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# Preparation of Pt/C-$In_2O_3.SnO_2$ Electrocatalysts by Borohydride Reduction Process for Ethanol Electro-Oxidation

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Pt/C-$In_2O_3.SnO_2$ electrocatalysts was prepared in the single step using $H_2PtCl_6.6H_2O$ as metal sources, sodium borohydride as reducing agent and a physical mixture of 85% Vulcan Carbon XC72 and 15% $In_2O_3.SnO_2$ (indium tin oxide – ITO) as support. The electrocatalysts were characterized by X-ray diffraction and transmission electron microscopy, cyclic voltammetry, chronoamperommetry, Attenuated Total Reflectance Fourier transform infrared (ATR-FTIR) spectroscopy and performance test on direct ethanol fuel cell. The diffractograms of the Pt/C showed four peaks associated the face-centered cubic (fcc) structure of platinum, while that Pt/C-$In_2O_3.SnO_2$ electrocatalysts showed peaks associated the face-centered cubic (fcc) structure of platinum and several others peaks associated with Indium-doped $SnO_2$ (ITO) used as supports. Transmission electron microscopy for Pt/C and Pt/C-$In_2O_3.SnO_2$ electrocatalysts showed that the metal particles were homogeneously distributed over the support with particles size of 3.0 nm. The electrochemical studies (cyclic voltammetry and chronoamperometry) showed that Pt/C-$In_2O_3.SnO_2$ had superior performance for ethanol electro-oxidation in comparison with Pt/C in all potential range of interest (0.05-0.9V). The experiments at 100°C on single direct ethanol fuel cells showed that the power density for the Pt/C-$In_2O_3.SnO_2$ was nearly 400% higher than the one obtained using Pt/C indicating an improved tolerance to intermediate adsorbed. The data from Fourier transform infrared spectroscopy showed that the addition of C-$In_2O_3.SnO_2$ to Pt favors a more complete oxidation of the ethanol molecule, where $In_2O_3.SnO_2$ provide an oxygen-containing species to oxidize acetaldehyde to acetic acid.

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**Keywords:** Pt/C-$In_2O_3.SnO_2$, borohydride reduction process, ethanol oxidation, ATR-FTIR *in-situ*, fuel cell

## 1. INTRODUCTION

Direct Ethanol Fuel Cell (DEFC) has been the focus of interest to many researchers for converting chemical energy into electrical energy, because the ethanol could be produced in large scale from renewable sources and it is less toxic than the methanol [1-5].

Platinum electrocatalysts are commonly used as anode or cathode in direct ethanol fuel cell, however the platinum alone is not a good electrocatalyst for the ethanol [6]. Platinum itself is rapidly poisoned on its surface by strongly adsorbed species coming from the dissociative adsorption of ethanol, consequently the efforts to mitigate the poisoning of Pt have been concentrated on the addition of co catalysts to platinum [7].

Recently, Pt electrocatalysts decorated with oxides such as $TiO_2$, $SnO_2$, $RuO_2$, $Sb_2O_5.SnO_2$, $In_2O_3$ and $CeO_2$ have showed an improvement on the catalytic activity and stability for the electro-oxidation of ethanol [6-10]. These oxides have showed corrosion resistance and smaller decrease in the electrochemical active surface area in comparison with the carbon support [6]. More recently, there has been considerable attention to Indium oxide ($In_2O_3$), where this material has been widely used to improve the catalytic performance for the steam reforming of methanol and dehydrogenation of ethanol [8, 11, 12].

Chue et al [10] showed that the Pd-$In_2O_3$/CNTs electrocatalyst it was more effective for ethanol oxidation in comparison with Pd/CNTs. Park et al [13] showed that indium tin oxide (ITO) supported Pt nanoparticles was more activity for methanol oxidation in relation Pt/C, while that Parrondo et al [6] showed Pt/C-$In_2O_3$ nanoparticles demonstrated a higher activity towards ethanol oxidation than Pt/C, the enhancement of activity could be attributed to the effects of $In_2O_3$ adjacent to Pt (bifunctional effect), however the mechanism of ethanol electro-oxidation was not studied for Pt/C-$In_2O_3$.

In this context, the aim of this work was to prepare Pt/C-$In_2O_3.SnO_2$ electrocatalysts by borohydride reduction process and to test these electrocatalysts for ethanol electro-oxidation in acidic medium by cyclic voltammetry, chronoamperometry and performance on direct ethanol fuel cell. The mechanism of ethanol oxidation on Pt/C-$In_2O_3.SnO_2$ electrocatalysts also was investigated by in situ FTIR spectroscopy to obtain information about intermediates and reaction products.

