

Preparation of PdPtSn/C-Sb₂O₅.SnO₂ electrocatalysts by Borohydride Reduction for Ethanol Electro-Oxidation in Alkaline Medium

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PdPt/C-Sb₂O₅.SnO₂ (80:20), PdPtSn/C-Sb₂O₅.SnO₂ (80:10:10) and PdPtSn/C-Sb₂O₅.SnO₂ (90:05:05) electrocatalysts were prepared in a single step using H₂PtCl₆.6H₂O, Pd(NO₃)₂.2H₂O and SnCl₂.2H₂O as metal sources, sodium borohydride as reducing agent and a physical mixture of 85% Vulcan Carbon XC72 and 15% Sb₂O₅.SnO₂ (antimony tin oxide – ATO) as support. The obtained electrocatalysts were characterized by X-ray diffraction (XRD) and cyclic voltammetry (CV). The activity for the ethanol electro-oxidation in alkaline medium was investigated at room temperature by cyclic voltammetry and chronoamperometry. The electrochemical studies showed that PdPtSn/C-Sb₂O₅.SnO₂ (80:10:10) electrocatalyst had superior performance for ethanol electro-oxidation at room temperature compared to the other electrocatalysts prepared. Pt/C-ATO, Pd/C-ATO, PdPt/C-ATO and PdPtSn/C-ATO electrocatalysts were also tested for ethanol electro-oxidation in acid medium and the final current values obtained after holding the cell potential at -0.4 V for 30 min were compared to the ones obtained in alkaline medium. The results confirmed that Pd-based electrocatalysts are emerging as an alternative to Pt-based catalysts for ethanol electro-oxidation in alkaline DEFCs, while that Pt-based electrocatalysts are effective for ethanol electro-oxidation in acidic DEFCs.

Keywords: Borohydride reduction process, PdPt/C, PdPtSn/C, ethanol electro-oxidation, alkaline medium

1. INTRODUCTION

The development of alkaline anion-exchange membranes (AEMs) evokes increasing interest on electrocatalysis in alkaline medium and the use of Pd/C has been an alternative to Pt/C electrocatalysts, because it is in the same group of Pt possessing similar electronic structure. Also, it is more abundant

in nature than Pt and considerably less expensive, consequently the cost final of electrocatalyst for alcohol oxidation could be reduced [1-2].

Ethanol has been considered as an interesting fuel for Direct Alcohol Fuel Cells (DAFC), because it could be produced in large scale from renewable sources and it is less toxic than methanol. [3-7].

PtSn/C electrocatalysts have been described to be more active than Pt/C and PtRu/C electrocatalysts for ethanol electro-oxidation in acid medium [8-9], while Pd/C electrocatalyst has been considered promising for the ethanol oxidation in alkaline medium, because the electrocatalytic activity is higher than that of Pt/C, the onset potential for ethanol oxidation on Pd shifted to lower potentials compared to that of Pt in alkaline medium and the Pd/C electrocatalysts shown high stability for alcohol electro-oxidation in alkaline medium [10]. The activity and stability order of alcohol oxidation on Pd/C is ethanol > EG > methanol [2], however, the activity of Pd/C for ethanol oxidation in alkaline medium needs to be improved.

Shen et al. [11-12] showed that PdCeO₂, PdNiO or PdCo₃O₄ were more active and stable compared to platinum for ethanol oxidation in alkaline medium. Pd₂Ni₃/C electrocatalyst also exhibited higher activity and stability for the ethanol oxidation reaction in alkaline medium than does Pd/C catalyst [1].

Demarconnay et al. [13] showed that PtBi/C electrocatalysts promoted the catalytic activity towards ethylene glycol electro-oxidation in alkaline medium when compared to Pt/C. Tusi et al [14] showed that PtBi/C electrocatalysts had a significant increase of performance for ethanol oxidation in alkaline medium compared to Pt/C, while Bi/C electrocatalyst showed no activity.

