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**Effect of Sb- Doped SnO<sub>2</sub> Supports Heat Treatment on the Oxygen Evolution Reaction**

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**ABSTRACT**

It has been recognized the role of supports in electrocatalysis as a way to increase both specific activity and lifetime of electrocatalysts. Due its stability, some doped SnO<sub>2</sub> supports could be used as an alternative to carbon black in PEM water electrolysis. In this work, IrO<sub>2</sub> catalyst was mixed in a colloidal mini-mill with SnO<sub>2</sub> supports doped with antimony (ATO) in a fixed proportion (50:50 wt %) and the mixtures were used as anode material for Oxygen Evolution Reaction (OER). ATO supports were obtained by reaction between Sn and Sb chloride precursors in alcoholic medium at moderate temperature, followed by an annealing procedure at 500 °C and different times of treatment (between 3 h and 15 h). The electrodes were evaluated in terms of OER by Linear Scan Voltammetry (LSV) and Electrochemical Impedance Spectroscopy (EIS) techniques. Electrokinetic parameters as Tafel Slope and Exchange Current Density for OER were obtained as a function of the different annealing times material support. Furthermore, the Charge Transfer Resistance (R<sub>ct</sub>) for oxygen evolution obtained from the Nyquist impedance spectra was compared. Although the LSV results showed a similar behavior for the OER of the several electrodes studied, the EIS analysis presented some distinctive R<sub>ct</sub> values for the electrodes assayed. The electrodes that showed minimum R<sub>ct</sub> values corresponded to those prepared with supports of 3 and 12 h of annealing time. These results could suggest that the ATO conductive properties depend strongly on the time of thermal treatment of the oxide in the synthesis procedure.

**1. INTRODUCTION**

In recent years, new technologies are being developed for energy generation in a clean, efficient and sustainable way. The fuel cells (FC), water electrolyzers (WE) and the unified regenerative fuel cells (URFC) that combines FC and WE in a single unit, represent viable options for electrochemical hydrogen production and power generation in an environmental friendly way. Although some of these devices are now commercially available, problems about the cost, availability and performance of catalysts and supports remain as the principal drawbacks of the hydrogen electrochemical energy conversion systems. The electrochemical reactions of oxygen: oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER) usually are the slowest reactions in FC, WE and



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URFC, representing thus limiting factors for these devices developing. In this sense, an important number of studies are currently dedicated to promote the electrochemical reactions of fuel cells and electrolyzers mainly based on the research and developing of new effective electrode and support materials for oxygen reactions [1-9].

Although it is commonly acknowledged the use of noble metals as catalysts in FC and WE, it has been found that Pt and other electrocatalytic metals show a better performance in the ORR than in the OER, presenting a high overpotential for the oxygen evolution. It has been noted that the oxides of Ir and Ru, and their combination with other metals; produce materials that are more convenient for OER catalysts. By the other side, despite of that the Vulcan coal and others carbonaceous materials show a well behavior as catalytic supports in FC, the high electrical potential used in an electrolyzer corrodes them, producing degradation of carbon material and a loss of electrical contact. Consequently, the research studies in electrochemical devices besides of finding catalysts with an activity enough for both oxygen reactions are focused in obtain support materials with the sufficient stability and electronic conductivity required in the anodic conditions of a WE [10, 11].

In the FC a potential near of 1 V vs. ENH is reached at the operation conditions, while in the WE is necessary to apply a potential proximate to 1.6 V vs. ENH for splitting the water into H<sub>2</sub> and O<sub>2</sub>. An oxygen electrode in a URFC operates alternatively at these two potential values, so that it is not advisable to use Vulcan carbon as support for the preparation of electrodes. The main disadvantage is that the operation with high potentials promotes the degradation of coal, limiting the electron transfer when a URFC operates mainly in the fuel cell mode. For this reason it is necessary to find an alternative support, which must be stable to a high potential of operation and it provides a higher electrical conductivity for the reactions of the oxygen electrode [12, 13].

Tin oxides have been used as transparent conductive films in liquid crystal displays, photodetectors, solar cells, gas sensors and protective films [14-17]. Recent studies have shown that the doped ceramic materials with a conductive material, as is the case of ATO, means a new field in the study of the electrode supports science [18-20]. The ATO has characteristics of high resistance to corrosion in acid media and when it is doped with conductive species as Sb<sup>5+</sup>, its electrical conductivity increases to 10<sup>2</sup> or 10<sup>3</sup> Ω<sup>-1</sup> cm<sup>-1</sup>. Studies indicate that the ATO could be used as catalyst support for OER in WE, being reported an improvement in the stability of the support as compared with an undoped oxide, in the conditions of oxygen evolution [18, 21]. Recent researches indicate that the characteristics of micro-structural and the nano-metric size of the ATO both depend strongly on the heat treatment of oxide in the stages of synthesis and the relative amount of doping agent [19].