## 2. EXPERIMENTAL

Pt/C-$In_2O_3.SnO_2$ electrocatalysts (20 wt.% of metals loading) was prepared using $H_2PtCl_6{\cdot}6H_2O$ (Chloroplatinic acid-Aldrich) as metal sources, sodium borohydride (Aldrich) as reducing agent and a physical mixture of 85% Vulcan Carbon XC72-15% $In_2O_3.SnO_2$ as support. In the borohydride reduction process the metal sources were dissolved in a mixture of water/2-propanol (50/50, v/v) and the Vulcan XC72 + $In_2O_3.SnO_2$ support was dispersed in the solution. The resulting mixture was submitted to an ultrasonic bath for 10 min, where a solution of sodium borohydride was added under stirring in one portion at room temperature. After, the mixture was filtered and the solid was washed with water and dried at 70 °C for 2 h [3].

The XRD analyses were realized in the RigaKu Miniflex II diffractometrer using Cu Kα radiation source (*l* = 0.15406 nm), where the all diffractograms were recorded from 2θ = 20° to 90° with a step size of 0.05° and a scan time of 2s per step [3]. Transmission electron microscopy (TEM) was carried out using a JEOL JEM-2100 electron microscope operated at 200 kV. The morphology, distribution, and mean particle size were determined by counting more than 200 particles from different regions of each sample.

The cyclic voltammetry and chronoamperommetry measurements were carried out using a Microquimica potenciostat, where the working electrodes (geometric area of 0.3 $cm^2$ with a depth of 0.3 mm) was prepared using the thin porous coating technique [7], the reference electrode was a reversible hydrogen electrode (RHE) and the counter electrode was a platinized Pt plate in presence of 1.0 mol $L^{-1}$ of ethanol in 0.5 mol $L^{-1}$ $H_2SO_4$ solutions saturated with $N_2$.

Direct ethanol fuel cell test were performed using Pt/C-$In_2O_3.SnO_2$ electrocatalysts as anode and Pt/C E-tek 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 $cm^{-2}$. The electrodes prepared contained 1 mg Pt $cm^{-2}$ in the anode and cathode. The 2 M ethanol aqueous solution was delivered at approximately 2 mL $min^{-1}$, and the oxygen flow was set to 500 mL $min^{-1}$ under 2 bar of pressure. The polarization curves were obtained using a electronic load [7].

The spectroelectrochemical ATR-FTIR in situ measurements were performed with a Varian® 660 IR spectrometer equipped with a MCT detector cooled with liquid $N_2$, ATR accessory (MIRacle with a Diamond/ ZnSe Crystal Plate Pike®) and a special cell [14]. 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 in accordance with Silva et al [14]. These experiments were performed at room temperature in presence of 0.1 mol $L^{-1}$ $HClO_4$ in 1.0 mol $L^{-1}$ ethanol. The absorbance spectra were collected as the ratio $R:R_0$, where R represents a spectrum at a given potential and $R_0$ is the spectrum collected at 0.05 V. The spectra were computed from 128 interferograms averaged from 2500 $cm^{-1}$ to 850 $cm^{-1}$ with the spectral resolution set to 4 $cm^{-1}$. Initially, a reference spectrum ($R_0$) 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 [14].

## 3. RESULTS AND DISCUSSION

Figure 1 shows X-ray diffractograms (XRD) for Pt/C and Pt/C-$In_2O_3.SnO_2$ electrocatalysts prepared by borohydride reduction process.

The diffractograms of the Pt/C showed a broad peak at about 25° that was associated with the Vulcan XC72 support material and four peaks in 2θ= 40°, 47°, 67° and 82°, which are associated with the (111), (200), (220) and (311) planes characteristic of Pt face-centered cubic (fcc) structure of platinum. For Pt/C-$In_2O_3.SnO_2$ electrocatalysts also was observed the planes characteristic of Pt face-centered cubic (fcc) structure and peaks at about 2θ= 31°, 36°, 51°, 60° correspond to the (222), (400),

(440) and (622) planes characteristic of $In_2O_3$ cubic structure. This result is in accordance with the work of Parrondo et al [6].