An efficient PdPt/C and PtPdBi/C electrocatalysts for the oxidation of ethylene glycol in alkaline solution also was prepared by Demarconnay et al [13], however the best electrical performances under the same experimental conditions are obtained with the PtPdBi/C anode. These authors have also studied the effect of the Pd:Pt ratio and of the overall metal loading on the electrode, discovering that the highest activity is attained with a 20% metal loading and a 1:1 Pd:Pt atomic ratio.

Jiang et al. [15] showed that the ethanol oxidation currents of Pt/C and PtSn/C electrocatalysts in alkaline medium were higher than those obtained in acid medium, while the onset potentials in alkaline medium were less positive than those obtained in acid medium.

Neto et al [6] showed that Pt nanoparticles supported on a physical mixture of carbon and Sb₂O₅.SnO₂ (antimony tin oxide-ATO) were more active for ethanol oxidation in acidic medium compared to Pt nanoparticles supported only on ATO or on carbon, while Lee et al [7] showed that the activities of Pt/ATO for methanol and ethanol electro-oxidation were greater than those of Pt/C electrocatalyst. The enhancement of activity was attributed to better dispersion of Pt particles on the ATO support, as well as to the effects of SnO₂ adjacent to Pt (bifunctional effect and/or the electronic effect)

In this context, the aim of this work was to prepare PdPtSn/C-Sb₂O₅.SnO₂ electrocatalysts with different Pd:Pt:Sn atomic ratios by borohydride reduction and to test these electrocatalysts for ethanol electro-oxidation in alkaline medium. The results obtained in alkaline medium also were compared to the ones obtained in acid medium.

2. EXPERIMENTAL

The atomic composition of the PdPt/C electrocatalysts prepared by borohydride reduction process was chosen to be close to (80:20), the most active composition for the ethanol electro-oxidation [16].

PdPt/C-Sb₂O₅.SnO₂ (80:20) and PdPtSn/C- Sb₂O₅.SnO₂ (20 wt.% of metals loading; Pd:Pt:Sn atomic ratios of 90:05:05 and 80:10:10) electrocatalysts were prepared using Pd(NO₃)₂.2H₂O (Palladium nitrate- Aldrich), H₂PtCl₆.6H₂O (Chloroplatinic acid-Aldrich) and SnCl₂.2H₂O (Tin chloride-Aldrich) as metal sources, sodium borohydride (Aldrich) as reducing agent and a physical mixture of 85% Vulcan Carbon XC72-15% Sb₂O₅.SnO₂ (ATO) as support. In this process the metal sources were dissolved in a mixture of water/2-propanol (50/50, v/v) and the Vulcan XC72+Sb₂O₅.SnO₂ support was dispersed in the solution. The resulting mixture was submitted to an ultrasonic bath for 10 min. After this, a solution of sodium borohydride was added under stirring in one portion at room temperature. Finally, the mixture was filtered and the solid was washed with water and dried at 70 °C for 2 h [17].

X-ray diffraction (XRD) analyses were performed using a Rigaku diffractometer model Miniflex II using Cu K α radiation source ($\lambda = 0.15406$ nm). The diffractograms were recorded from $2\theta = 20^\circ$ to 90° with a step size of 0.05° and a scan time of 2 s per step.

Electrochemical studies of electrocatalysts were carried out using the thin porous coating technique [14]. An amount of 20 mg of the electrocatalyst was added to a solution of 50 mL of water containing 3 drops of a 6% solution polytetrafluoroethylene (PTFE) suspension. The resulting mixture was treated in an ultrasound bath for 10 min, filtered and transferred to the cavity (0.30 mm deep and 0.47 cm² area) of the working electrode. In cyclic voltammetry and chronoamperometry experiments the current values (I) were expressed in amperes and were normalized per gram of platinum ($A\ g\ Pt^{-1}$). The quantity of platinum was calculated considering the mass of the electrocatalyst present in the working electrode multiplied by its percentage of platinum. The reference electrode was an Ag/AgCl electrode and the counter electrode was a Pt plate.

