

## Ethanol Electro-Oxidation on PtSn/C-ATO Electrocatalysts

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PtSn/C-ATO electrocatalysts with different Pt:Sn atomic ratios (90:10, 70:30 and 50:50) were prepared in a single step by an alcohol-reduction process using  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  and  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  as metal sources and ethylene glycol as solvent and reducing agent and a physical mixture of carbon Vulcan XC72 (85 wt%) and  $\text{Sb}_2\text{O}_5 \cdot \text{SnO}_2$  (15 wt%) as support (C-ATO). The obtained materials were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The catalytic activity for ethanol electro-oxidation in acid medium was investigated by cyclic voltammetry and chronoamperometry and in single direct ethanol fuel cell (DEFC). XRD analyses showed that Pt(fcc),  $\text{SnO}_2$ , carbon and ATO phases coexist in the obtained materials. The electrochemical studies showed that PtSn/C-ATO electrocatalysts were more active for ethanol electro-oxidation than PtSn/C electrocatalyst. The experiments at 100°C on a single DEFC showed that the power density of the cell using PtSn/C-ATO (90:10) was nearly 100% higher than the one obtained using PtSn/C (50:50). FTIR measurements showed that the addition of ATO to PtSn/C favors the formation of acetic acid as a product while for PtSn/C acetaldehyde was the principal product formed.

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**Keywords:** PtSn/C-ATO,  $\text{Sb}_2\text{O}_5 \cdot \text{SnO}_2$ , alcohol-reduction process, ethanol electro-oxidation, FTIR, fuel cells

### 1. INTRODUCTION

Direct Alcohol fuel cell (DAFC) has received much attention in recent years due to the advantages of using liquid combustible. Methanol and ethanol have been utilized as fuel due to their low cost and high theoretical energy density; in addition, ethanol has been considered more interesting

because it could be produced in large scale from renewable sources and it is less toxic than methanol [1].

PtSn-based electrocatalysts have been shown the best results for ethanol electro-oxidation. Despite of the increase of the activity of these electrocatalysts, acetaldehyde and acetic acid are the principal products formed and the complete ethanol electro-oxidation to CO<sub>2</sub> in a DEFC continues to be a great challenge [2-16].

Lee et al [17] showed that the activities of Pt/ATO (antimony doped tin oxide-Sb<sub>2</sub>O<sub>5</sub>.SnO<sub>2</sub>-ATO) for ethanol electro-oxidation were greater than those of Pt/C electrocatalyst, however, the products formed using these electrocatalysts were not determined.

Recently, Oliveira Neto et al [18] showed that Pt nanoparticles supported on a physical mixture of carbon and ATO (Pt/C-ATO) were more active for ethanol electro-oxidation in acidic medium than Pt nanoparticles supported on ATO (Pt/ATO), on carbon (Pt/C) or using physical mixtures of Pt/ATO plus Pt/C. The enhancement of activity of Pt/C-ATO electrocatalyst was attributed to Pt nanoparticles, ATO and carbon supports in close proximity.

In this context, the aim of this work was to evaluate the activity of PtSn/C-ATO electrocatalysts with different Pt:Sn atomic ratios prepared in a single step by an alcohol-reduction process for ethanol electro-oxidation and to investigate the products formed by in situ FTIR spectroscopy.

## 2. EXPERIMENTAL

PtSn/C-ATO electrocatalysts (20% of PtSn metal loading and Pt:Sn atomic ratios of 90:10, 70:30 and 50:50) were prepared in a single step by an alcohol-reduction process using H<sub>2</sub>PtCl<sub>6</sub>.6H<sub>2</sub>O (Aldrich) and SnCl<sub>2</sub>.2H<sub>2</sub>O (Aldrich) as metal sources, ethylene glycol as solvent and reducing agent a physical mixture of carbon Vulcan XC72 (85 wt%) and Sb<sub>2</sub>O<sub>5</sub>.SnO<sub>2</sub> (15 wt%) as support (C-ATO). The metal sources were dissolved in a solution of ethylene glycol/ water (3:1, v/v), the carbon Vulcan XC72 (Cabot) and ATO (Aldrich, nanopowder, antimony pentoxide 7-11 wt%, tin(IV) oxide 89-93 wt%) supports were dispersed in the solution and the resulting mixture was submitted to reflux for 3h.

XRD analyses were performed in a Rigaku Miniflex II diffractometer using Cu K $\alpha$  radiation source ( $\lambda = 0.15406$  nm). The diffractograms were recorded from  $2\theta = 20^\circ$  to  $90^\circ$  with a step size of  $0.05^\circ$  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. Mean particle sizes were determined by counting more than 200 particles from different regions of each sample.

The cyclic voltammetry and chronoamperometry measurements were carried out under controlled temperatures of 25 and  $50 \pm 0.1^\circ\text{C}$  using a Nova Ética thermostat. These studies were performed using a Microquímica potenciostat, where the working electrodes (geometric area of 0.3 cm<sup>2</sup> with a depth of 0.3 mm) were prepared using the thin porous coating technique [6]. An amount of 20 mg of the electrocatalyst 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 reference electrode was a reversible

hydrogen electrode (RHE) and the counter electrode was a Pt plate. The experiments were performed in a solution of 1.0 mol L<sup>-1</sup> of ethanol in 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> saturated with N<sub>2</sub>.