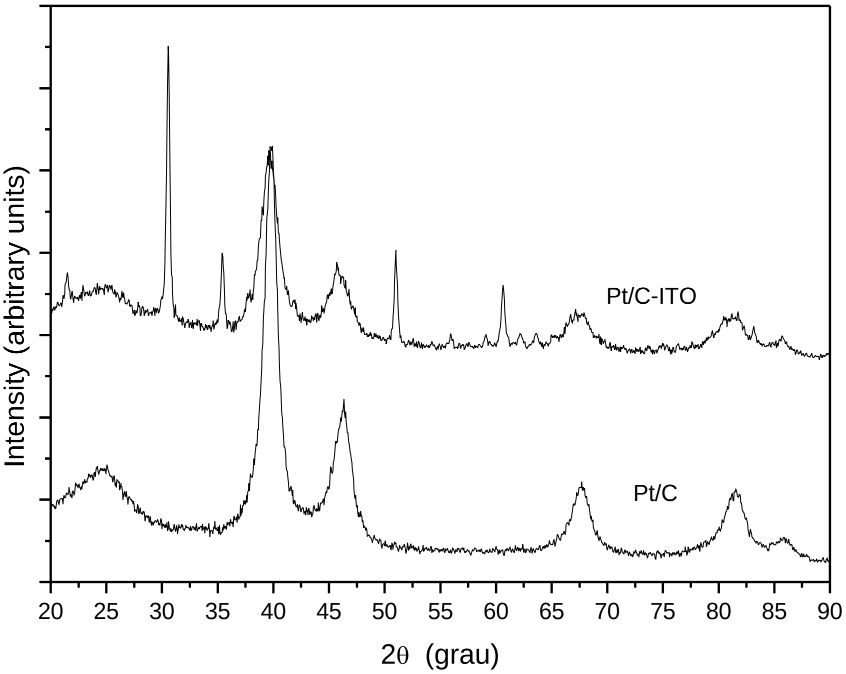

**Figure 1.** X-ray diffractograms of the Pt/C and Pt/C-$In_2O_3.SnO_2$ electrocatalysts.

Figure 2 presents TEM micrographs and a histogram of the Pt/C (2a) and Pt/C-$In_2O_3.SnO_2$ electrocatalyst (2b). The microscopic measurements were carried out to provide information on the morphology, particle size and particle size distribution.

In all electrocatalysts it was observed a good dispersion of the particles in the support, however some agglomerates also were observed. Pt/C electrocatalysts and Pt/C-$In_2O_3.SnO_2$ electrocatalyst showed particles with average sizes of 3 nm. TEM results are in agreement with Oliveira Neto et al [9], while Parrondo et al [6] has observed an average particle size of 5 nm for Pt/C and Pt/C-$In_2O_3$. Parrondo et al [6] also observed for Pt/C-$In_2O_3$ that the Pt electrocatalysts and the agglomerated $In_2O_3$ particles were distributed uniformly on the carbon support, while that for only $In_2O_3$ was observed an agglomerated.

Figure 3 shows the cyclic voltammetry in acid media for Pt/C and Pt/C-$In_2O_3.SnO_2$ electrocatalyst. The cyclic voltammetry responses were normalized per gram of platinum, considering that ethanol adsorption and dehydrogenation occur only on platinum sites at ambient temperature [3].

Pt/C-$In_2O_3.SnO_2$ electrocatalyst showed an increase in the current values in the double layer (0.4–0.8 V) in comparison with Pt/C, this effect may be attributed to contribution of Pt and ITO oxide species [15]. The anodic peaks appeared around 0.6V indicates the oxidation of In-O species [6]. Pt/C-$In_2O_3.SnO_2$ electrocatalyst do not show a well-defined hydrogen adsorption–desorption region (0.05–

0.4 V) in comparison with Pt/C electrocatalysts, this effect also could be attributed a presence or the oxidation of In-O species.