Cyclic voltammetry experiments were performed in 1.0 mol L⁻¹ KOH solution saturated with N₂ using a Microquímica (model MQPG01, Brazil) potentiostat/galvanostat in presence and absence of 1.0 mol L⁻¹ of ethanol, while that the chronoamperometry curves of the PdPt/C-Sb₂O₅.SnO₂ (80:20), PdPtSn/C-Sb₂O₅.SnO₂ (80:10:10) and PdPtSn/C-Sb₂O₅.SnO₂ (90:05:05) electrocatalysts were performed holding the cell potential at -0.4 V vs Ag/AgCl electrode (0.5 V vs RHE) in 1.0 mol L⁻¹ KOH and 1.0 mol L⁻¹ C₂H₅OH solutions at room temperature.

3. RESULTS AND DISCUSSION

The mean crystallite sizes determined using Scherrer equation [5] for all electrocatalysts prepared were in the range of 2–3 nm, except for Pt/C-ATO electrocatalyst that was 3.5 nm. The X-ray diffractograms of the Pt/C-ATO, Pd/C-ATO, PdPt/C-ATO (80:20), PdPtSn/C-ATO (80:10:10) and PdPtSn/C-ATO (90:05:05) are shown in Fig. 1.

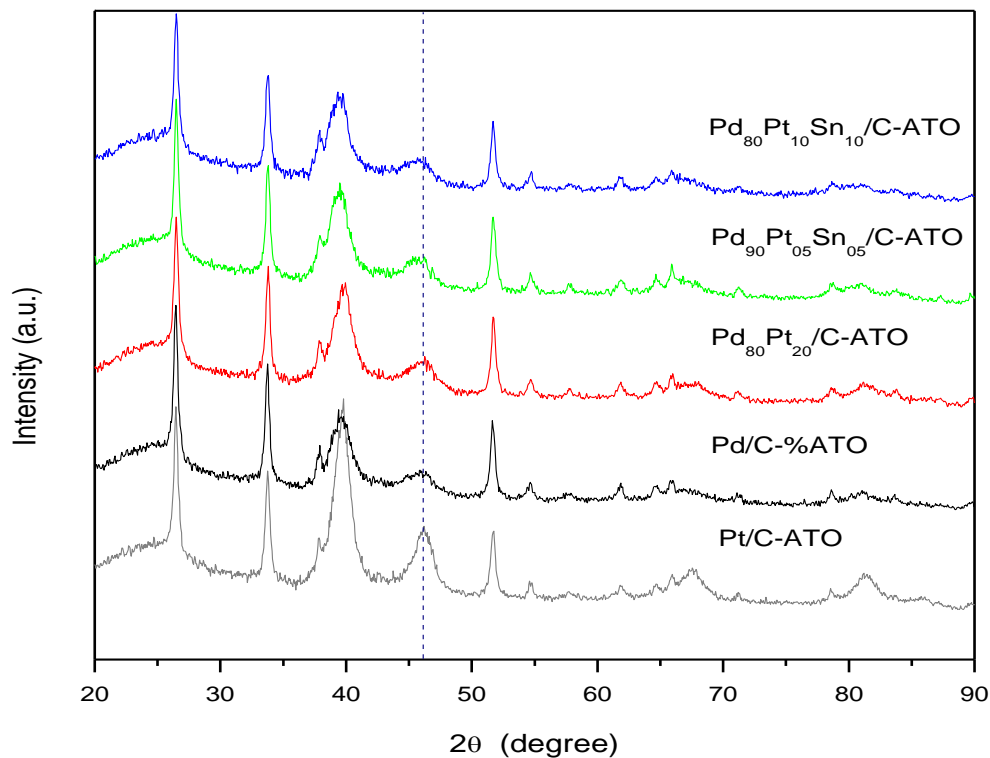


Figure 1. X-ray diffractograms of the Pt/C-ATO, Pd/C-ATO, PdPt/C-ATO (80:20), PdPtSn/C-ATO (80:10:10) and PdPtSn/C-ATO (90:05:05).

