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# Electro-Oxidation of Formic Acid on PdIr/C-$Sb_2O_5$.$SnO_2$ Electrocatalysts Prepared by Borohydride Reduction

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PdIr/C-$Sb_2O_5$.$SnO_2$ electrocatalysts with different atomic ratio (90:10, 70:30 and 50:50) were prepared by borohydride reduction method using a water/2-propanol mixture as solvent, $Pd(NO_3)_2.2H_2O$ and $IrCl_3.3H_2O$ as metal sources, a physical mixture of 85% Vulcan Carbon XC72 and 15% $Sb_2O_5$.$SnO_2$ (ATO) as support and $NaBH_4$ as reducing agent. The obtained materials were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM), while the catalytic activity for formic acidic electro-oxidation was investigated by cyclic voltammetry and chronoamperometry. X-ray diffractograms of PdIr/C-$Sb_2O_5$.$SnO_2$ electrocatalysts showed the presence of Pd(fcc) phase, carbon and ATO phases. These electrocatalysts did not show peaks related to Ir, however the presence of Ir oxides in small amounts and amorphous forms cannot be discarded. TEM micrographs and histograms of the particle size distributions showed that the nanoparticles of PdIr electrocatalysts where not well dispersed on the support and some agglomerates were present. The electrochemical studies showed that PdIr/C-$Sb_2O_5$.$SnO_2$ (90:10) and PdIr/C-$Sb_2O_5$.$SnO_2$ (50:50) had superior performance for formic acid electro-oxidation at 25$^{o}$C compared to Pd/C-$Sb_2O_5$.$SnO_2$. These result indicated that addition of Ir to Pd could favor the electro-oxidation of formic acid, therefore this effect could be attributed to bifunctional mechanism associated to electronic effect.

**Keywords:** PdIr/C-$Sb_2O_5$.$SnO_2$ electrocatalysts; formic acid oxidation, borohydride reduction process

## 1. INTRODUCTION

Fuel cell has been considered as attractive option for power generation due to their high efficiency and little or no pollution [1]. Among various types of fuel cells, direct liquid fuel cell has been considering very attractive as power sources for stationary, mobile and portable applications [2], while Methanol has been the fuel most studied for polymer electrolyte membrane fuel cells (DMFC)

due to their low cost, low pollutant emissions and high theoretical energy density. Nevertheless the use of methanol is not safe because it is a toxic, evaporable and burnable compound [3].

Therefore, formic acid has been proposed as an alternative to methanol, because it exhibits a smaller crossover flux through Nafion® than methanol, allowing the use of highly concentrated fuel solutions. Moreover, formic acid is also not inflammable and its storage and transportation are safe [4].

For the formic acid electro-oxidation, Pt-based and Pd-based catalysts have been most frequently employed. On Pt based electrocatalysts the formic acid oxidation has been mainly via an indirect path, where the electrocatalyst is easily poisoned by the adsorbed CO at low potential [5, 6]. Pd electrocatalysts has been able to catalyze formic acid oxidation and it is less inclined to CO poisoning and deactivation, in comparison with Pt, because the electro-oxidation of formic acid on these materials is mainly through the direct pathway. Nevertheless, the catalytic activity and durability of Pd catalysts still need to be substantially improved, consequently, the addition of co-catalysts to palladium is yet necessary [6, 7].

Considering Pd binary electrocatalysts, it has been suggested that the second atom can increase the adsorption ability of the active oxygen and then the oxidation rate of formic acid. Another suggestion is that the co-catalysts could also prevent from the formation of strongly adsorbed CO [8].

Wang *et. al.* [8] showed that the electrocatalytic activity of Pd–Ir/C was better than only Pd/C electrocatalyst, although Ir has no electrocatalytic activity for the oxidation of formic acid. These authors concluded that Ir could promote the oxidation of formic acid at Pd through the direct pathway, because Ir can decrease the adsorption strength of CO on Pd. The use of iridium is interesting for direct liquid fuel cell, since iridium oxide shows an excellent corrosion resistance in acidic medium, good electrical conductivity, and high electrocatalytic activity towards oxygen evolution.