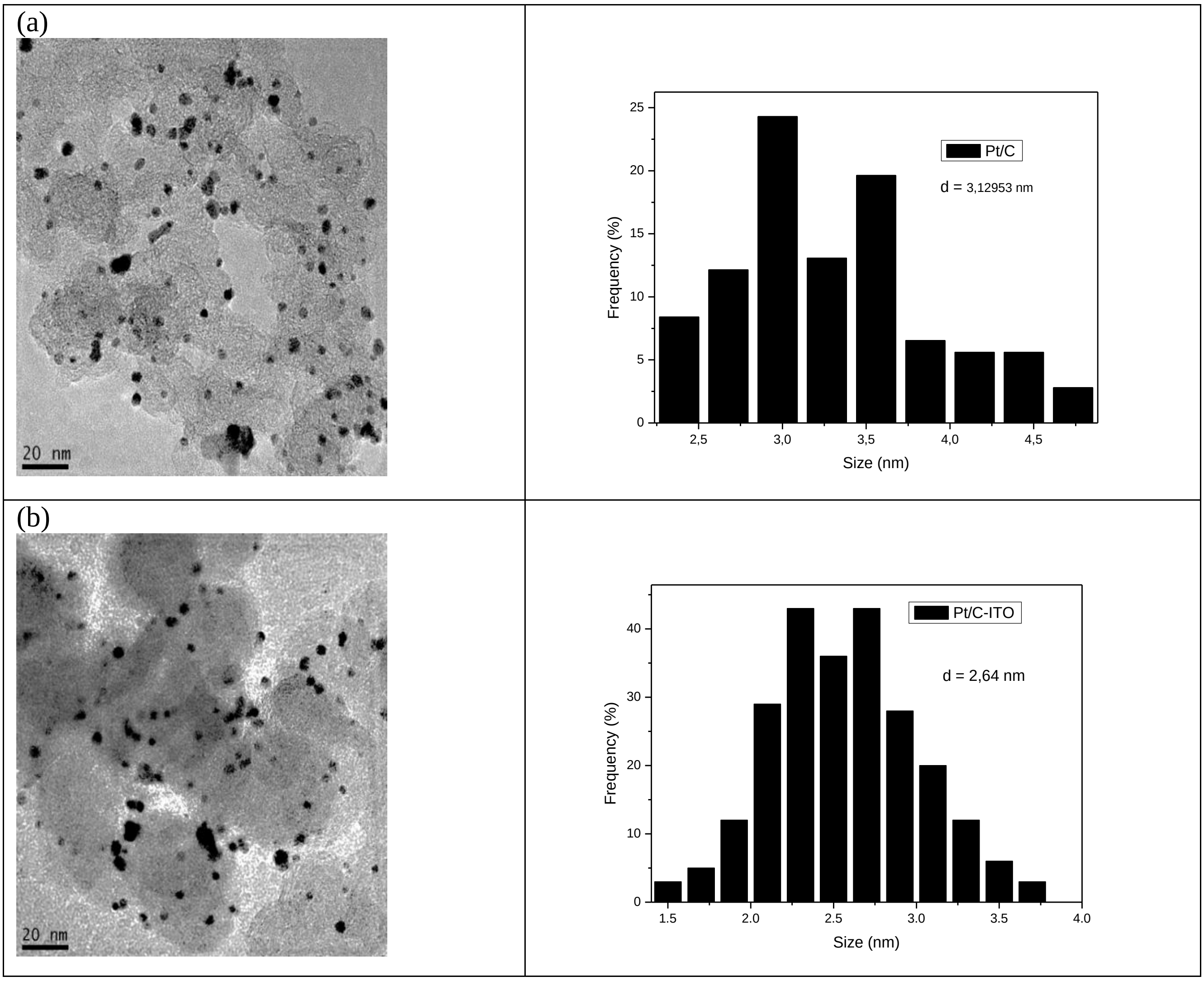

**Figure 2.** TEM micrograph of the Pt/C (2a) and Pt/C-$In_2O_3.SnO_2$ electrocatalyst (2b).

Figure 4 shows the cyclic voltammetry for ethanol oxidation using Pt/C and Pt/C-$In_2O_3.SnO_2$ electrocatalyst obtained in a half cell at a scan rate of 10 mV $s^{-1}$ between 0.05 and 0.8 V in 1.0 mol $L^{-1}$ of ethanol and 0.5 mol $L^{-1}$ $H_2SO_4$.

Pt/C-$In_2O_3.SnO_2$ electrocatalyst showed the highest current values in all potential range in comparison with Pt/C. The electro-oxidation of ethanol started at approximately 0.23 V for Pt/C-$In_2O_3.SnO_2$ electrocatalysts, while that Pt/C the electro-oxidation of ethanol started at approximately 0.4 V. Thus results confirmed that the Pt is not an efficient electrocatalyst for the direct ethanol fuel cells [15].

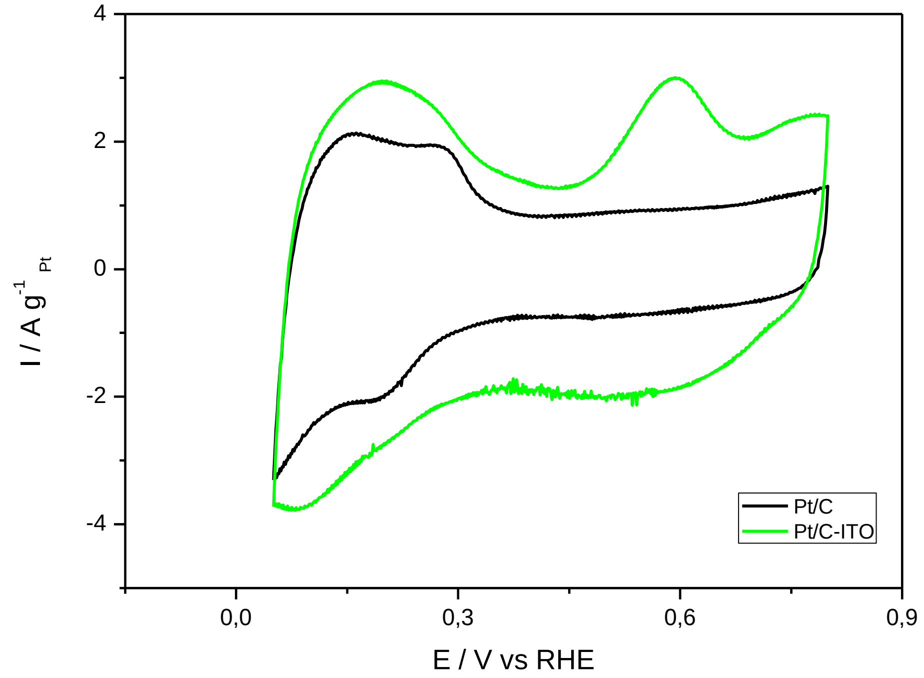

**Figure 3.** Cyclic voltammograms of Pt/C and Pt/C-$In_2O_3.SnO_2$ electrocatalyst in 0.5 mol $L^{-1}$ $H_2SO_4$, sweep rate of 10 mV $s^{-1}$.