This paper shows the preliminary results of the study of the OER kinetics of an IrO<sub>2</sub> catalyst supported on ATO. The catalytic materials composed of IrO<sub>2</sub> with ATO obtained at different times of heat treatment (between 3 h



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and 15 h) were used to evaluate the dispersibility of catalyst and kinetic parameters as Tafel slope and transfer charge resistance respect to OER in acid medium. The study was based in the electrochemical techniques of cyclic voltammetry (CV), linear voltammetry (LV) and electrochemical impedance spectroscopy (EIS).

## **2. EXPERIMENTAL SECTION**

### **2.1 Synthesis of antimony doped tin oxide (ATO)**

ATO supports were obtained by reaction between Sn and Sb chloride precursors in alcoholic medium at moderate temperature, followed by an annealing procedure at 500 °C and heat treatment times of 3 h, 6 h, 9 h, 12 h and 15 h. The supports prepared by this procedure are denoted as ATO (nh) where n means the number of hours of thermal treatment.

### **2.2 Electrochemical characterization**

#### **2.2.1 Electrodes preparation**

The electrodes were prepared from a catalytic ink comprising 90  $\mu\text{L}$  of Nafion® (5 wt. %, Aldrich), 540  $\mu\text{L}$  of ethanol spectroscopic grade, 6 mg of  $\text{IrO}_2$  and 6 mg of ATO. The ink was obtained using a FRITSCH/PULVERISETTE 23 mini-mill for a period of 0.5 h in order to homogenize the mixture and promote dispersion of the ink. Later, the resulting suspensions were hold in an ultrasonic bath for 0.5 h in aim to gain additional dispersion of mixture. Subsequently, a volume of each ink was deposited on a clean polished glassy carbon disk electrode (GCE) ( $A = 0.07068 \text{ cm}^2$ ). The coated GCEs were dried in a furnace at 80°C for 10 min. In order to comparison a Pt supported on ATO (3h) electrode and  $\text{IrO}_2$  supported on Vulcan carbon electrode were used. Finally,  $\text{IrO}_2$  and Pt films supported on ATOs were used as working electrodes for the OER kinetic studies. All the current values reported in this paper are normalized to the electrode geometric area.

#### **2.2.2 Electrochemical characterization of electrodes**

All the experiments were performed in a double-compartment electrochemical glass cell. An  $\text{Hg}/\text{Hg}_2\text{SO}_4/0.5 \text{ M H}_2\text{SO}_4$  (ESM = 0.69V vs. NHE) electrode was used as reference which was positioned as close to the working electrode as possible by means of a Luggin capillary. A Pt-mesh was used as counter-electrode and the aqueous electrolytic medium was 0.5 M  $\text{H}_2\text{SO}_4$  at room temperature. The electrochemical measurements were performed using an EG&G PAR VersaSTAT 3 Potentiostat/Galvanostat. In this study, all measured values of potential are reported respect to the normal hydrogen electrode (NHE).



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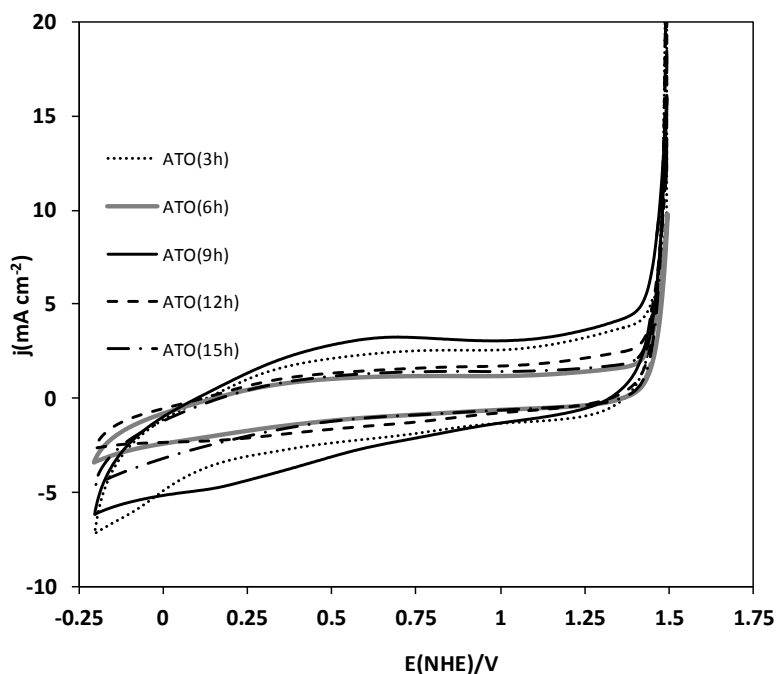
Cyclic voltammetry (CV) was carried out to evaluate the effect of different ATO in the IrO<sub>2</sub> or Pt electrodes by scanning the potential at a rate of 50 mV s<sup>-1</sup> between -0.16 V and 1.54 V under a N<sub>2</sub> atmosphere electrolyte solution. Oxygen evolution experiments were performed by linear scan voltammetry (LSV) at a scan rate of 5 mV s<sup>-1</sup> in the anodic direction from 0.59 V to 1.69 V in O<sub>2</sub>-free electrolyte solution at a constant electrode rotation frequency of 1000 rpm. The rotation rate was controlled by a PINE MSR<sub>X</sub> precision rotating system.