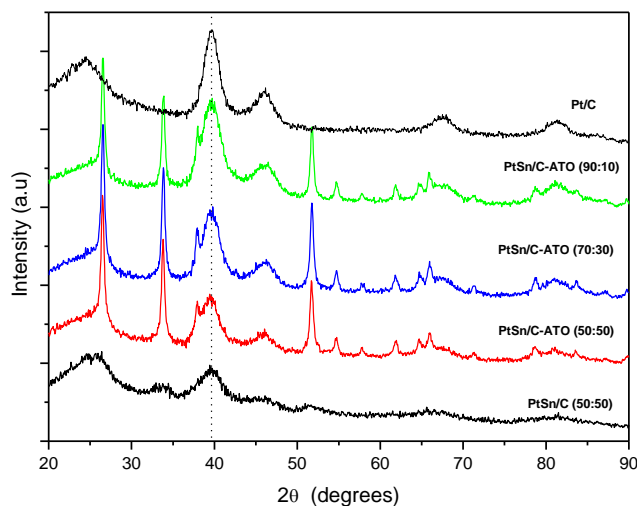
Direct ethanol fuel cell tests were performed using PtSn/C-Sb<sub>2</sub>O<sub>5</sub>.SnO<sub>2</sub> electrocatalysts as anode and Pt/C electrocatalysts as cathode. For DEFC studies it was utilized the carbon-cloth Teflon-treated (Electrochem ECCC1-060T) as a gas diffusion layer and a Nafion 117 membrane as electrolyte. The electrodes (anode or cathode) were hot pressed on both sides of a Nafion 117 membrane at 100°C for 2 min under a pressure of 225 kgf cm<sup>-2</sup>. The electrodes prepared contained 1 mg Pt cm<sup>-2</sup> in the anode and cathode. An aqueous solution of ethanol 2 mol L<sup>-1</sup> was delivered at 2 mL min<sup>-1</sup>, and the oxygen flow was set to 500 mL min<sup>-1</sup> under 2 bar of pressure. The polarization curves were obtained using an electronic load.

The spectroelectrochemical ATR-FTIR in situ measurements were performed with a Varian® 660 IR spectrometer equipped with a MCT detector cooled with liquid N<sub>2</sub>, ATR accessory (MIRacle with a Diamond/ ZnSe Crystal Plate Pike®) and a special cell [9]. The working electrodes were constructed by dispersing 8 mg of the electrocatalyst powder in 1 mL water and mixing for 5 min in an ultrasonic bath, and then 20 µL of 5% Nafion® solution was added to the suspension, which was mixed again for 15 min in an ultrasonic bath. Aliquots of 4 µL of the dispersion fluid were pipetted onto the Glass Carbon surface. These experiments were performed at 25°C in presence of 0.1 mol L<sup>-1</sup> HClO<sub>4</sub> in 1.0 mol L<sup>-1</sup> ethanol. The absorbance spectra were collected as the ratio R:R<sub>0</sub>, where R represents a spectrum at a given potential and R<sub>0</sub> is the spectrum collected at 0.05 V. A Positive and negative directional bands represent gain and loss of species at the sampling potential, respectively. The spectra were computed from 128 interferograms averaged from 2500 cm<sup>-1</sup> to 850 cm<sup>-1</sup> with the spectral resolution set to 4 cm<sup>-1</sup>. Initially, a reference spectrum (R<sub>0</sub>) was measured at 0.05 V, and the sample spectra were collected after applying successive potential steps from 0.2 V to 1.0 V [9].

### 3. RESULTS AND DISCUSSION

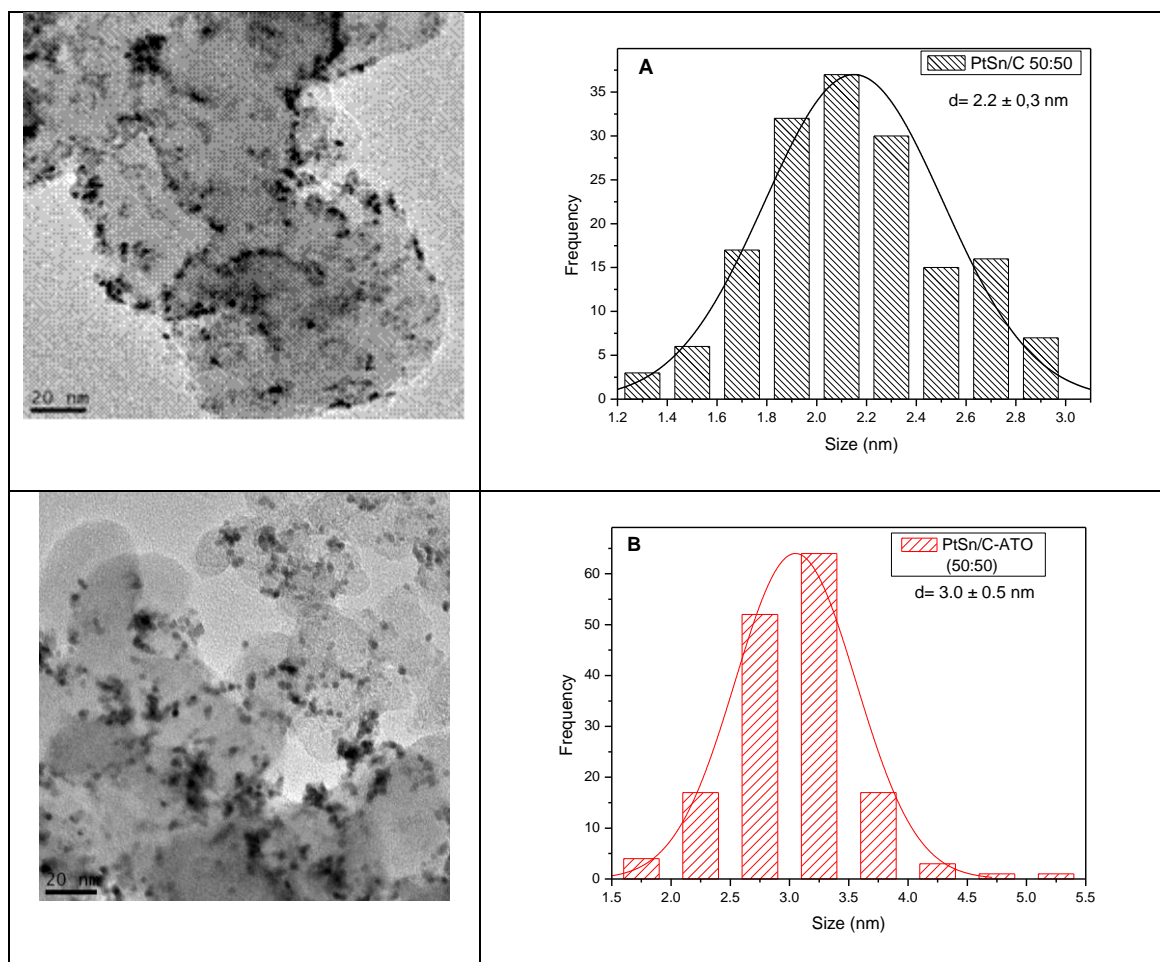
Figure 1 shows X-ray diffractograms (XRD) for PtSn/C and PtSn/C-ATO electrocatalysts prepared with different Pt:Sn atomic ratios.