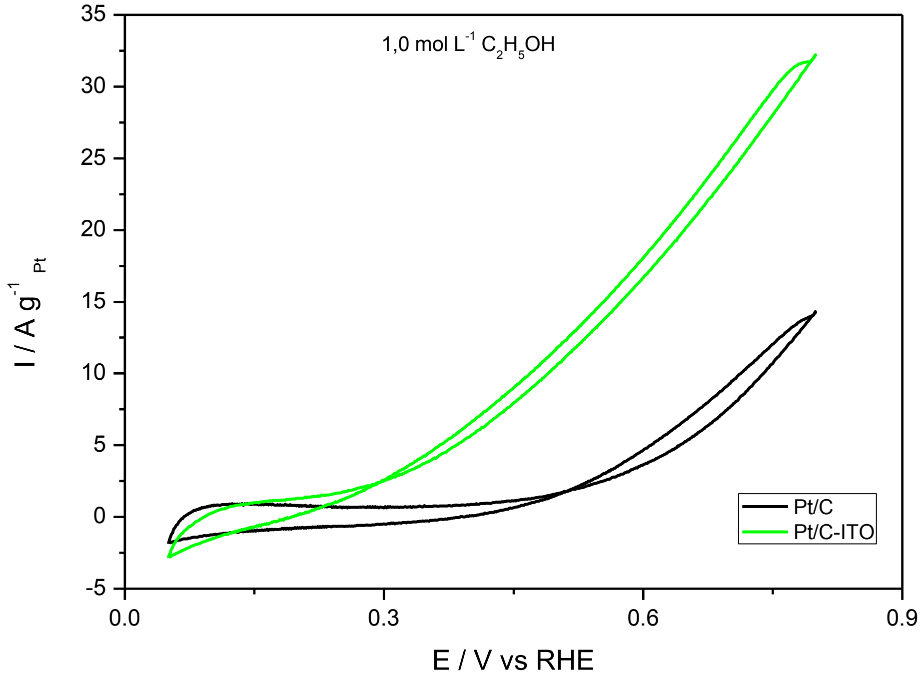

**Figure 4.** Cyclic voltammograms of Pt/C and Pt/C-$In_2O_3.SnO_2$ electrocatalyst in 1 mol $L^{-1}$ methanol solution in 0.5 mol $L^{-1}$ $H_2SO_4$ with a sweep rate of 10 mV s–$^1$.

The better activity of Pt/C-$In_2O_3.SnO_2$ electrocatalyst could be attributed to the bifunctional mechanism, where ITO enhances the formation of chemisorbed oxygen species and promotes the oxidation of intermediate adsorbed on the surface of platinum [9]. In accordance Parrondo et al [6] showed that the catalytic activity of 60%Pt/C-40%$In_2O_3$ was approximately 2.5 times higher than that of Pt/C for ethanol oxidation and the potentials of Pt/C-$In_2O_3$ electrocatalysts were slightly lower when compared to that of Pt/C catalyst.

Figure 5 shows the chronoamperometric curves for ethanol oxidation using Pt/C and Pt/C-$In_2O_3.SnO_2$ electrocatalyst in the potential of 0.5 V by 30 minutes.