In addition, electrochemical impedance spectroscopy (EIS) experiments were carried out in the potentiostatic mode in the 100 kHz to 10 mHz frequency range. The impedance spectra were registered with a logarithmic data collection scheme at 10 steps per decade at 1.57 V of potential with alternate signal amplitude of 10 mV.

### 3. RESULTS AND DISCUSSION

#### 3.1 Evaluation of the supports by cyclic voltammetry

Figure 1 shows cyclic voltammograms obtained for IrO<sub>2</sub> supported on ATOs in N<sub>2</sub> saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. The CV diagrams reveal that the electrochemical response for IrO<sub>2</sub> is practically unchanged with the use of different ATO as support. Also is showed that the current density (*j*) attributed to IrO<sub>2</sub> supported on ATO (3h) and ATO (9h) are greater than the rest of the ATOs, this enhancement may be considered evidence that the dispersion of IrO<sub>2</sub> is improved with the use of this supports. The off-peak potential for oxygen evolution on all the IrO<sub>2</sub>/ATO electrodes appears near to 1.45 V, although on the ATO(3h) and ATO(9h) supported electrodes the onset was about 50 mV more negative than the rest of ATOs as showed in Figure 1.



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Figure 1. Cyclic voltammograms of GCEs coated with  $\text{IrO}_2/\text{ATOs}$  (with different heat treatment times: 3h, 6h, 9h, 12h, 15h) in 0.5 M  $\text{H}_2\text{SO}_4$  at 50 mV s<sup>-1</sup>. 50 wt %  $\text{IrO}_2/\text{ATOs}$ , with atmosphere:  $\text{N}_2$  and room temperature.

The Figure 2 compares the cyclic voltammograms obtained for  $\text{IrO}_2$  and Pt supported on ATO (3h) and  $\text{IrO}_2$  supported on Vulcan carbon in  $\text{N}_2$  saturated 0.5 M  $\text{H}_2\text{SO}_4$  solution. The CV of Pt supported on ATO (3h) shows that the reactions associated with the surface of Pt in an acid medium are limited by the support, avoiding identify the characteristic peaks of Pt on a clearly way [22], nevertheless the general electrochemical behavior in acid medium of platinum is still outlined in the voltammogram. The voltammograms corresponding to  $\text{IrO}_2$  catalyst show broad waves corresponding to the redox reactions over the Ir surface, these waves are more evident when Vulcan is used as support. In the voltammograms of Figure 2 also can be observed that the potential onset for oxygen evolution in the Pt/ATO electrode appears near to 1.7 V, while the corresponding oxygen evolution peaks of  $\text{IrO}_2/\text{ATO}$  and  $\text{IrO}_2/\text{C}$  electrodes appear at potential values about 300 mV more negative.