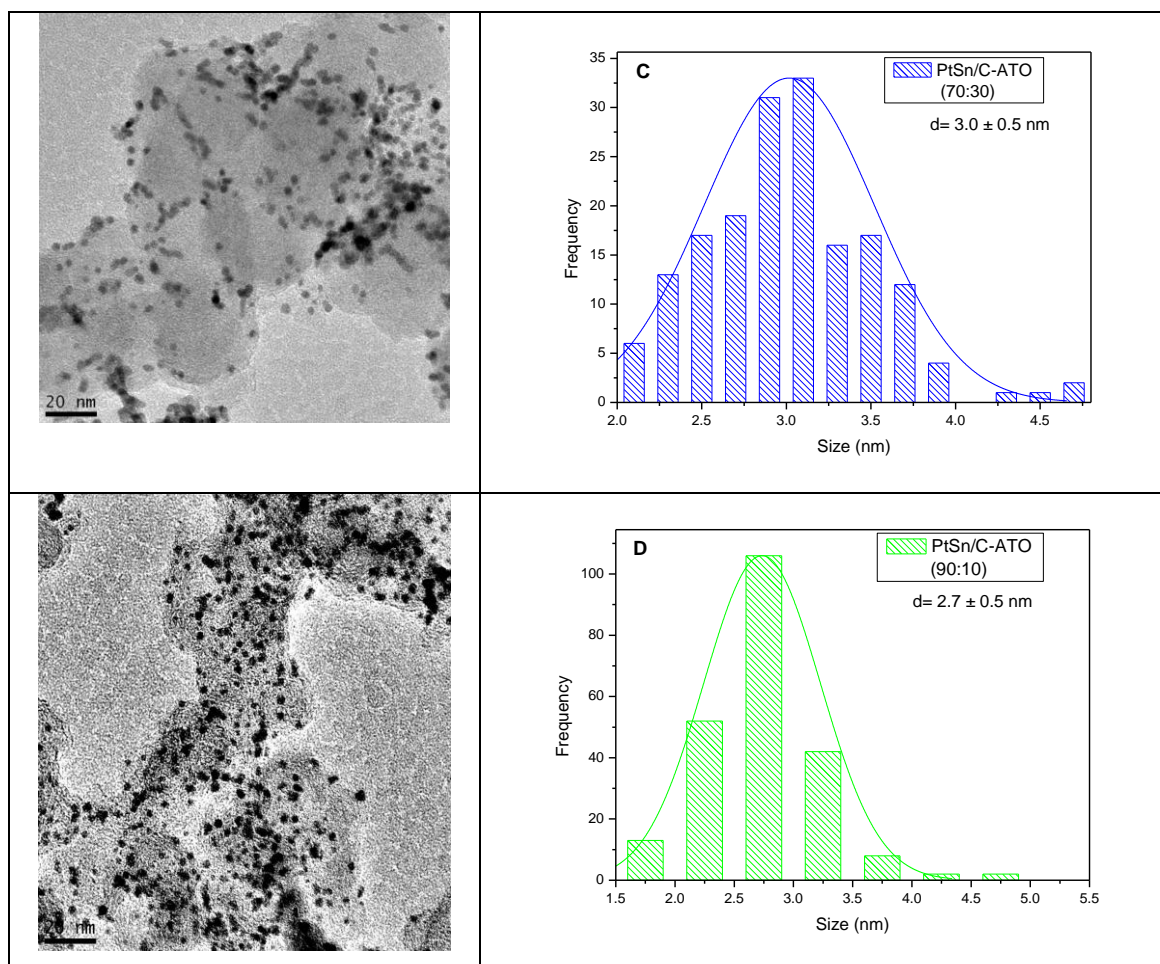
The diffractogram of the PtSn/C electrocatalyst showed a broad peak at about 2θ= 25° that was associated with Carbon Vulcan XC72 support material and four peaks at about 2θ= 40°, 47°, 67° and 82°, which are associated with the (111), (200), (220) and (311) planes characteristic of face-centered cubic (fcc) structure of Pt [18]. It was also observed in the diffractogram two broad peaks at about 2θ= 34° and 52° which were identified as a cassiterite SnO<sub>2</sub> phase [18]. For PtSn/C-ATO electrocatalysts besides the peaks of carbon material and Pt(fcc) structure it was also observed peaks at about 2θ= 27°, 34°, 38°, 52°, 55°, 62°, 65° and 66°, which were also characteristic of cassiterite SnO<sub>2</sub> phase and were associated with ATO used as support [18]. Comparing the peaks of Pt(fcc) phase of the PtSn/C and PtSn/C-ATO electrocatalysts with the ones of Pt/C electrocatalyst (see line at about 2θ= 40°, Fig. 1) no shifting of these peaks was observed, which suggest that PtSn alloys were not formed. Thus, the obtained materials showed the peaks characteristic of Pt (fcc), carbon, SnO<sub>2</sub> and ATO phases.