Considering also the addition of oxides into carbon as support, it can enhance the catalytic activity for small organic molecule electro-oxidation through synergetic interaction between oxides, the carbon and noble metals. Among those, $Sb_2O_5.SnO_2$ (ATO) exhibit a number of characteristics that make them interesting for catalytic studies due to enhancement of electrical conductivity compared with others oxides. The presence of ATO oxides could also be beneficial to the oxidation of some poisoning intermediates adsorbed on palladium (bifunctional mechanism) [5, 9, 10].

In this context, the aim of this work was prepare PdIr/C-$Sb_2O_5.SnO_2$ electrocatalysts by borohydride reduction and test these materials for formic acid electro-oxidation in acidic medium by cyclic voltammetry and chronoamperometry.

## 2. EXPERIMENTAL

PdIr/C-$Sb_2O_5.SnO_2$ (20 wt.% of metals loading, with Pd:Ir atomic ratio of 90:10, 70:30 and 50:50) were prepared by borohydride reduction method using a water/2-propanol mixture as solvent (3:1), $Pd(NO_3)_2.2H_2O$ and $IrCl_3.3H_2O$ as metal sources, a physical mixture of 85% Vulcan Carbon XC72 and 15% $Sb_2O_5.SnO_2$ (ATO) as support and $NaBH_4$ as reducing agent. The preparation of electrocatalysts was realized in accordance with reference 9.

X-ray diffraction (XRD) analyses were performed using a Rigaku diffractometer model Miniflex II using Cu Kα radiation source ($l$ = 0.15406 nm). The diffractograms were recorded from 2θ = 20° to 90° with a step size of 0.05° and a scan time of 2s per step, while transmission electron microscopy (TEM) was carried using a JEOL JEM-2100 electron microscope operated at 200 kV. The mean nanoparticle sizes were determined by counting more than 200 particles from different regions of each sample.

The cyclic voltammetry and chronoamperommetry measurements were carried out at room temperature using a Microquimica potentiostat. These study were performed using a working electrodes (geometric area of 0.3 $cm^2$ with a depth of 0.3 mm) prepared using the thin porous coating technique [11]. The reference electrode was a reversible hydrogen electrode (RHE) and the counter electrode was a Pt plate. The electrochemical measurements were realized in presence of 0.5 $molL^{-1}$ $H_2SO_4$ or 1.0 mol $L^{-1}$ of formic acid + 0.5 mol $L^{-1}$ $H_2SO_4$ solutions saturated with $N_2$. .

## 3. RESULTS AND DISCUSSION

The X-ray diffractograms of PdIr/C-$Sb_2O_5$.$SnO_2$ electrocatalysts prepared with different Pd:Ir atomic ratio are shown in Fig. 1. All diffractograms showed a broad peak at about 25º associated with the Vulcan XC72 support, four peaks at approximately 2θ = 40º, 47º, 67º and 82º, which are associated with the fcc structure characteristic of Pd (JCPDF # 89-4897) or Pd alloys and peaks at about 2θ= 27º, 34º, 38º, 52º, 55º, 62º, 65º, 66º, which were also characteristic of ATO used as support.