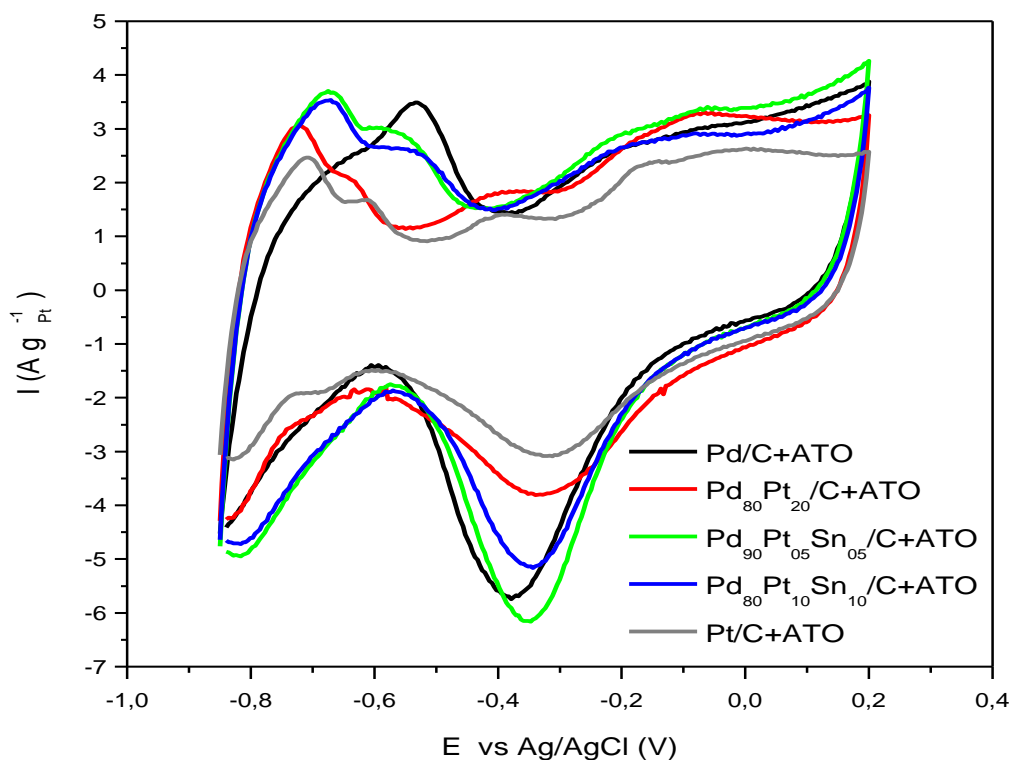


Figure 2. Cyclic voltammograms of Pt/C-ATO, Pd/C-ATO, PdPt/C-ATO (80:20), PdPtSn/C-ATO (80:10:10) and PdPtSn/C-ATO (90:05:05) in 1.0 mol L⁻¹ KOH with a sweep rate of 10 mV s⁻¹.

In all diffractograms can be clearly seen a broad peak at about 25° associated with the Vulcan XC72 support and four peaks at approximately $2\theta = 40^\circ, 47^\circ, 67^\circ$ and 82° , which are associated with the (111), (200), (220) and (311) planes, respectively, of the fcc structure characteristic of palladium and palladium alloys [6]. It was also observed peaks at about $2\theta = 27^\circ, 34^\circ, 38^\circ, 52^\circ, 55^\circ, 62^\circ, 65^\circ$ and 66° , which were associated with SnO_2 and $\text{Sb}_2\text{O}_5 \cdot \text{SnO}_2$ (ATO) used as supports [6-7]. For PdPtSn/C-ATO (80:10:10) and PdPtSn/C-ATO (90:05:05) electrocatalysts the diffraction peaks of Pd (fcc) phase are shifted to small angles compared to Pd/C-ATO electrocatalyst, which indicates some lattice expansion and that part of Sn atoms could be incorporated into the PdPt lattice.

The CV of Pt/C-ATO, Pd/C-ATO, PdPt/C-ATO (80:20), PdPtSn/C-ATO (80:10:10) and PdPtSn/C-ATO (90:05:05) in 1.0 mol L^{-1} KOH are shown in Fig. 2. The cyclic voltammetry responses were normalized per gram of platinum, considering that ethanol adsorption and dehydrogenation occur only on platinum or palladium sites at ambient temperature.