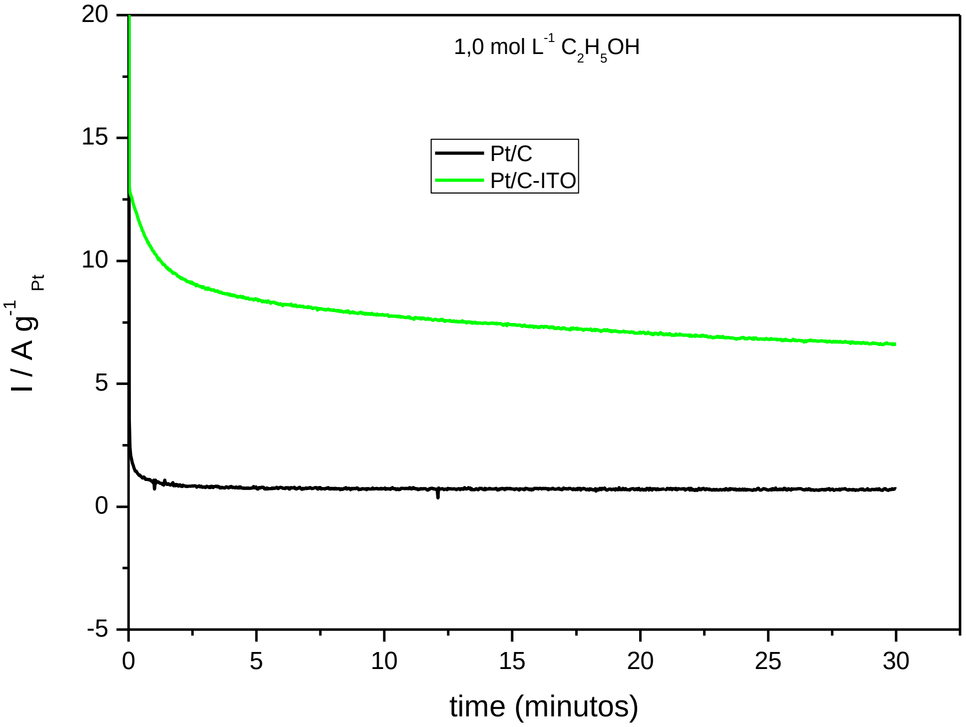

**Figure 5.** Current-time curves at 0.5 V in 1 mol $L^{-1}$ ethanol solution in 0.5 mol $L^{-1}$ $H_2SO_4$ for Pt/C and Pt/C-$In_2O_3.SnO_2$ electrocatalys.

Chronoamperometric curves for ethanol oxidation on Pt/C-$In_2O_3.SnO_2$ electrocatalyst showed a decay of current densities faster in the first 2 minutes followed by a slower decay. The current density of ethanol oxidation at the Pt/C-$In_2O_3.SnO_2$ electrocatalys was higher than that at the Pt/C in accordance with cyclic voltammograms results.

The results also reveal that the performance of the Pt/C-$In_2O_3.SnO_2$ electrocatalys for ethanol oxidation is remarkably improved by 800% as compared to that on Pt/C. The effect may be due to the synergetic interaction between Pt and $In_2O_3$ and the surface effect of the nanoparticles $In_2O_3$ [10]. The $In_2O_3$ oxides also showed to be active sites for the formation of oxygen-containing species, which will help to oxidize the adsorbed intermediate species according to the bifunctional mechanism [10].

Figure 6 shows the performances of a single cell with Pt/C and Pt/C-$In_2O_3.SnO_2$ electrocatalyst as anode.

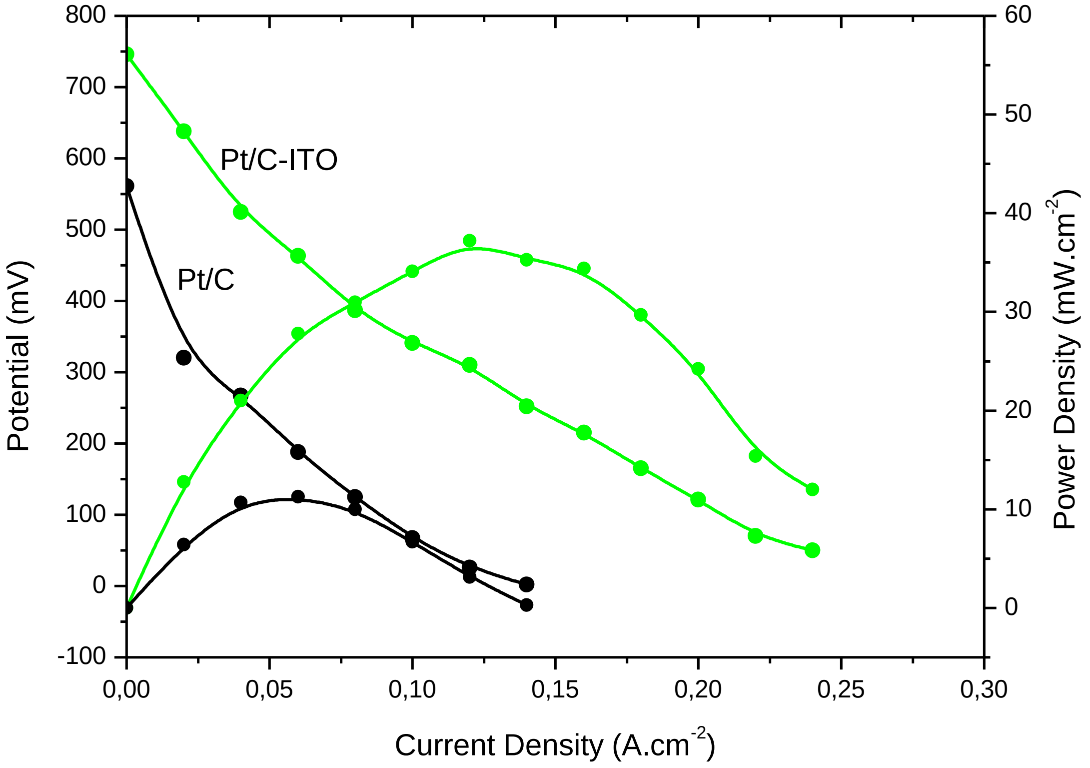

**Figure 6.** I–V curves and the power density at 100 °C of a 5 $cm^2$ DEFC using Pt/C and Pt/C-$In_2O_3.SnO_2$ electrocatalyst anodes (1 mgPt $cm^{-2}$ catalyst loading) and Pt/C ETEK electrocatalyst cathode (1 mgPt $cm^{-2}$ catalyst loading, 20 wt.% Pt loading on carbon), Nafion® 117 membrane, ethanol (2.0 mol $L^{-1}$), and oxygen pressure (2 bars).

