) and $Pt(SnO_2)/C$ (Fig. 6c and d) as anodic electrocatalysts. For both electrocatalysts there was no worthy difference in electrical performance when 0.5 mol L^{-1} of acetic acid was added into the ethanol solution in contrast to the results observed by Prieto and Tremiliosi-Filho [27]. It is

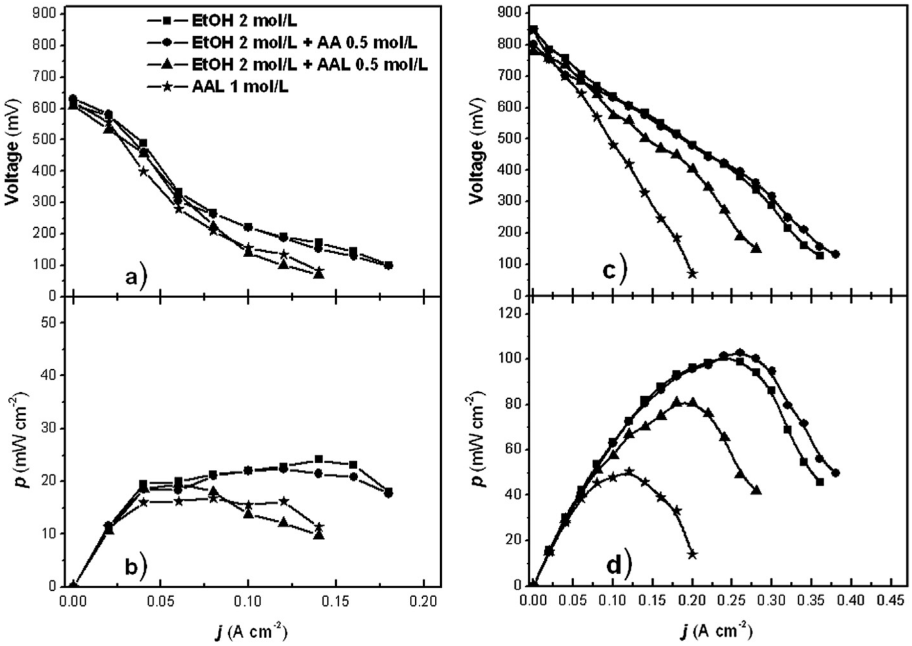

Fig. 6 – Electrical performances of different fuel mixtures a) polarization curves and b) power density curves using Pt/C in both anode and cathode, c) polarization curves and d) power density curves employing Pt(SnO_2)/C as anode and Pt/C in cathode. Catalytic loading 2 $mg_{Pt}\ cm^{-2}$, $T_{cell} = 100$ °C; Fuel flux = 2 mL min^{-1}; $P_{O2} = 2$ bar; Nafion117 membrane. AA acetic acid, AAL acetaldehyde and EtOH ethanol.

necessary to emphasize that such quantity of acetic acid is much larger than that produced in the single cell using pure ethanol solution (Table 2). On the other hand, for both electrocatalysts, a sharp drop in electrical performance was verified when the ethanol/acetaldehyde mixture was employed; although the concentration of acetaldehyde was lower than that of ethanol.

The cell voltage stability was studied for a DEFC using the fuel mixtures at a constant current. In these experiments the fuel mixtures were recirculated into the fuel cell anode and the cell voltage was continuously measured as shown in Fig. 7a. Using only ethanol solution, it was observed a decrease from 572 V to 470 V in the first 10 min and, after this time, a small decrease occurred until 1 h of operation. Using the ethanol/acetic acid mixture as a fuel, practically the same cell voltage behavior was observed when compared to pure ethanol solution. Beside this, the quantities of formed acetaldehyde (Fig. 7b) were very similar showing that acetic acid caused no interference on the DEFC performance. For both cases, no CO_2 was detected over these fuel cell conditions. Using an ethanol/acetaldehyde mixture as a fuel, a cell voltage decrease was also observed in the first 10 min and it was greater than the one observed for ethanol/acetic acid mixture. After this period, the voltage continued to decrease progressively. Furthermore, a pronounced voltage drop was observed when pure acetaldehyde solution was used as a fuel leading to the fuel cell deactivation at approximately 30 min of operation. Considering the linear regression, a cell voltage rate