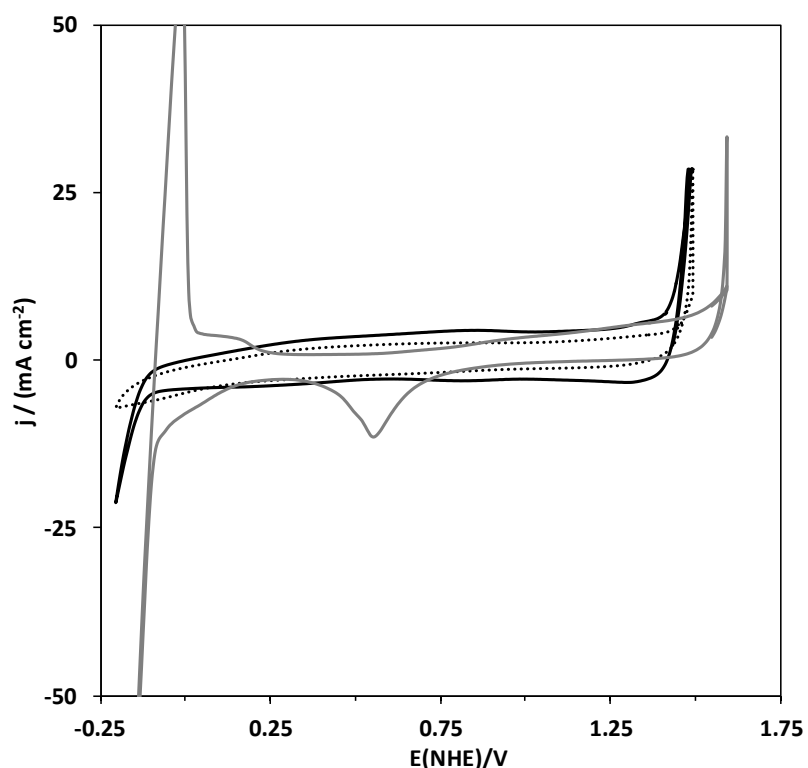
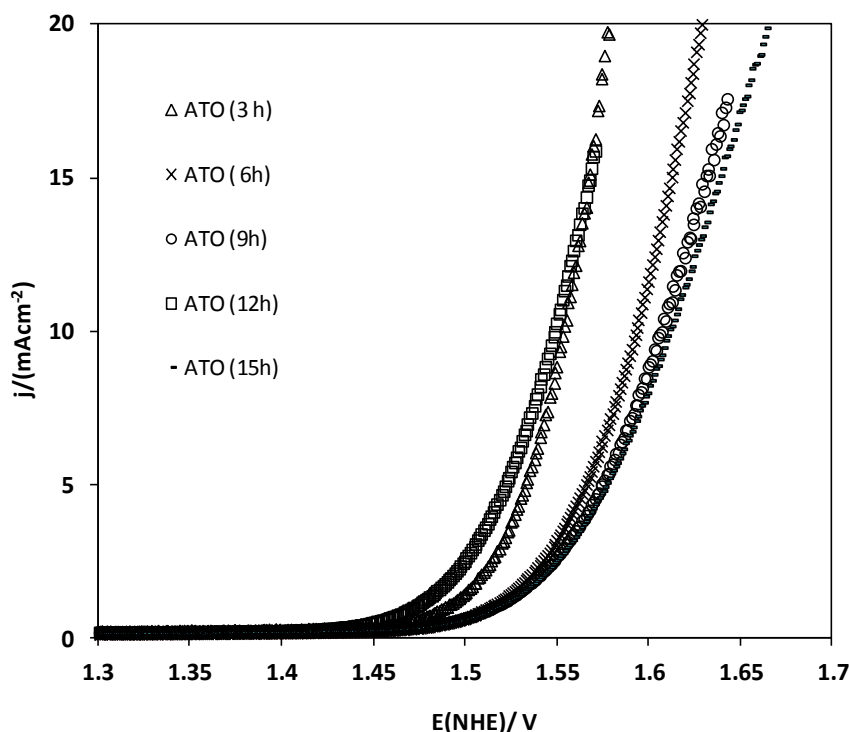


Figure2. Cyclic voltammograms of  $\text{IrO}_2/\text{ATO}$  (3h) (....),  $\text{Pt}/\text{ATO}$  (3h) (dashed line) and  $\text{IrO}_2/\text{C}$  (solid line) electrodes in  $\text{N}_2$  saturated 0.5 M  $\text{H}_2\text{SO}_4$  at  $50 \text{ mV s}^{-1}$ .