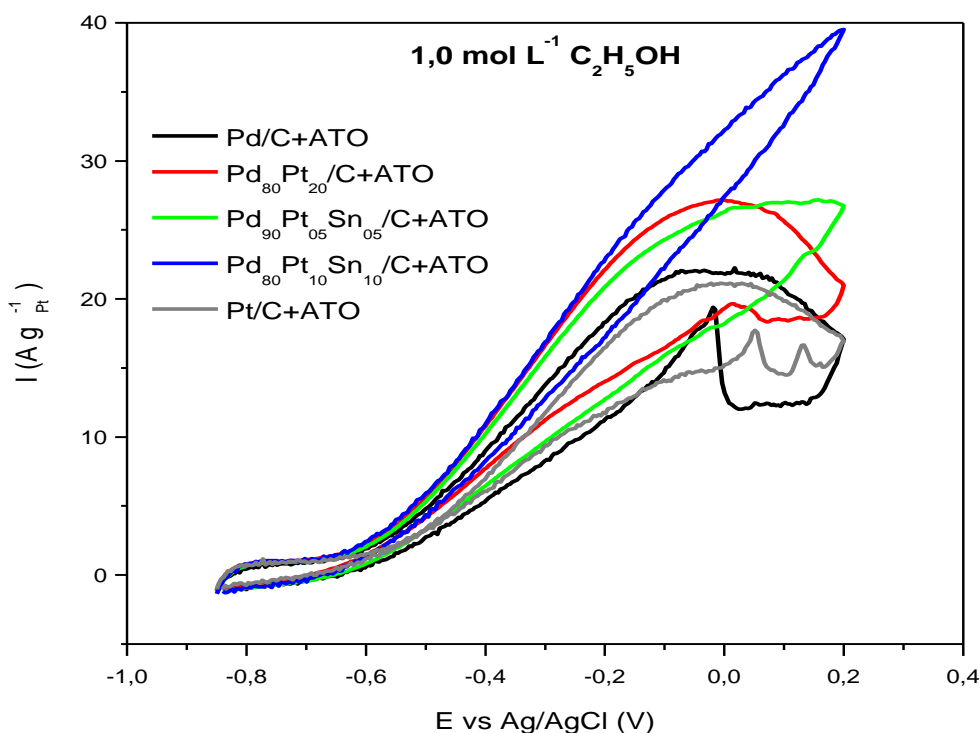


Figure 3. Cyclic voltammograms of Pt/C-ATO, Pd/C-ATO, PdPt/C-ATO (80:20), PdPtSn/C-ATO (80:10:10) and PdPtSn/C-ATO (90:05:05) in 1.0 mol L^{-1} KOH and 1.0 mol L^{-1} $\text{C}_2\text{H}_5\text{OH}$ with a sweep rate of 10 mV s^{-1} .

The humps in the potential region -850 to -450 mV on Pt/C-ATO, Pd/C-ATO, PdPt/C-ATO (80:20), PdPtSn/C-ATO (80:10:10) and PdPtSn/C-ATO (90:05:05) are associated with hydrogen adsorption process in the anodic scan. All electrocatalysts prepared showed a well-defined hydrogen adsorption-desorption region which is characteristic of Pt or Pd electrocatalysts (-850 to -450 mV) in alkaline medium. The process which emerges above -0.20 V , can be attributed to the formation of the palladium or platinum oxide layer on the surface of the electrocatalyst, although the mechanism of this

oxidation process for palladium remains unclear, it has been widely accepted that OH^- ions are first chemisorbed in the initial stage of the oxide formation and then they are transformed into higher valence oxides at higher potentials [18]. The cathodic peaks, at around -0.35 V, is attributed to the reduction of the palladium, palladium or thin oxide during the cathodic scan. Pd/C-ATO, PdPt/C-ATO and PdPtSn/C-ATO electrocatalysts also showed an increase in the current values in the double layer (-0.3 to 0.0 V) in comparison with Pt/C-ATO electrocatalyst, which may be attributed to the formation of oxide species.