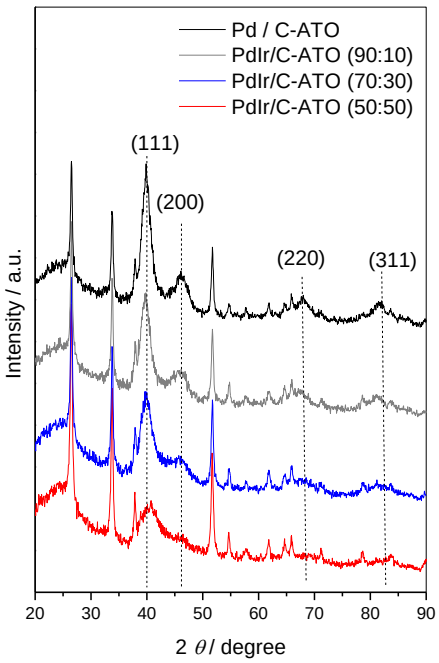
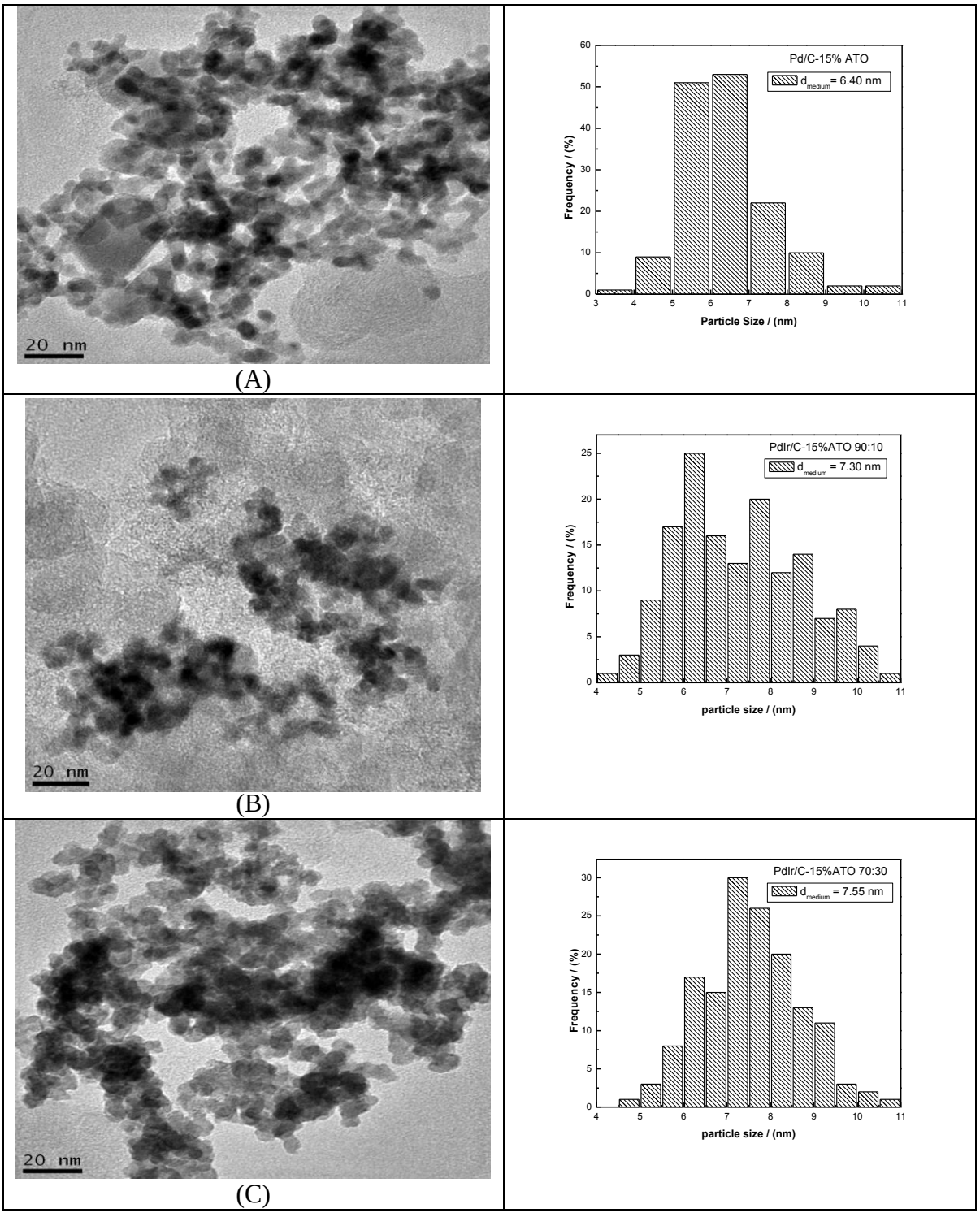
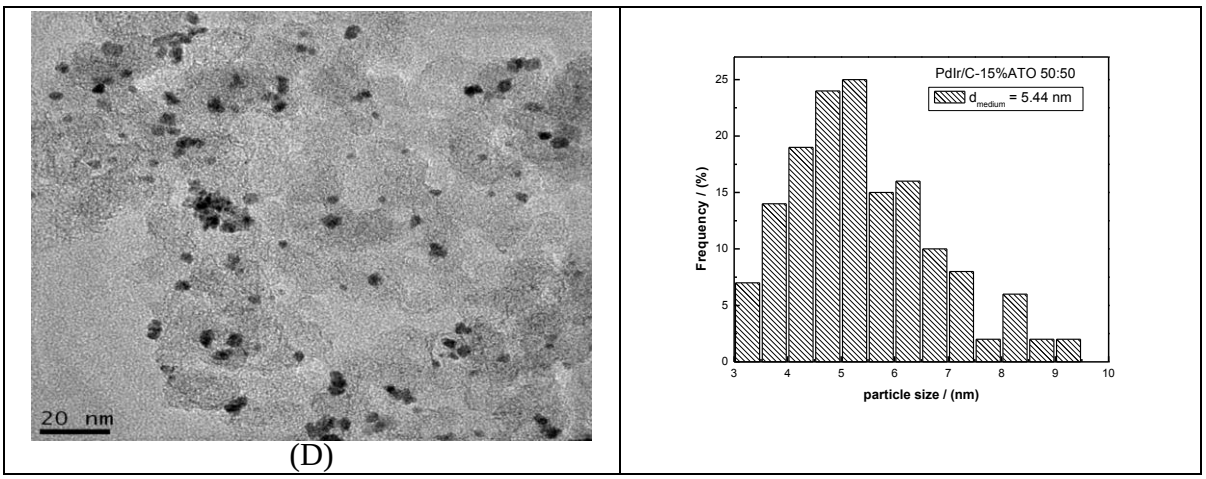