### 3.2 Oxygen evolution activity of the $\text{IrO}_2$ supported on ATO

The Figure 3 shows linear scan voltammograms for OER with  $\text{IrO}_2$  support on ATO (with different heat treatment times: 3h, 6h, 9h, 12 h, 15h) in 0.5 M  $\text{H}_2\text{SO}_4$  at a scan rate of  $5 \text{ mVs}^{-1}$ . Since the  $\text{IrO}_2$  catalyst used in the electrode preparation was the same in the different mixtures, and the proportion catalyst-support was maintained fixed in a 50:50 weight percent ratio, the voltammograms displacement observed in Figure 3 indicate that the OER depend on the ATO annealing times used in the electrodes. It is observed that the OER begins in a potential near to 1.45 V when the  $\text{IrO}_2$  is supported on ATO (3h) and ATO (12h), while that for the  $\text{IrO}_2$  supported on other ATO the EOR onset occurs near to 1.5 V. It is means that EOR is facilitated when ATO 3h or 12h annealed is used as support for  $\text{IrO}_2$ . As a consequence, the higher current densities are obtained when the ATO (3h) and ATO (12h) are used as supports for EOR. In Table 1, the values of current density obtained at a potential of 1.57 V corresponding to the different  $\text{IrO}_2/\text{ATO}$  electrodes studied, are showed.



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Figure 3. Linear scan voltammograms for OER of IrO<sub>2</sub>/ATO (with different heat treatment times) electrodes in N<sub>2</sub> saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> at  $v=5 \text{ mVs}^{-1}$ .

In Figure 4 the linear scan voltammograms for OER with IrO<sub>2</sub> supported on ATO (3h) and IrO<sub>2</sub> supported on carbon are shown [23]. In order to comparison the voltammogram corresponding to EOR on Pt/ATO (3h) is included. It can be observed that the oxygen evolution occurs in a potential about 100 mV more negative when the IrO<sub>2</sub> is supported on carbon respect to the onset OER potential obtained with the IrO<sub>2</sub>/ATO (3h) electrode. This little difference in overpotential could be put sideways in considering the disadvantage of carbon supports that suffer an easy corrosion at the high potentials used in the electrolysis process. Then the IrO<sub>2</sub> supported on ATO (3h) and finally Pt supported on ATO (3h). In Figure 4 also can be seen the poor catalytic activity of Pt for OER.

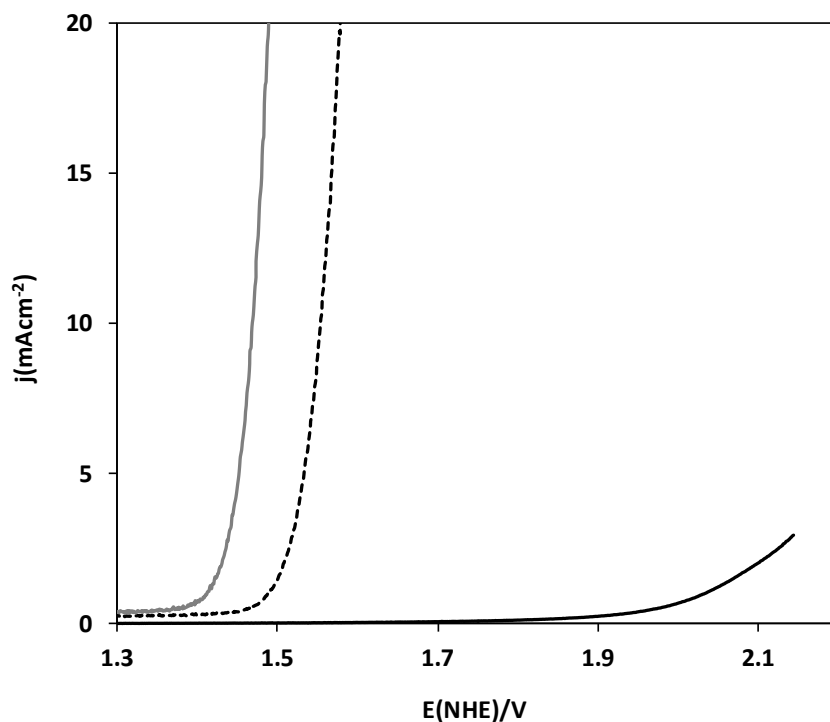


Figure 4. Linear voltammograms for OER on IrO<sub>2</sub>/ATO (3h) (-----), Pt/ATO (3h) (solid line) and IrO<sub>2</sub>/C (dashed line) electrodes in N<sub>2</sub> saturated 0.5 M H<sub>2</sub>SO<sub>4</sub>, at  $v=5 \text{ mVs}^{-1}$ .