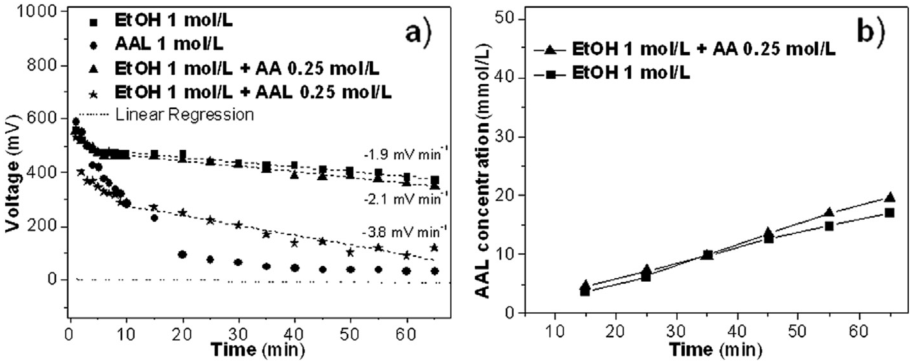

Fig. 7 – Recirculation of different fuel mixtures. a) Cell voltage stability and b) acetaldehyde production with time, using Pt(SnO_2)/C (2 mg Pt cm^{-2}) as anode and Pt/C (2 mg Pt cm^{-2}) as cathodic catalyst. $T_{cell} = 100$ °C; Fuel flux = 2 mL min^{-1}; $P_{O2} = 2$ bar; Nafion 117 membrane. AA acetic acid, AAL acetaldehyde and EtOH ethanol.

drop for ethanol/acetaldehyde mixture was found to be 3.8 mV min^{-1}, twice than ethanol and ethanol/acetic acid mixture, both around 2.0 mV min^{-1}. Once again, these tests showed that acetic acid practically did not affect the DEFC performance whereas the presence of acetaldehyde leads to its deactivation.

3.6. Discussion

We propose a mechanism of ethanol electro-oxidation based upon the identified products and some previous works [28,29], as shown in Fig. 8. The Pt active sites act as nuclei of adsorption and dehydrogenation of ethanol molecule to acetaldehyde, releasing two electrons for external circuit. The acetaldehyde can desorbs to the bulk or remains adsorbed, forming $\text{acetyl}_{(ads)}$ species, which could be oxidized to acetic acid with the aid of oxygenated species from Sn or SnO_2. Also, the C–C breaking bond of $\text{acetyl}_{(ads)}$ species could lead to the formation of $CO_{(ads)}$ and $CH_{3(ads)}$species. The $CO_{(ads)}$ species could be subsequently oxidized to CO_2 with the aid of the oxygenated species. In a similar way, $CH_{3(ads)}$ species could be oxidized to CO_2. There is also the possibility of ethanol molecule to oxidize directly to acetic acid.

Our results showed that Pt/C and $Pt_3Sn/C_{(alloy)}$ electrocatalysts were more selective for acetaldehyde production than $Pt_3(SnO_2)/C$ and $Pt(SnO_2)/C$ electrocatalysts, which were more selective for acetic acid production. This means that the presence of SnO_2 phase could contribute to oxidize ethanol directly to acetic acid and/or to further oxidize the acetaldehyde coming from ethanol oxidation to acetic acid, while the Sn present in the form of alloy in the $Pt_3Sn/C_{(alloy)}$ electrocatalyst was not too efficient in this case.