The CV of Pt/C-ATO, Pd/C-ATO, PdPt/C-ATO (80:20), PdPtSn/C-ATO (80:10:10) and PdPtSn/C-ATO (90:05:05) in 1.0 mol L^{-1} KOH and 1.0 mol L^{-1} $\text{C}_2\text{H}_5\text{OH}$ are shown in Fig. 3.

The cyclic voltammogram of the all electrocatalysts showed the hydrogen desorption/sorption region was significantly suppressed in the presence of ethanol in the solution. The ethanol electro-oxidation started at approximately -0.65 V for PdPtSn/C-ATO (80:10:10), PdPtSn/C-ATO (90:05:05) and PdPt/C-ATO (80:20), -0.6 V for Pd/C-ATO, while that for Pt/C-ATO the ethanol electro-oxidation started at approximately -0.55 V. In the potential range of interest for a direct ethanol fuel cell (-0.6 to -0.3 V), the current values of the PdPtSn/C-ATO (80:10:10), PdPtSn/C-ATO (90:05:05) and PdPt/C-ATO (80:20) were higher than that of Pd/C-ATO and Pt/C-ATO. The cyclic voltammetry also showed that the current densities are higher at corresponding potentials on Pd/C-ATO than that on Pt/C-ATO. The most significant phenomenon is that the onset potential for ethanol oxidation on Pd/C-ATO is more negative for 50 mV compared with that on Pt/C-ATO at the same condition.

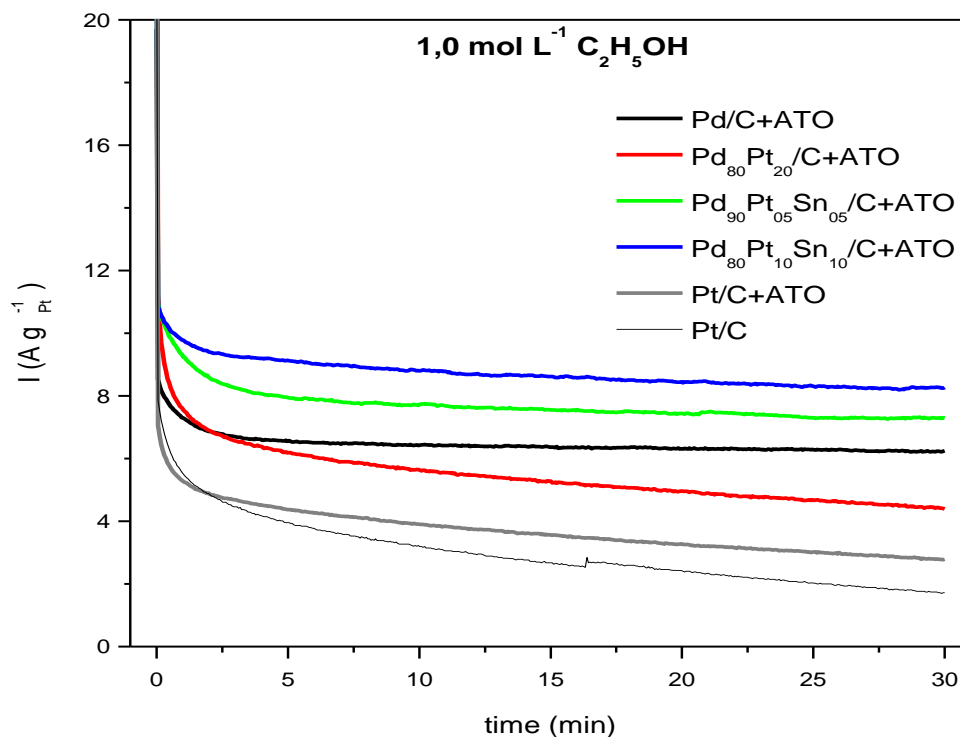


Figure 4. Current–time curves at -0.4 V in 1.0 mol L^{-1} KOH and 1.0 mol L^{-1} $\text{C}_2\text{H}_5\text{OH}$ for Pt/C-ATO, Pd/C-ATO, PdPt/C-ATO (80:20), PdPtSn/C-ATO (80:10:10) and PdPtSn/C-ATO (90:05:05) electrocatalysts.