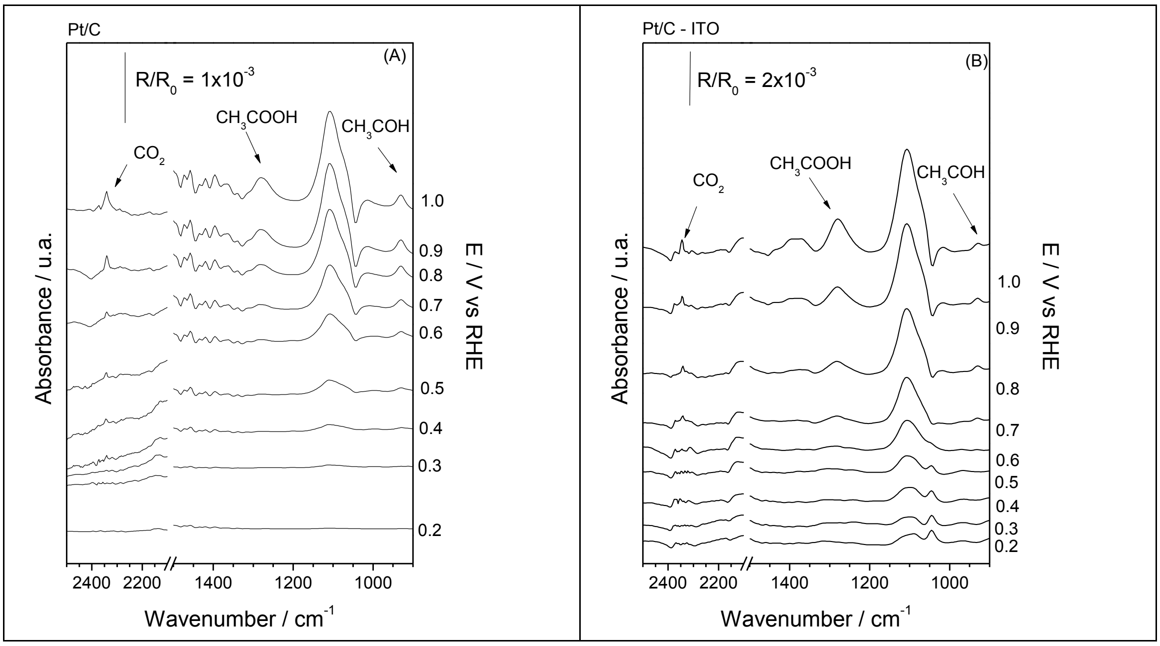

**Figure 7.** In situ FTIR spectra taken at several potentials (indicated) in 0.1 M $HClO_4$ + 1.0 M EtOH for (A) Pt/C and (B) Pt/C-$In_2O_3.SnO_2$. The backgrounds were collected at 0.05 V (RHE scale) with a sweep rate of 1 mV $s^{-1}$.

The open circuit voltage of the fuel cell using Pt/C-$In_2O_3.SnO_2$ electrocatalyst was 0.75 V, while the corresponding value for Pt/C was 0.56 V. The maximum power density of Pt/C-$In_2O_3.SnO_2$ electrocatalyst (37 mWcm$^{-2}$) was higher that than Pt/C (11 mWcm$^{-2}$). The use of Pt/C-$In_2O_3.SnO_2$ electrocatalyst increased the cell performance in agreement to the observed by cyclic voltammetry and chronoamperometry electrochemical techniques. In accordance Neto et al [9] showed that Pt/ATO-C electrocatalyst prepared by alcohol reduction process was more active for ethanol oxidation than Pt/C electrocatalysts and that the presence of Pt nanoparticles, oxides and carbon supports in close proximity seems to be essential for a good catalytic activity.

Figure 7 shows the FTIR spectra collected during ethanol electro-oxidation for Pt/C (7 a) and Pt/C-$In_2O_3.SnO_2$ (7b) electrocatalyst as a function of the potential in 0.1 M $HClO_4$. The principal bands observed in the FTIR were at 2344, 1282 and 933 cm$^{-3}$, which are characteristic of the presence of $CO_2$, acetic acid and acetaldehyde. Figure 8 shows the integrated band intensities in function of the potential for acetic acid, acetaldehyde and $CO_2$ for (A) Pt/C and (B) Pt/C-$In_2O_3.SnO_2$.