**Figure 1.** X-ray diffractograms of the Pd/C-$Sb_2O_5$.$SnO_2$ and PdIr/C-$Sb_2O_5$.$SnO_2$ electrocatalysts.

For all PdIr/C-$Sb_2O_5$.$SnO_2$ no peaks related to Ir were observed, however the presence of Ir oxides in small amounts and amorphous forms cannot be discarded. PdIr/C-$Sb_2O_5$.$SnO_2$ (50:50) electrocatalyst showed a shift to higher angles of the peak associated to the (220) plane compared to Pd/C-$Sb_2O_5$.$SnO_2$ indicating the insertion of Ir in the Pd structure. Also it was found that the peaks of Pd particles in the Pd/C-$Sb_2O_5$.$SnO_2$ electrocatalysts are higher and sharper than that of the PdIr/C-$Sb_2O_5$.$SnO_2$ (50:50), consequently the average size and crystallinity of PdIr/C-$Sb_2O_5$.$SnO_2$ (50:50) is smaller than that of the Pd/C-$Sb_2O_5$.$SnO_2$.






(D)

**Figure 2.** TEM micrograph and a histogram of (2a) Pd/C-$Sb_2O_5$.$SnO_2$, (2b) PdIr/C-$Sb_2O_5$.$SnO_2$ (90:10), (2c) PdIr/C-$Sb_2O_5$.$SnO_2$ (70:30) and (2d) PdIr/C-$Sb_2O_5$.$SnO_2$ (50:50) electrocatalyst with the mean diameter and particle distribution.

Therefore, the presence of Ir could prevent from the aggregation of the particles as an observed by Wang *et al.* [8].

TEM micrographs and histograms of the particle size distributions of Pd/C-$Sb_2O_5$.$SnO_2$ and PdIr/C-$Sb_2O_5$.$SnO_2$ electrocatalysts are shown in Figure 2.