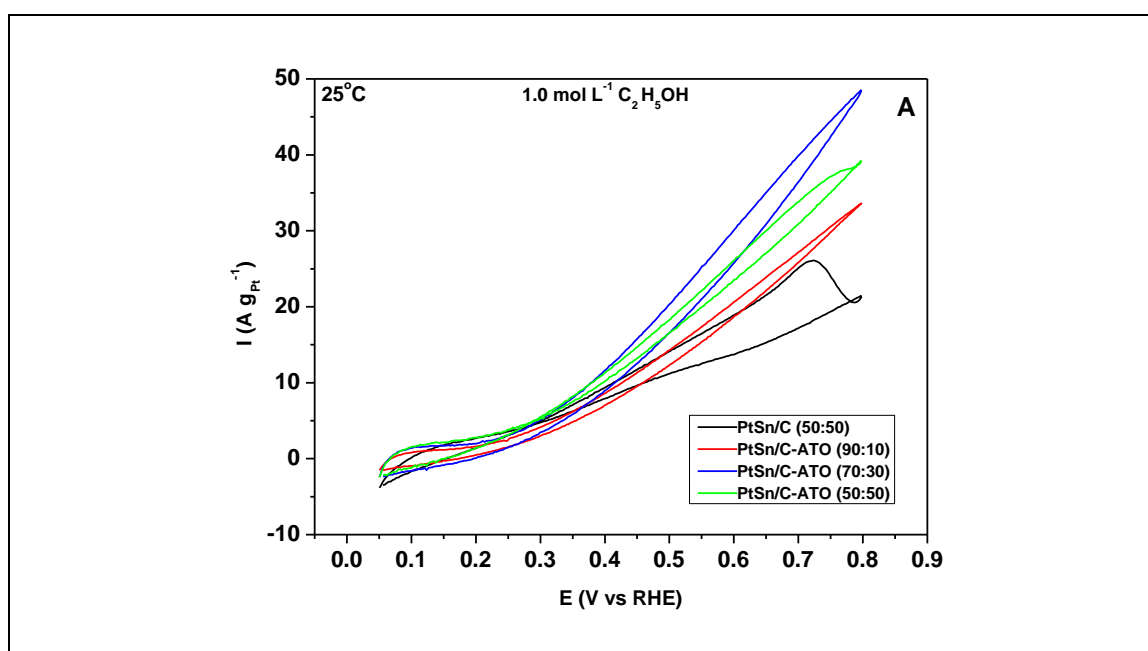
**Figure 1.** X-ray diffractograms of Pt/C, PtSn/C (50:50), PtSn/C-ATO (90:10), PtSn/C-ATO (70:30) and PtSn/C-ATO (50:50).

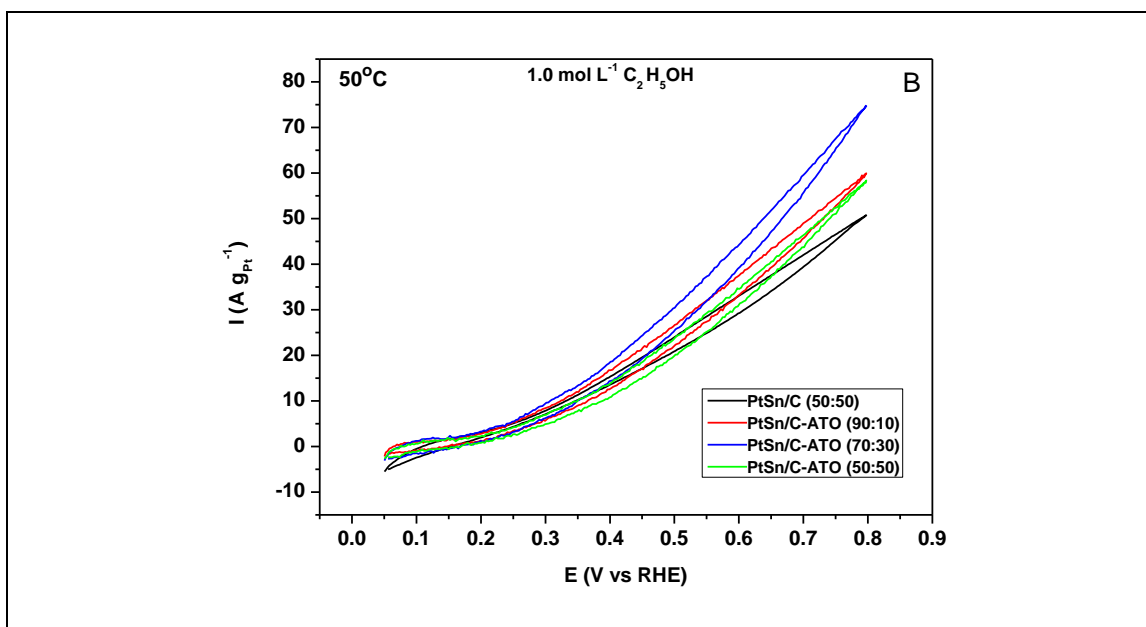
Figure 2 presents TEM micrographs and histograms of PtSn/C (50:50) (Fig 2A), PtSn/C-ATO (50:50) (Fig 2B), PtSn/C-ATO (70:30) (Fig 2C) and PtSn/C-ATO (90:10) (Fig 2D).