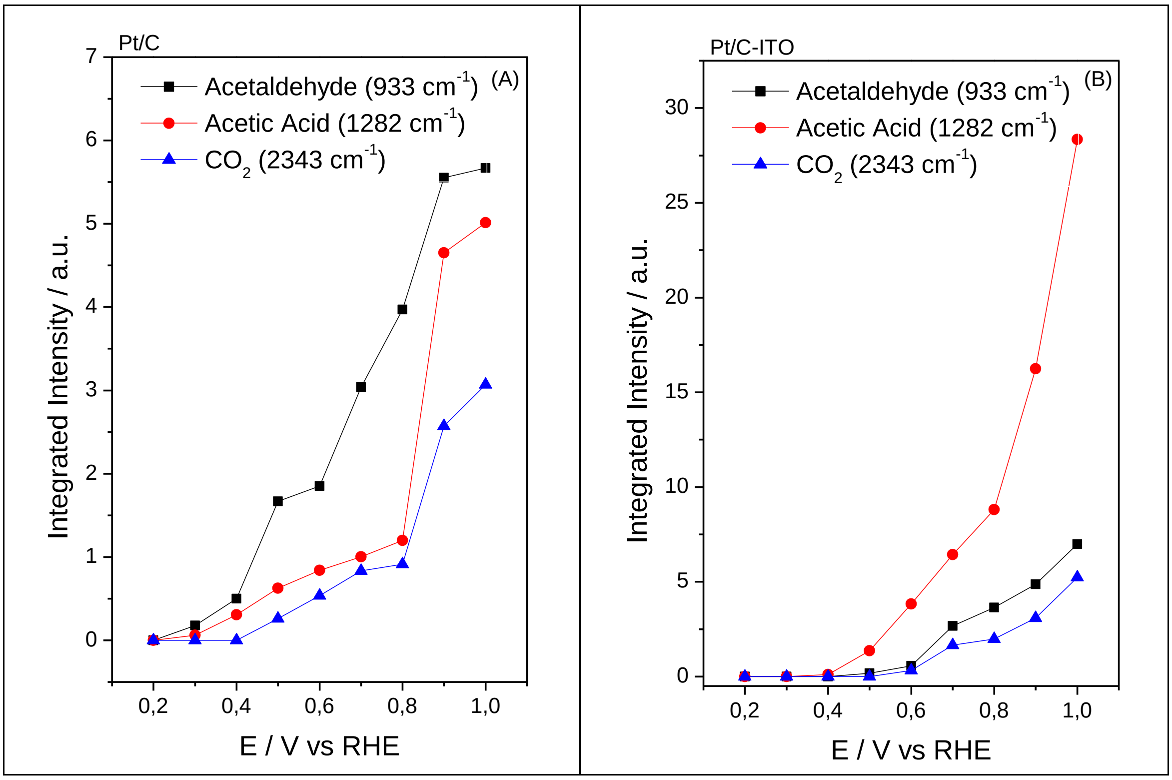

**Figure 8.** Integrated $CO_2$, acetic acid and acetaldehyde band intensity as a function of the electrode potential for: (A) Pt/C and (B) Pt/C-$In_2O_3.SnO_2$.

For Pt/C-$In_2O_3.SnO_2$ electrocatalysts acetic acid was the main product in the potential range studied as indicated by the integrated band intensities, while that for Pt/C electrocatalysts the acetaldehyde was the principal product. These result indicating that the addition of ITO to Pt seems to favor a transference of more electrons during ethanol oxidation process, where ITO provide oxygen-containing species to oxidize acetaldehyde to acetic acid or oxidize ethanol directly to acetic acid. Neto et al [8] showed that addition of oxide cerium to PtSn leads to a transference of more electrons during the ethanol oxidation process.

## 4. CONCLUSIONS

The borohydride reduction showed to be an effective method for producing active Pt/C-$In_2O_3.SnO_2$ electrocatalysts for ethanol oxidation in acidic medium. Pt/C-$In_2O_3.SnO_2$ electrocatalysts showed peaks associated the face-centered cubic (fcc) structure of platinum and several others peaks associated with Indium-doped $SnO_2$ (ITO) used as supports. Transmission electron microscopy for Pt/C-$In_2O_3.SnO_2$ electrocatalysts showed that the metal particles were homogeneously distributed over the support with particles size of 3.0 nm.

Pt/C-$In_2O_3.SnO_2$ had superior performance for ethanol electro-oxidation in comparison with Pt/C in all potential range of interest (0.05-0.9V). The experiments at $100^oC$ on single direct ethanol fuel cells showed that the power density for the Pt/C-$In_2O_3.SnO_2$ was nearly 400% higher than the one obtained using Pt/C indicating an improved tolerance to intermediate adsorbed. The data from Fourier transform infrared spectroscopy showed that the addition of C-$In_2O_3.SnO_2$ to Pt favors a more complete oxidation of the ethanol molecule or oxidize ethanol directly to acetic acid.

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