Pd/C-$Sb_2O_5$.$SnO_2$, PdIr/C-$Sb_2O_5$.$SnO_2$ (90:10) and PdIr/C-$Sb_2O_5$.$SnO_2$ (70:30) showed that the nanoparticles where not well dispersed on the support and some agglomerates were present, while PdIr/C-$Sb_2O_5$.$SnO_2$ (50:50) electrocatalyst showed the nanoparticles well dispersed on the support. The mean particle sizes of Pd/C-$Sb_2O_5$.$SnO_2$, PdIr/C-$Sb_2O_5$.$SnO_2$ (90:10), PdIr/C-$Sb_2O_5$.$SnO_2$ (70:30) and PdIr/C-$Sb_2O_5$.$SnO_2$ (50:50) electrocatalysts were 6.4 nm, 7.3 nm, 7.6 nm and 5.4 nm, respectively. The addition of 50% Ir to Pd/C-$Sb_2O_5$.$SnO_2$ resulted in a decrease of mean particle size indicating that higher concentration of Ir could prevent an aggregation of the particles. This result is in accordance with X-ray diffractogram study.

According to Marinšek *et al.* [12] catalytic activity of Pd-based catalysts depends strongly on the size, shape and size distribution of the metal particles and generally, the smaller the Pd-particles enhanced the electro-activity for formic acid oxidation. In terms of beneficial particle size effects, 5-7 nm Pd-nanopartcles were reported to be the most favorable for formic acid electro-oxidation [12, 13].

The cyclic voltammograms of Pd/C-$Sb_2O_5$.$SnO_2$, PdIr/C-$Sb_2O_5$.$SnO_2$ (90:10), PdIr/C-$Sb_2O_5$.$SnO_2$ (70:30) and PdIr/C-$Sb_2O_5$.$SnO_2$ (50:50) electrocatalysts in presence of 0.5 mol $L^{-1}$ of $H_2SO_4$ solution are shown in Figure 3.

The voltammograms of PdIr/C-$Sb_2O_5$.$SnO_2$ (70:30) and PdIr/C-$Sb_2O_5$.$SnO_2$ (50:50) electrocatalysts do not display a well-defined hydrogen oxidation region (0.0–0.4V versus RHE) in comparison with Pd/C-$Sb_2O_5$.$SnO_2$, PdIr/C-$Sb_2O_5$.$SnO_2$ (90:10). The current densities of all PdIr/C-$Sb_2O_5$.$SnO_2$ in the double layer region (between 0.45 and 0.65V versus RHE) are larger than those on Pd/C-$Sb_2O_5$.$SnO_2$, this behavior is characteristic of binary and ternary electrocatalysts [14].