**Figure 2.** TEM micrographs of the of PtSn/C (50:50) (Fig 2A), PtSn/C-ATO (50:50) (Fig 2B), PtSn/C-ATO (70:30) (Fig 2C) and PtSn/C-ATO (90:10) (Fig 2D).





**Figure 3.** Cyclic voltammograms of PtSn/C (50:50), PtSn/C-ATO (90:10), PtSn/C-ATO (70:30) and PtSn/C-ATO (50:50) at 25°C (A) and 50°C (B) in 1 mol L<sup>-1</sup> ethanol solution in 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> with a sweep rate of 10 mV s<sup>-1</sup>.

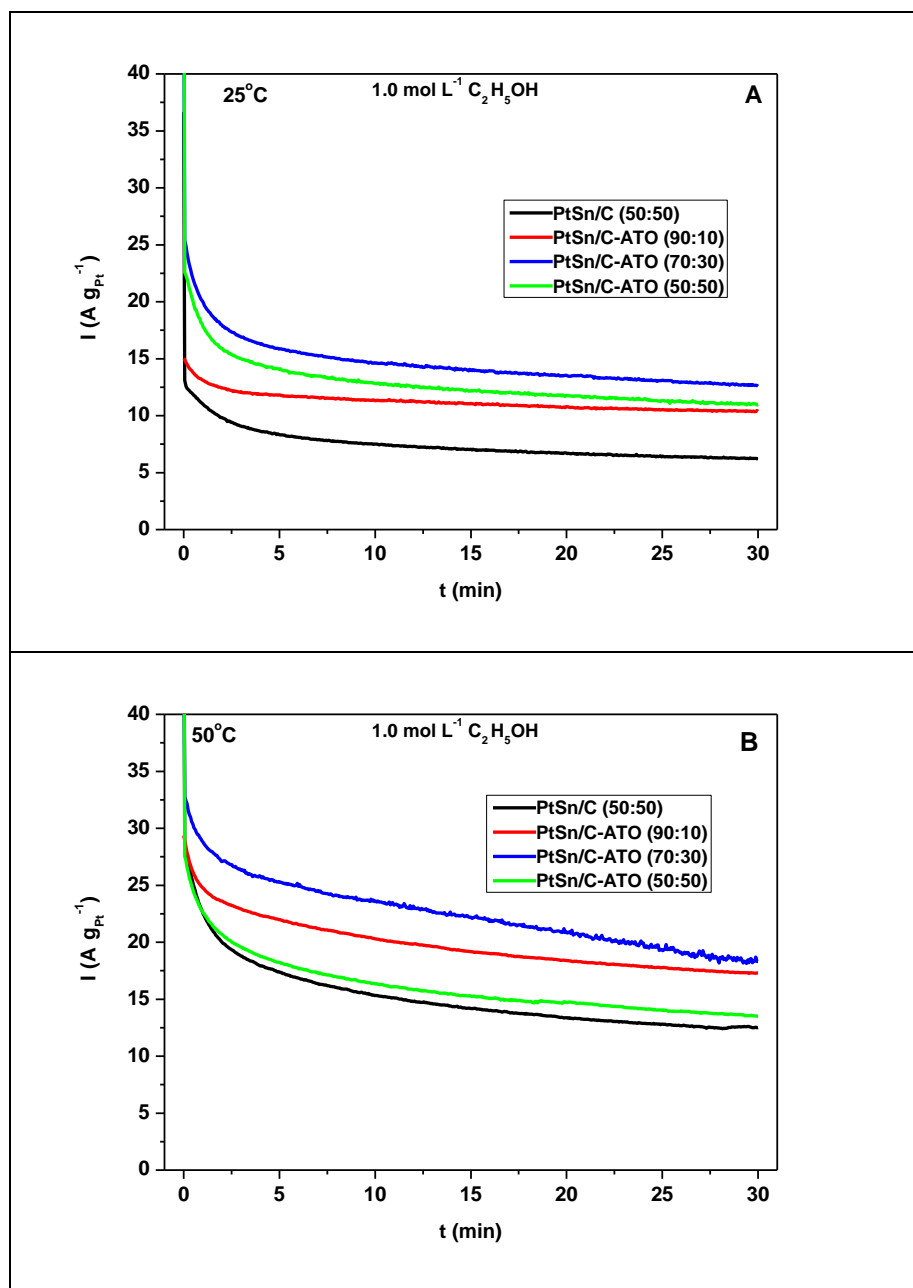
For all electrocatalysts it was observed a good distribution of the nanoparticles on the support; however some agglomerates were also observed. The mean particles sizes were in the range of 2 – 3 nm for all electrocatalysts.

Figure 3 shows the cyclic voltammograms (normalized by mass of Pt) of PtSn/C and PtSn/C-ATO electrocatalysts at 25°C (Fig. 3A) and 50°C (Fig. 3B) in presence of 1.0 mol L<sup>-1</sup> of ethanol and 0.5 mol L<sup>-1</sup> of H<sub>2</sub>SO<sub>4</sub>.

It was observed that the ethanol electro-oxidation started at approximately 0.25 V at 25°C and 50°C for all electrocatalysts; while below potentials of 0.2V it is largely blocked by poisoning CO and/or intermediates adsorbed. At 25°C PtSn/C-ATO (70:30) and (50:50) electrocatalysts showed the highest current values in all potential range, while PtSn/C-ATO (70:30) and (90:10) showed superior electrocatalytic activities at 50°C.