The results showed that Pd had higher catalytic activity for ethanol electro-oxidation in comparison with Pt. The XRD results showed that little alloy occurs between Sn, Pt and Pd, which suggests that the electronic effect brought by the addition of Sn also contributes little to the high catalytic activity of the PdPtSn/C electrocatalysts. Also is generally believed that these Sn species are oxophilic i.e. they have the capacity to generate OH_{ads} at a lower potential, and facilitate the oxidative desorption of the intermediate (bifunctional mechanism).

The chronoamperometry experiments were carried out to examine the electrochemical stability of the Pt/C-ATO, Pd/C-ATO, PdPt/C-ATO (80:20), PdPtSn/C-ATO (80:10:10) and PdPtSn/C-ATO (90:05:05) electrocatalysts (Fig. 4).

The final current values after holding the cell potential at -0.4 V vs Ag/AgCl for 30 min were the following: PdPtSn/C-ATO (80:10:10) > PdPtSn/C-ATO (90:05:05) > Pd/C-ATO > PdPt/C-ATO (80:20) > Pt/C-ATO. The results show that PdPtSn, Pd and PdPt had higher catalytic activity for ethanol electro-oxidation than Pt i.e. they are in agreement with cyclic voltammetry experiments.

In this experiment, the current values also decays rapidly on Pt/C-ATO and PdPt/C-ATO, however the current values decays slowly on PdPtSn/C-ATO (80:10:10), PdPtSn/C-ATO (90:05:05) and Pd/C-ATO. These results show that PdPtSn/C-ATO (80:10:10), PdPtSn/C-ATO (90:05:05) and Pd/C-ATO had better steady-state electrolysis than Pt/C-ATO and PdPt/C-ATO for ethanol oxidation in alkaline medium [19].