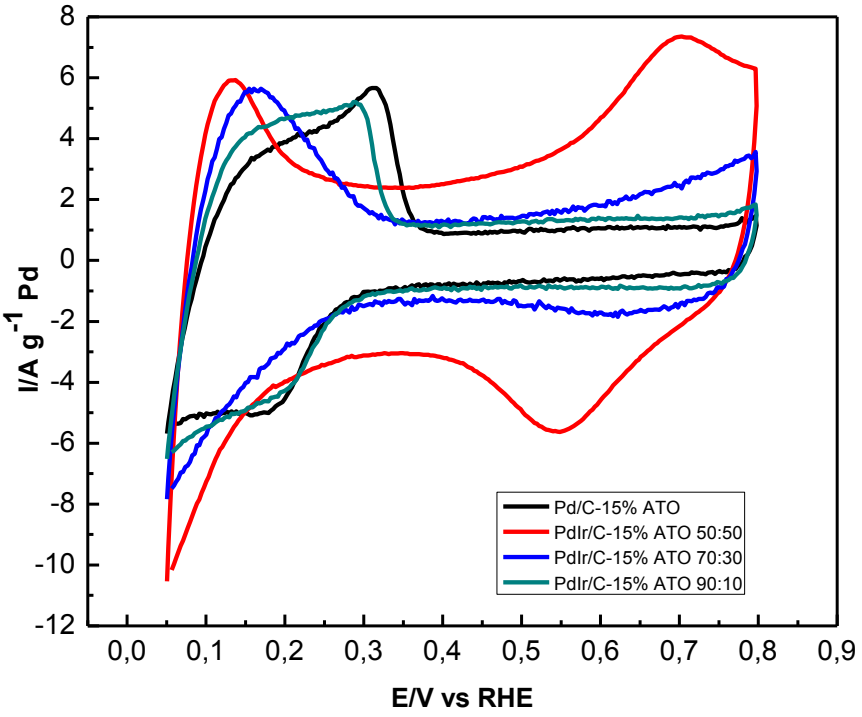



**Figure 3.** Cyclic voltammograms of Pd/C-$Sb_2O_5$.$SnO_2$ and PdAu/C-$Sb_2O_5$.$SnO_2$ electrocatalysts in 0.5 mol $L^{-1}$ $H_2SO_4$ with a sweep rate of 10 mV $s^{-1}$.

The charge–discharge current of the double layer at the PdIr/C-$Sb_2O_5$.$SnO_2$ (50:50) electrocatalyst was largest among all electrocatalyts, this behavior could be attributed to smallest average size of the metal particles and the largest surface area. The voltammograms of PdIr/C-$Sb_2O_5$.$SnO_2$ (70:30) PdIr/C-$Sb_2O_5$.$SnO_2$ (50:50) electrocatalysts are also suppressed in comparison with Pd/C-$Sb_2O_5$.$SnO_2$ indicating partial coverage of Pd by Ir.

PdIr/C-$Sb_2O_5$.$SnO_2$ (50:50) and PdIr/C-$Sb_2O_5$.$SnO_2$ (70:30) electrocatalysts also showed the clear shifts of the peak positions for the hydrogen adsorption-desorption in comparison with others electrocatalysts prepared, therefore this negative shift is an indication of the electronic modification of Pd atoms by the neighboring Ir atoms [12].

The presence of an oxidation process in potential (0.7V) could be related as Ir oxide species, where Juodkazis et al [15] has reported the existence of reversible metal-oxide layers for noble metals such as iridium, oxidized anodically in the range of potentials before $O_2$ evolution.

Fig. 4 shows the cyclic voltammograms of Pd/C-$Sb_2O_5$.$SnO_2$ and PdIr/C-$Sb_2O_5$.$SnO_2$ electrocatalysts prepared at 25°C in presence of 1.0 mol $L^{-1}$ formic acidic in 0.5 mol $L^{-1}$ $H_2SO_4$. All PdIr/C-$Sb_2O_5$.$SnO_2$ electrocatalysts showed highest current values in all potential range in comparison with Pd/C-$Sb_2O_5$.$SnO_2$. PdIr/C-$Sb_2O_5$.$SnO_2$ (70:30) electrocatalyst showed a best performance in potential of 0.05 to 0.45 V, while that PdIr/C-$Sb_2O_5$.$SnO_2$ (50:50) showed higher currents values in comparison to PdIr/C-$Sb_2O_5$.$SnO_2$ (70:30) and PdIr/C-$Sb_2O_5$.$SnO_2$ (90:10) electrocatalysts for

potentials above of 0.45V. The high activity of PdIr/C-$Sb_2O_5$.$SnO_2$ (50:50) electrocatalysts could be attributed to smaller average sizes particle in comparison with others electrocatalysts prepared.