The chronoamperometry curves of the electrocatalysts at 0.5 V are shown in Fig. 4. At 25°C (Fig. 4A). It can be seen in all current-time curves an initial current drop in the first minutes followed by a slower decay. The final current values were the following: PtSn/C-ATO (70:30) > PtSn/C-ATO (50:50) ≈ PtSn/C-ATO (90:10) > PtSn/C (50:50). At 50°C (Fig. 4B) it was also observed in all current time curves an initial current drop in the first minutes, however, the final current values are greater than the ones observed at 25°C showing the following order of activity: PtSn/C-ATO (70:30) > PtSn/C-ATO (90:10) > PtSn/C-ATO (50:50) ≈ PtSn/C (50:50).

Figure 5 shows the performances of a single DEFC operating at 100°C with PtSn/C and PtSn/C-ATO as anode electrocatalysts.



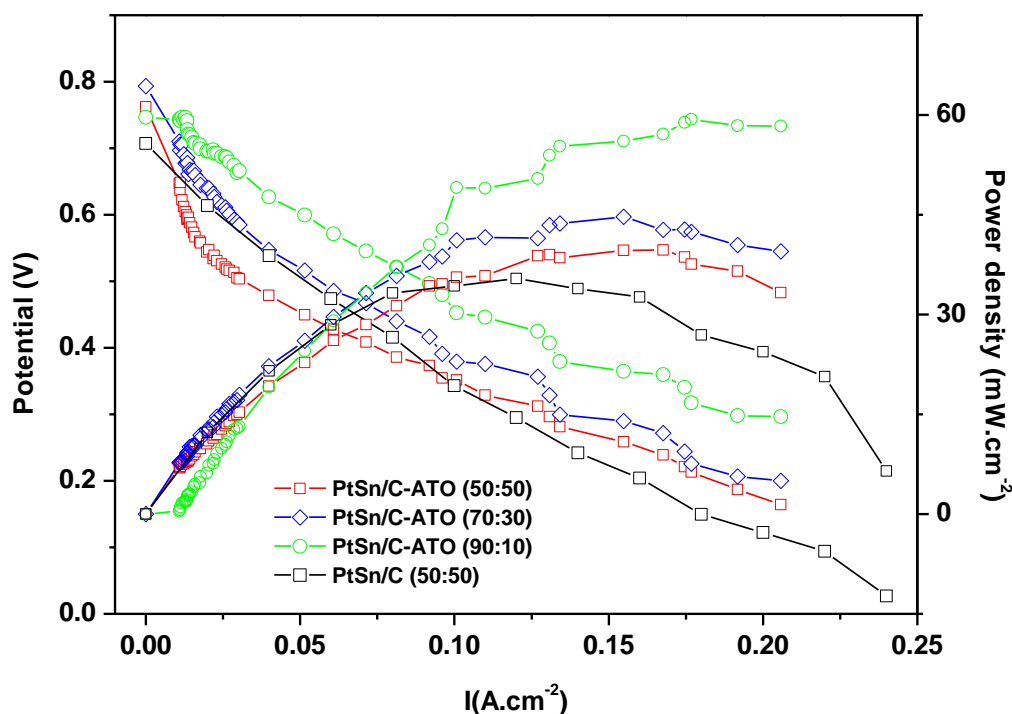
**Figure 4.** Current-time curves at 0.5 V in  $1 \text{ mol L}^{-1}$  methanol solution in  $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  for PtSn/C (50:50), PtSn/C-ATO (90:10), PtSn/C-ATO (70:30) and PtSn/C-ATO (50:50) at  $25^\circ\text{C}$  (A) and  $50^\circ\text{C}$  (B).

PtSn/C-ATO (90:10) electrocatalyst showed the higher value of maximum power density ( $60 \text{ mWcm}^{-2}$ ) in comparison with PtSn/C-ATO (70:30) ( $44 \text{ mWcm}^{-2}$ ), PtSn/C-ATO (50:50) ( $40 \text{ mWcm}^{-2}$ ) and PtSn/C ( $36 \text{ mWcm}^{-2}$ ). Using Pt/C-ATO in the same conditions [18] the maximum power density observed was  $38 \text{ mW cm}^{-2}$ , which shows that the addition of small quantities of Sn in the synthesis leads to an increase of activity for ethanol electro-oxidation.

The alcohol-reduction process used in this work to prepare PtSn/C electrocatalysts leads to the formation of Pt(fcc) and  $\text{SnO}_2$  (see XRD Fig.1). Thus, the difference of Pt/C-ATO and PtSn/C-ATO is

that: for Pt/C-ATO, Pt (fcc) nanoparticles were deposited on carbon and ATO supports [18], thus for PtSn/C-ATO, Pt(fcc) and SnO<sub>2</sub> phases could be deposited on carbon and ATO supports.