Many results described in the literature [10,22,30] using different PtSn electrocatalysts showed that acetaldehyde was the major product formed. On the other hand, our results showed that acetaldehyde was responsible for the loss performance of DEFC and, in this case, this could suggest that acetaldehyde adsorbs preferentially on Pt sites avoiding ethanol adsorption. Moreover, the C–C acetaldehyde breaking bond could take place on Pt sites leading to the formation of $CO_{(ads)}$ and $CH_{x(ads)}$groups. Lai and Koper [31] studied the electrochemical oxidation of ethanol and acetaldehyde at Pt single-crystal electrodes using electrochemical techniques and spectroscopic methods. They observed that acetaldehyde was the main specie in which the C–C breaking bond occurred, although slow C–C breaking bond in ethanol and ethoxy could not be excluded. Farias et al. [32] studied the electro-oxidation of isotope-labeled ethanol on Pt using FTIR spectroscopy and concluded that CO_2 coming from $CH_{x(ads)}$ species were only produced at higher overpotentials than those observed for CO_2 coming from $CO_{(ads)}$ species and attributed such difference to a major difficulty to oxidize CH_x groups. In a similar way, Shimada et al. [33] studied the ethanol electro-oxidation at 250 °C using a membrane of CsH_2PO_4 and observed that even at such high temperature both C–C breaking bond and $CH_{x(ads)}$oxidation groups were the rate limiting step. By this way, the preferential adsorption of acetaldehyde and/or the resulting fragments of its C–C breaking bond could lead to the deactivation of the electrocatalysts and the presence of acetaldehyde on ethanol electro-oxidation should be avoided.

It was also claimed in the literature that acetic acid must be avoided [34,35], however, our results showed that acetic acid did not influence the cell performance even in great quantities. Thus, if it is possible to prepare PtSn electrocatalysts that produce only acetic acid from ethanol oxidation (Eq. (5)), we can obtain a DEFC operating at temperatures ≤100 °C with current density and durability higher than those where acetaldehyde was the main product formed. Obviously, the complete electro-oxidation of ethanol to CO_2 would be much more

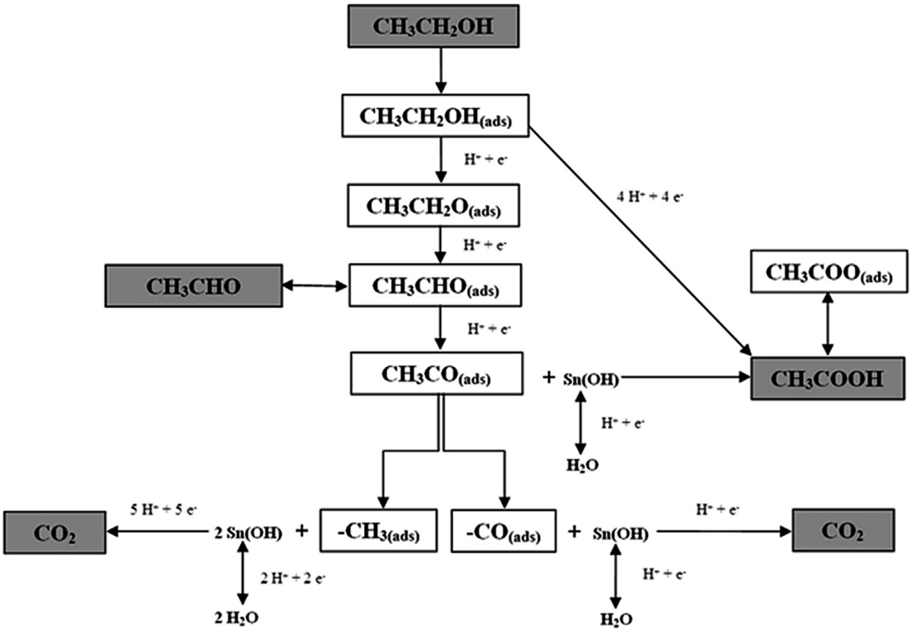

Fig. 8 – Proposed ethanol electro-oxidation mechanism over $PtSnO_2/C$, indicating the products ▨ from the bulk and □ adsorbed on surface catalyst.

interesting, however, the development of the electrocatalysts capable to promote the C–C breaking bond and to oxidize the resulting $CO_{(ads)}$ and $CH_{x(ads)}$ species with great efficiency remains a challenge to be overcome.

4. Conclusions

DEFC experiments showed that $PtSnO_2/C$ electrocatalysts have superior electrical performance compared to commercial $Pt_3Sn/C_{(alloy)}$ and Pt/C electrocatalysts. Acetic acid was the main product formed using $PtSnO_2/C$ electrocatalysts while acetaldehyde was the major product formed using $Pt_3Sn/C_{(alloy)}$ and Pt/C electrocatalysts. The addition of acetaldehyde into the ethanol solution leads to an electrical performance decrease and a poor durability of the fuel cell. On the other hand, the addition of acetic acid did not modify the fuel cell performance.

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