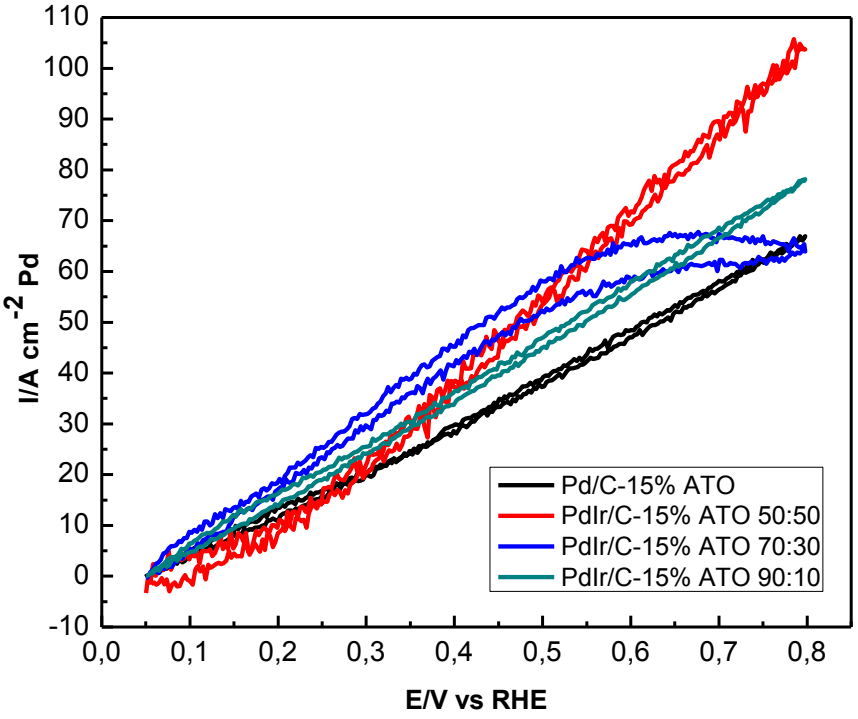



**Figure 4.** Cyclic voltammograms of the Pd/C-$Sb_2O_5$.$SnO_2$, PdIr/C-$Sb_2O_5$.$SnO_2$ (90:10), PdIr/C-$Sb_2O_5$.$SnO_2$ (70:30) and PdIr/C-$Sb_2O_5$.$SnO_2$ (50:50) electrocatalysts in 1 mol $L^{-1}$ formic acid solution in 0.5 mol $L^{-1}$ $H_2SO_4$ with a sweep rate of 10 mV $s^{-1}$ at 25°C.

The introduction of Ir leads to an increase in the electro-activity of the binary electrocatalysts(PdIr) compared to pure Pd. This effect could be also explained by the activation of interfacial water molecules at lower potentials than in the case of pure Pd due to the presence of preferential sites for $OH_{ads}$ adsorption, where the presence of $OH_{ads}$ species is necessary for the complete oxidation of poisoning intermediates adsorbed [14]. The electro-oxidation of formic acid on PdIr/C-$Sb_2O_5$.$SnO_2$ electrocatalysts could also occur in the direct pathway, where formic acid is directly oxidized to $CO_2$. In accordance, Wang et. al. [7] showed that the electrocatalytic activity of the PdIr/C (50:50) and PdIr/C (70:30) for the oxidation of formic acid was highest among all the electrocatalysts prepared.

Fig. 5 shows the current-time curves for formic acidic electro-oxidation for Pd/C-$Sb_2O_5$.$SnO_2$, PdIr/C-$Sb_2O_5$.$SnO_2$ (90:10), PdIr/C-$Sb_2O_5$.$SnO_2$ (70:30) and PdAu/C-$Sb_2O_5$.$SnO_2$ (50:50) electrocatalysts at 25°C in the potential of 0.5 V for 30 min.

All of the catalysts featured a pronounced current decay in the first 2 min due to the accumulation of poisonous intermediates, and the current values of PdIr/C-$Sb_2O_5$.$SnO_2$ (50:50), PdIr/C-$Sb_2O_5$.$SnO_2$ (90:10) and Pd/C-$Sb_2O_5$.$SnO_2$ decay slowed down at longer times, while that PdIr/C-$Sb_2O_5$.$SnO_2$ (70:30) electrocatalyst showed a decay sharply.