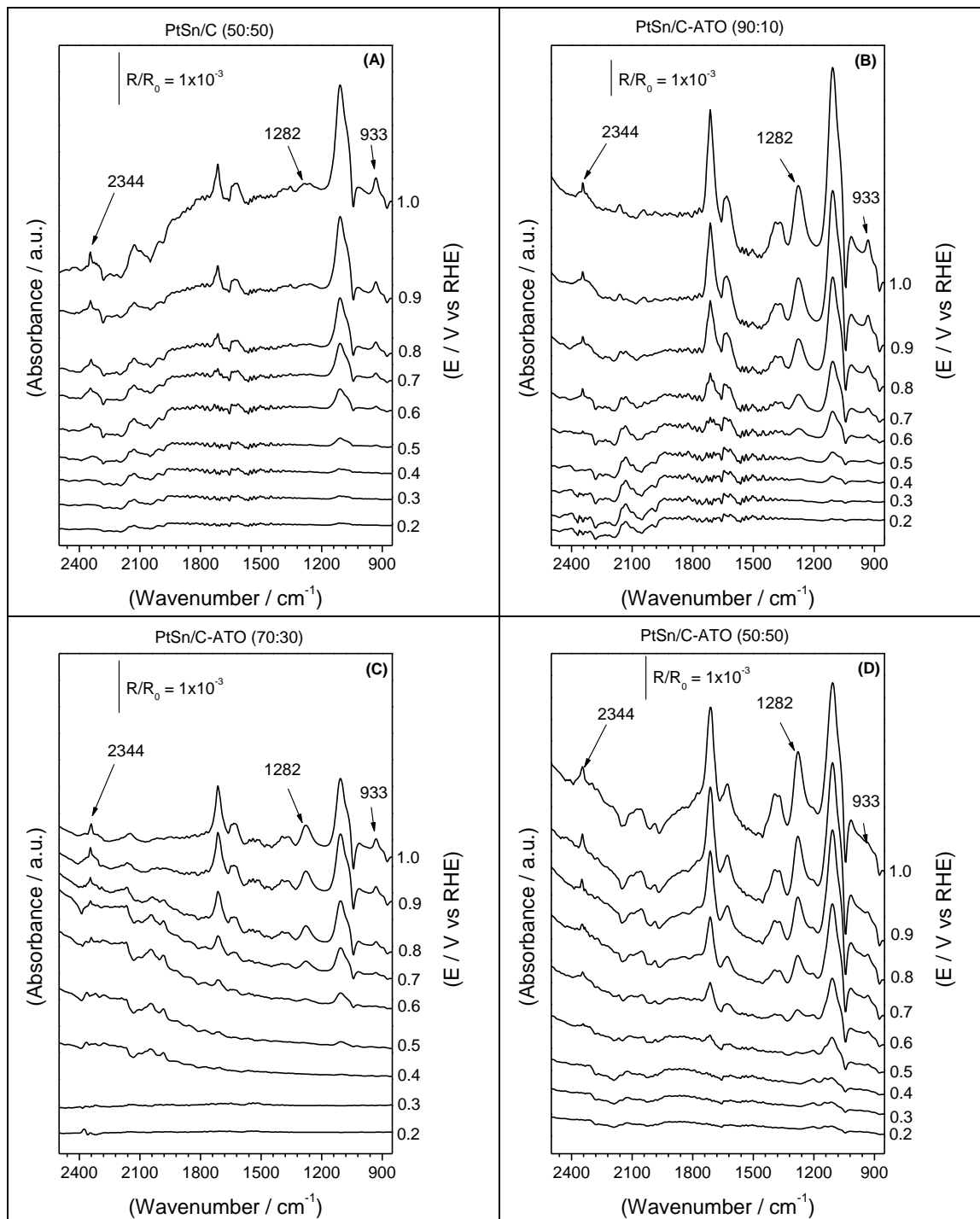
Figure 6 shows the FTIR spectra collected during ethanol electro-oxidation for PtSn/C (50:50), PtSn/C-ATO (90:10), PtSn/C-ATO (70:30) and PtSn/C-ATO (50:50), (Fig. 6 A-D), respectively, as a function of the potential in 0.1 M HClO<sub>4</sub>. The experiments were performed in the presence of solutions containing 1 mol L<sup>-1</sup> of ethanol.



**Figure 5.** I–V curves and power densities at 100 °C of a 5 cm<sup>2</sup> DEFC using PtSn/C (50:50), PtSn/C-ATO (90:10), (70:30) and (50:50) electrocatalysts anodes (1 mg<sub>Pt</sub> cm<sup>-2</sup> of catalyst loading) and Pt/C E-TEK electrocatalyst cathode (1 mg<sub>Pt</sub> cm<sup>-2</sup> catalyst loading, 20 wt.% Pt loading on carbon), Nafion® 117 membrane, ethanol (2.0 mol L<sup>-1</sup>) and oxygen pressure (2 bar).

The principal bands of the species from ethanol adsorption and oxidation observed in the FTIR spectra were observed at 2344, 1282 and 933 cm<sup>-1</sup>, which are characteristic of the presence of CO<sub>2</sub>, acetic acid and acetaldehyde [19]. In these spectra is possible to see others important bands as a 1715 cm<sup>-1</sup> corresponding to carbonyl group, 1635 cm<sup>-1</sup> referent to the water deformation and 1110 cm<sup>-1</sup> to the perchlorate group [20]. However to make a better comparison between data obtained for each electrode it were considered the bands referents to acetaldehyde (933 cm<sup>-1</sup>), acetic acid (1282 cm<sup>-1</sup>) and CO<sub>2</sub> (2343 cm<sup>-1</sup>), these bands were deconvoluted to Lorentzian line forms [9] and normalized using the band intensities at all potentials, where the bands were divided by the band intensity obtained at bigger intensity for each electrode [20]. The integrated band intensities in function of the potential for acetic acid, acetaldehyde and CO<sub>2</sub> for PtSn/C (50:50), PtSn/C-ATO (90:10), (70:30) and (50:50) are showed in the Fig. 7 A-D, respectively.