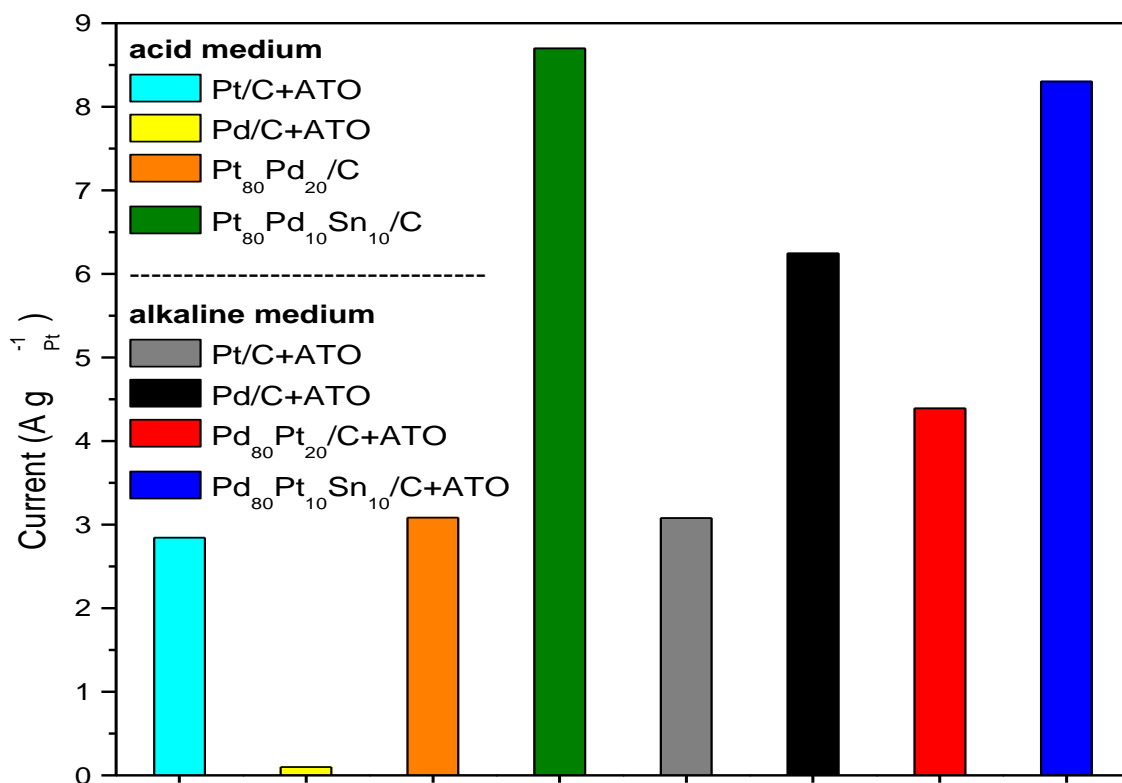


Figure 5. Current values at -0.4 V after 30 min for Pt/C-ATO, Pd/C-ATO, PtPd/C-ATO and PdPtSn/C-ATO electrocatalysts in alkaline and acid medium.

The results confirmed that Pd is a good electrocatalyst for ethanol oxidation in alkaline medium in comparison with Pt and that these results also are important to develop direct ethanol fuel cells. All electrocatalysts prepared were more active for ethanol oxidation than Pt/C indicating the beneficial effect of the addition of ATO. The presence of Pd and PdPtSn nanoparticles, ATO and carbon supports in close proximity seems to be essential for a good catalytic activity, however, the reason why Pd/C-ATO and PdPtSn/C-ATO showed better performance is still not very clear [6].

Pt/C-ATO, Pd/C-ATO, PtPd/C-ATO and PdPtSn/C-ATO electrocatalysts were also tested for ethanol electro-oxidation in acid medium and the final current values obtained after holding the cell at -0.4 V for 30 min were compared to the ones obtained in alkaline medium (Figure 5).

The results confirmed that Pd is not a good electrocatalyst for ethanol oxidation in acidic medium, however it is a good electrocatalyst for ethanol oxidation in alkaline medium, because the final current value in alkaline medium was about sixty times higher than the current value obtained in acidic medium. Pt/C-ATO electrocatalysts showed similar current value in alkaline and acidic medium. These results showed that the presence of the tin oxides and antimony oxides (ATO) in the electrocatalysts (acidic medium) promote the formation of oxygenated species in a potential region less positive than the pure platinum, and these species play a crucial role in the oxidation of adsorbed intermediates, releasing the active sites of Pt. The results also showed that PtPd/C-ATO (80:20) and PtPdSn/C (80:10:10) are effective in acidic medium, while that for alkaline medium PdPt/C-ATO (80:20) and PdPtSn/C-ATO (80:10:10) are more effective. The results also confirmed that Pd-based electrocatalysts are emerging as an alternative to Pt-based catalysts for ethanol electro-oxidation in alkaline DEFC, while that Pt-based electrocatalysts are effective for ethanol electro-oxidation in acidic DEFC.

4. CONCLUSIONS

The borohydride reduction showed to be an effective method for producing active PdPtSn/C-ATO (80:10:10) for ethanol oxidation in alkaline medium. The X-ray diffractograms of Pt/C-ATO, Pd/C-ATO, PdPt/C-ATO (80:20), PdPtSn/C-ATO (80:10:10) and PdPtSn/C-ATO (90:05:05) electrocatalysts showed the presence of characteristic peaks of Pt, Pt alloys, Pd, Pd alloys, SnO₂ and Sb₂O₅.SnO₂ phases. The chronoamperometry experiments showed that PdPtSn/C-ATO (80:10:10) electrocatalyst was more active than others electrocatalysts prepared for ethanol oxidation in alkaline medium at room temperature. These results suggest that the electronic effect brought by the addition of Sn also contributes to the high catalytic activity of the PdPtSn/C electrocatalysts and a presence of Sn species facilitate the oxidative desorption of the intermediate. Further work is now necessary to investigate the PdPtSn/C electrocatalysts surface by different techniques and to elucidate the mechanism of ethanol electro-oxidation in alkaline medium.

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