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Tafel plots were obtained from LSV curves for OER after ohmic drop (IRs) correction due to the electrolyte resistance ( $R_s$ ). This correction was done by subtracting the IR to the applied potential [24]. The  $R_s$ -values were obtained by electrochemical impedance spectroscopy (EIS) for each electrode.  $R_s$  values were in the  $3\ \Omega - 7.5\ \Omega$  interval which are mainly attributed to a combined resistance between the solution resistance and the electrode film resistance. Figure 5 shows the Tafel curve for OER on  $\text{IrO}_2$  supported on ATO (3h) electrode after IR correction, a Tafel slope ( $b$ ) value of  $62\ \text{mV dec}^{-1}$  was obtained. A value close to  $60\ \text{mV dec}^{-1}$  has been observed for OER on some metal oxides in the low overpotential region ( $\eta_{\text{low}}$ ) [25, 26], for this slope value has been proposed the following mechanism [27]:



Being the reaction limiting step (rls) for the oxygen evolution process, the reorganization of the oxygen-species over the surface Ec. (1) before transfer of the first electron. Similarly to the graph shown in Figure 5, Tafel were plots obtained for each of the support under study, showing similar Tafel slope values. These results are presented in Table 1.



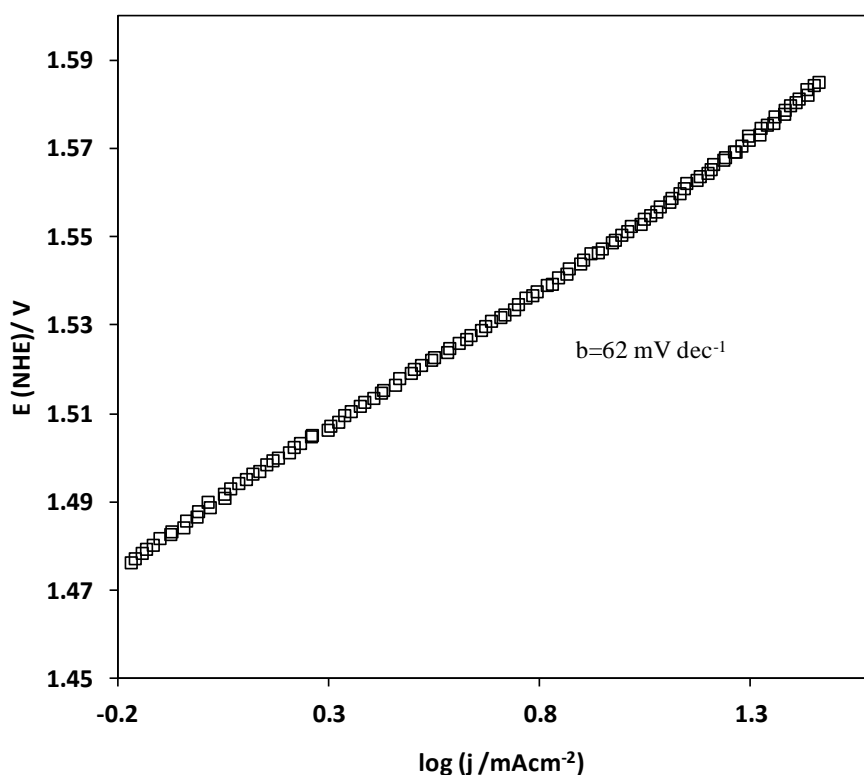


Figure 5. Tafel Plot for OER for IrO<sub>2</sub>/ATO (3h) after IR correction.

Figure 6 shows a comparison of Tafel curves for OER on IrO<sub>2</sub>/ATO (3h), IrO<sub>2</sub>/ATO (15h) and IrO<sub>2</sub>/C electrodes after IR correction. In the potential interval shown, some Tafel curves exhibit two linear slopes related with changes in the EOR kinetic mechanism, in this case the Tafel slope data at high overpotential ( $\eta_{\text{high}}$ ) show values close to 120 mV dec<sup>-1</sup>. These results indicate a change in mechanism where the rls is the first transfer electron in the electrolysis of the water molecule. In Figure 5 this behavior is clearly observed for IrO<sub>2</sub>/ATO (15h) and IrO<sub>2</sub>/C electrodes. The two Tafel slope behavior in OER has been observed in other metal oxide electrodes. The similar values of  $b$  observed in the IrO<sub>2</sub>/ATO and IrO<sub>2</sub>/C electrodes, could mean that the OER mechanism is the same in both supports and that the oxygen evolution is developed mainly on the Ir surface.