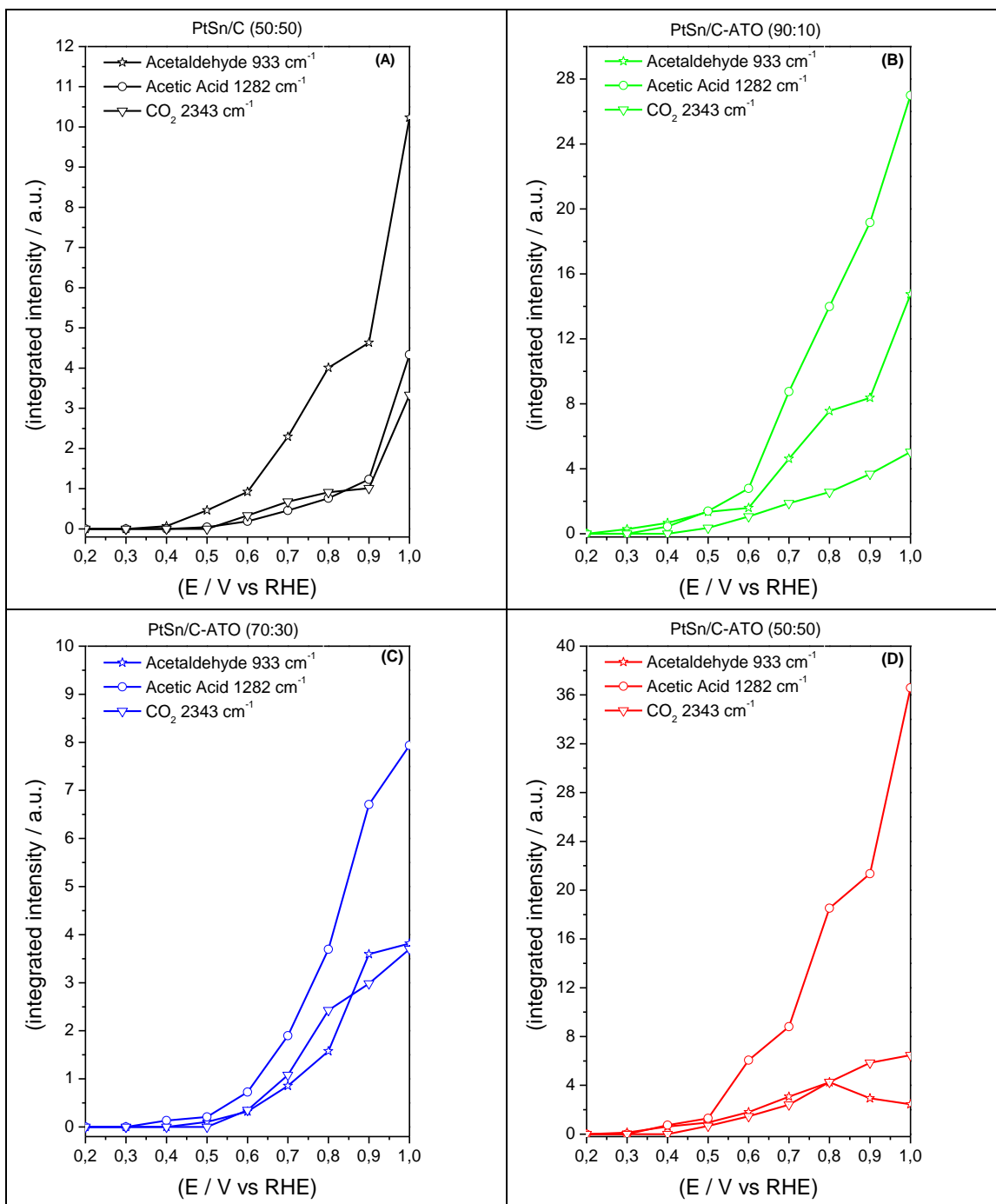




**Figure 6.** In situ FTIR spectra taken at several potentials (indicated) in 0.1 M  $\text{HClO}_4$  + 1.0 M EtOH for (A) PtSn/C (50:50), (B) PtSn/C-ATO (90:10), (C) PtSn/C-ATO (70:30) and (D) PtSn/C-ATO (50:50). The backgrounds were collected at 0.05 V (RHE scale) with a sweep rate of  $1 \text{ mV s}^{-1}$ .

For all PtSn/C-ATO electrocatalysts acetic acid is the main product in the potential range studied as indicated by the integrated band intensities, while that for PtSn/C electrocatalysts the acetaldehyde is the principal product.

These results indicates that the increase of the power density of DEFC using PtSn/C-ATO electrocatalyst is related to the formation of acetic acid (transference of 4 electrons per molecule ethanol) as a principal product while using PtSn/C electrocatalyst acetaldehyde (transference 2 electrons per molecule de ethanol) is the principal product formed.



**Figure 7.** Integrated CO<sub>2</sub>, acetic acid and acetaldehyde band intensity as a function of the electrode potential for: (A) PtSn/C (50:50), (B) PtSn/C-ATO (90:10), (C) PtSn/C-ATO (70:30) and (D) PtSn/C-ATO (50:50).

Thus, these results suggest that the presence of Pt(fcc) and SnO<sub>2</sub> phases supported on ATO could favor further electro-oxidation of acetaldehyde (produced on sites of Pt(fcc) and SnO<sub>2</sub> phases supported on carbon) to acetic acid and/or that ethanol could be directly oxidized to acetic acid on these sites.

#### 4. CONCLUSIONS

PtSn/C-ATO electrocatalysts prepared by an alcohol-reduction process comprising Pt(fcc) and SnO<sub>2</sub> phases dispersed on carbon and ATO supports. Electrochemical experiments and tests on single DEFC showed that PtSn/C-ATO electrocatalysts exhibited higher performance for ethanol electro-oxidation than PtSn/C electrocatalyst. FTIR studies identified that acetic acid is the principal product formed on PtSn/C-ATO electrocatalysts while acetaldehyde was formed on PtSn/C electrocatalyst. Thus, the addition of ATO on PtSn/C electrocatalysts leads to an increase of overall efficiency and power density of DEFC, however, modifications are still needed in the electrocatalysts in order to obtain the complete electro-oxidation of ethanol to CO<sub>2</sub>.

#### ACKNOWLEDGMENTS

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