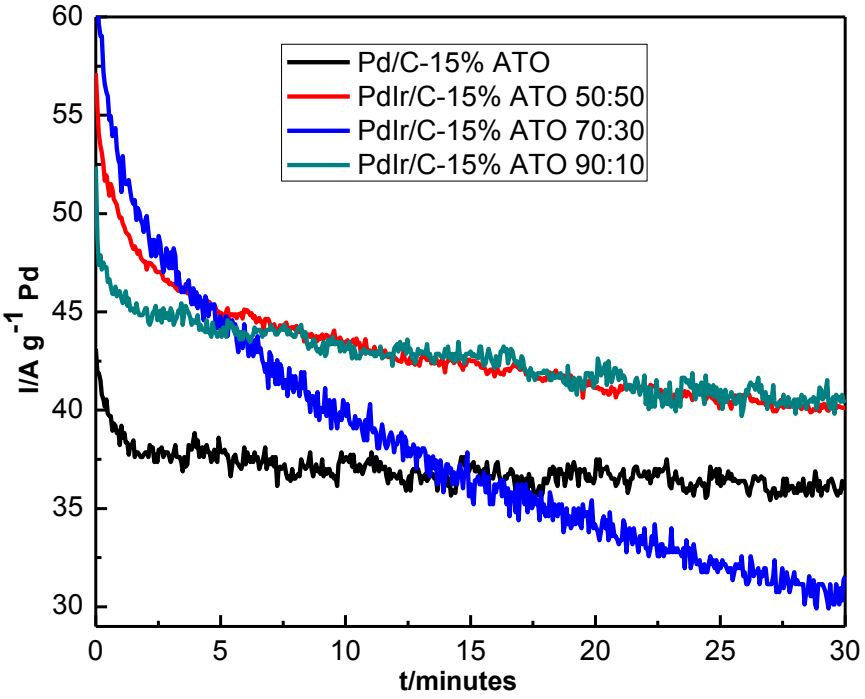



**Figure 5.** Current-time curves at 0.5 V in 1 mol $L^{-1}$ ethanol solution in 0.5 mol $L^{-1}$ $H_2SO_4$ for Pd/C-$Sb_2O_5$.$SnO_2$ and PdIr/C-$Sb_2O_5$.$SnO_2$ electrocatalysts at 25°C.

The final current values at 0.5 V (T= 25°C) increase in the following order: PdIr/C-$Sb_2O_5$.$SnO_2$ (50:50) ≈ PdIr/C-$Sb_2O_5$.$SnO_2$ (90:10) > Pd/C-$Sb_2O_5$.$SnO_2$ > PdIr/C-$Sb_2O_5$.$SnO_2$ (70:30). The activity of PdIr/C-$Sb_2O_5$.$SnO_2$ (50:50) and PdIr/C-$Sb_2O_5$.$SnO_2$ (90:10) was higher that of the Pd/C-$Sb_2O_5$.$SnO_2$ indicating that the activity and stability of Pd could be improved due to the co-presence of Ir. The electronic modification of Pd might be the possible reasons for the enhanced activity, as the proximity of Ir and Pd atoms on the surface of the C- $Sb_2O_5$.$SnO_2$ (mechanism bifunctional).

## 4. CONCLUSIONS

The borohydride reduction method was an efficient process to produce of PdIr/C-$Sb_2O_5$.$SnO_2$ for formic acid electro-oxidation.

PdIr/C-$Sb_2O_5$.$SnO_2$ electrocatalysts showed a broad peak at about 25º associated with the Vulcan XC72 support, four peaks at approximately 2θ = 40º, 47º, 67º and 82º, which are associated with the fcc structure characteristic of Pd or Pd alloys and peaks at about 2θ= 27°, 34°, 38°, 52°, 55°, 62°, 65°, 66°, which were also characteristic of ATO used as support. PdIr/C-$Sb_2O_5$.$SnO_2$ also no showed peaks related to Ir, however the presence of Ir oxides in small amounts and amorphous forms cannot be discarded.

PdIr/C-$Sb_2O_5$.$SnO_2$ (50:50) exhibited superior performance for formic acid electro-oxidation in comparison with others electrocatalysts prepared. The highest catalytic activity of PdIr/C-$Sb_2O_5$.$SnO_2$ (50:50) seems to be related to the combination of the bifunctional mechanism and the electronic effect. Further work is now necessary to investigate the mechanism of formic acid electro-oxidation using these electrocatalysts.

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