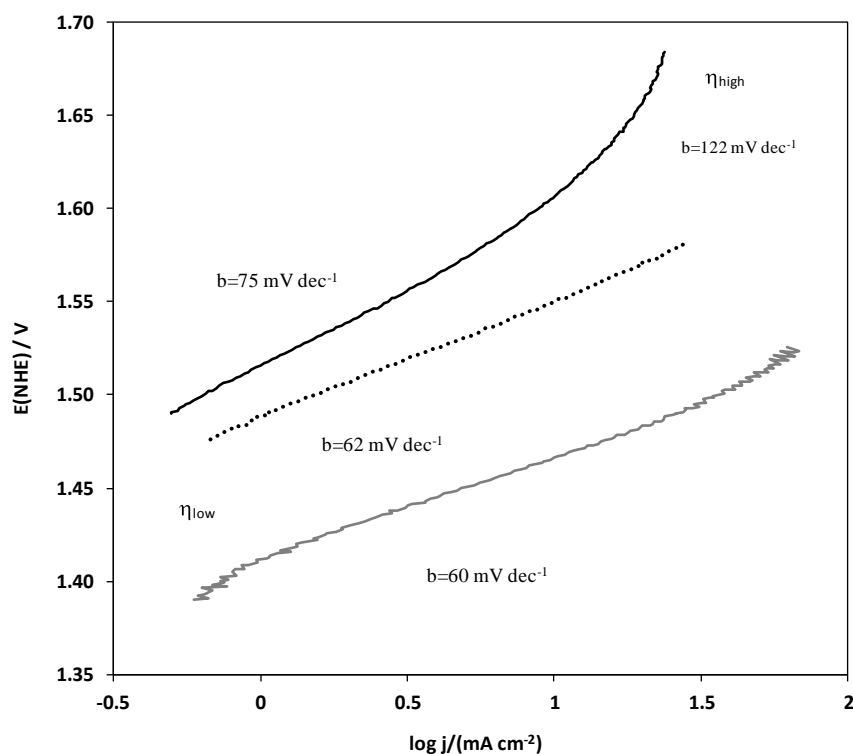
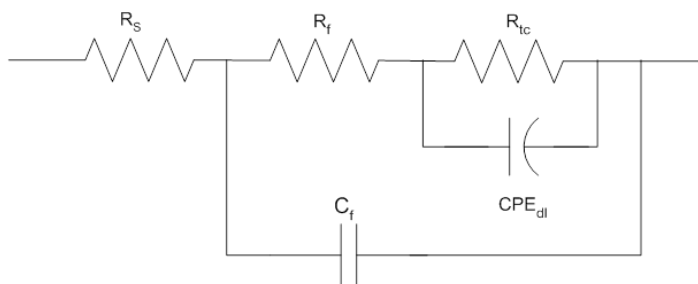


Figure 6. Tafel Plots comparison for OER on IrO<sub>2</sub>/ATO (3h) (.....), IrO<sub>2</sub>/ATO (15h) (solid line) and IrO<sub>2</sub>/C (dashed line) after IR correction.

### 3.3 Electrochemical impedance spectroscopy performance for OER

EIS measurements for oxygen evolution was carried out on IrO<sub>2</sub>/ATO electrodes in O<sub>2</sub>-free 0.5 M H<sub>2</sub>SO<sub>4</sub> solution, in the potentiostatic mode at an anodic potential of 1.57 V. Figure 7 shows the Nyquist plots for OER on IrO<sub>2</sub> supported on ATO. The depressed semicircles presented in Figure 7 were adjusted by a CNLS fitting to the following equivalent circuit [28]:



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Where  $R_s$  is the electrolytic solution resistance,  $R_f$  and  $C_f$  the resistance and capacitance of the film of catalyst/support/Nafion system, and  $R_{tc}$  the resistance of charge transfer associated with the OER in parallel with  $CPE_{dl}$  the constant phase element corresponding to the impedance of a double layer over an heterogeneous material electrode surface [28]. The values of  $R_s$  and  $R_{tc}$  calculated for the  $IrO_2$ /ATO electrodes are resumed in Table 1 along with other OER kinetic parameter values.

In consistency with the LSV results, the Nyquist plots of Figure 7 show that OER is faster when the  $IrO_2$  is supported on ATO (3h), followed by supporting on ATO (12h) as can be seen by their smaller semicircles in the complex impedance plane. In contrast, the ATO (15h) support shows the bigger  $R_{tc}$  value (c.a. 577  $\Omega$ ) that means the slowest reaction rate for oxygen evolution on the support materials studied in this work. The rest of ATO supports obtained at other heat treatment times showed intermediate  $R_{tc}$  values.

With the results of this study it was not possible to explain the non-linear behavior obtained for the annealing times of ATO preparation effect on the OER catalytic activity obtained over the  $IrO_2$ /ATO electrodes.

Table 1. Onset potential and kinetics parameters for OER on  $IrO_2$ /ATO electrodes in  $O_2$  free 0.5 M  $H_2SO_4$ .

	$E_{OER}$ (NHE)/V	$j / (mA\ cm^{-2})$ @ 1.57 V	$R_s / \Omega$	$R_{ct} / \Omega$ @ 1.57 V	$b / (mV\ dec^{-1})$	
					$\eta_{low}$	$\eta_{high}$
<b><math>IrO_2</math>/ATO(3h)</b>	1.5	16.2	4	42	62	-
<b><math>IrO_2</math>/ATO(6h)</b>	1.55	5.7	3	230	68	-
<b><math>IrO_2</math>/ATO(9h)</b>	1.55	4.5	3.5	321	78	120
<b><math>IrO_2</math>/ATO(12h)</b>	1.5	15.8	7.5	184	65	-
<b><math>IrO_2</math>/ATO(15h)</b>	1.55	4.5	4.5	577	75	122
<b><math>IrO_2</math>/C</b>	1.41	-	4.1	284 @ (1.49V)	60	-
<b>Pt/ATO(3h)</b>	2	-	6.8	1050 @ (2V)	-	-

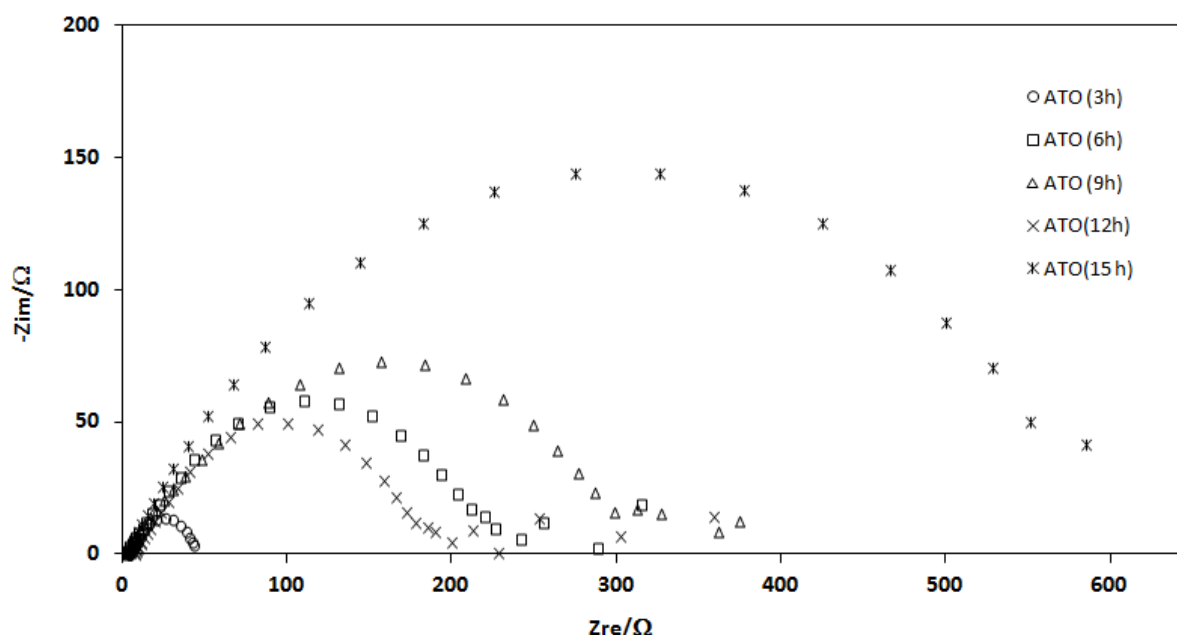


Figure 7. Nyquist plots for OER on IrO<sub>2</sub>/ATO electrodes at anodic potential value of 1.57 V, in O<sub>2</sub>-free 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions

#### 4. CONCLUSIONS

Electrochemical studies were performed for the OER on IrO<sub>2</sub>/ATO electrodes. The OER was assessed using the ATO with different heat treatment time as support. The results show that the catalytic activity of the electrocatalyst depend on the annealing time of ATO supports, the best behavior corresponding to ATO (3h) followed by the ATO(12h) one. Further characterization of ATO is necessary to explain the non-linear behavior of thermal times respect to its performance as a support for the OER.

The study has showed that the Sb-doped SnO<sub>2</sub> (ATO) is a promising supports for WE and URFC. The OER onset potential of IrO<sub>2</sub> on ATO is near to observed on the Vulcan carbon, this could mean that the electronic conductivity and catalyzer dispersion properties are similar in both support materials.

#### 5. ACKNOWLEDGMENTS

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