

Electrochemical Evaluation of IrO₂ and Pt Supported on ATO-Vulcan Mixtures for Reduction and Evolution Oxygen Reactions

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ABSTRACT

In the search of get better supports for PEM electrolyzers and fuel cells, one approach is to prepare a mixture of different supports in order to obtain an improvement in the global performance by taking advantage of their individual properties. In this work it is reported the evaluation of the electrochemical response of mixtures ATO-Vulcan as catalytic supports for ORR and OER. Pt and IrO₂ were used as catalysts in the electrochemical oxygen reactions. The ATO was synthesized by a co-precipitation reaction and the supports mixture was prepared mechanically in a fixed proportion (50:50 wt %). The using of IrO₂ on the mixed support showed an improvement near to 50 mV in the onset potential of oxygen evolution respect to the Vulcan only support. While mixed support with Pt for RRO showed an increase in the current density, near to the response obtained when Vulcan alone was used as support. The ATO presence in the mixture got better stability to the support. The electrochemical study was carried out by using CV, VL, RDE, EIS and chronoamperometry techniques.

1. Introduction

The operating conditions of ORR and EOR set the properties of materials that must have to be used as electrocatalysts or supports in PEM electrolyzers and fuel cells. Catalyst development is critical in these fields. The best catalysts for the ORR consist of Pt but this has only moderate activity for the OER. Ru and Ir oxides are the best OER catalysts, but they are not as active for the ORR as Pt. Alloys of Pt, Ir, and Ru have consequently been evaluated for bifunctional oxygen electrode activity, and they were shown to perform better than the pure metals or metal oxides. Although it is commonly acknowledged the use of this metals show a better performance in the ORR than in the OER, presenting a high overpotential for the oxygen evolution[1-3]. Nevertheless, bifunctional catalyst development remains a major challenge as the best catalysts require significant overpotentials for both reactions and consist of precious metals that are both scarce and expensive[4, 5]. In the other hand, despite of that the Vulcan coal and others carbonaceous materials show a well behavior as catalytic supports in FC, the high electrical potential (1.6 V vs. ENH) used in an electrolyzer corrodes them, producing degradation of carbon material and a loss of



electrical contact, this reason it is necessary to find an alternative support or experimenting with mixtures of these, which must be stable to a high potential of operation and it provides a higher electrical conductivity for the reactions of the oxygen electrode. 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[6-13].

Tin dioxide (SnO_2) is an important semiconducting material which has been widely used in an extensive range of applications such as catalysts, gas sensors, heat mirrors, varistors, transparent electrodes for solar cells [14-16]. The SnO_2 powder have been much attention since they are highly conducting, recently, some research have pointed out the need for more detailed study including nanocrystalline size and impurity effect of pure SnO_2 , the impurity – doped SnO_2 powders have been found to be more active as conductive fillers then pure SnO_2 [17, 18]. The electrical and optical properties of SnO_2 can increase significantly as it is doped with suitable dopants, such as antimony, fluorine or indium, etc. When the tin dioxide is doped with antimony its known as ATO, and different studies show that the ATO has characteristics of high resistance to corrosion in acid media and when it is doped with conductive species as Sb^{5+} , its electrical conductivity increases to 10^2 or $10^3 \Omega^{-1} \text{cm}^{-1}$ [19-21]. 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 recent year, enormous efforts have been made towards synthesis of ultrafine ATO nanoparticles, one of them is by co- precipitation, this route gives high yield and relatively low cost [22-24].

In the search for find support that can be used in the oxygen reactions, in this paper shows the results of the electrochemical evaluation of vulcan-ATO mixture for ORR and OER, to obtain an improvement in the global performance by taking advantage of their individual properties.

2. EXPERIMENTAL SECTION

2.1 Preparation of ink: Vulcan-ATO mixture and electrocatalyst

The ATO was synthesized by a co-precipitation reaction and the supports mixture was prepared mechanically with the following proportion: 100 μL of Nafion® (5 wt. %, Aldrich), 600 μL of ethanol spectroscopic grade, 6 mg of IrO_2 or Pt, 3 mg of ATO and 3 mg of vulcan. The ink was obtained using a FRITSCH/PULVERISETTE 23 mini-mill for a period of 1 h in order to homogenize the mixture and promote dispersion of the ink. Later, the resulting suspensions were hold in an ultrasonic bath for 1 h in aim to gain additional dispersion of mixture.

2.2 Electrochemical characterization



2.2.1 Electrodes preparation

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 60°C for 10 min. In order to comparison a Pt or IrO_2 supported on vulcan-ATO mixture electrodes were used as working electrodes for the OER and ORR 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 = 0.694V 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 $0.5 \text{ M H}_2\text{SO}_4$ 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).

Cyclic voltammetry (CV) was carried out to evaluate the effect of vulcan-ATO mixture in the IrO_2 or Pt electrodes by scanning the potential at a rate of 50 mV s^{-1} between -0.1 V and 1.54 V under a N_2 atmosphere electrolyte solution. OER experiments were performed by linear scan voltammetry (LSV) at a scan rate of 5 mV s^{-1} in the anodic direction from 0.59 V to 1.69 V in O_2 -free electrolyte solution at a constant electrode rotation frequency of 1000 rpm. The rotation rate was controlled by a PINE MSR-X precision rotating system.

For the ORR used RDE scanning the potential at a rate of 5 mV s^{-1} between 1 V and 0.39 V under a O_2 atmosphere electrolyte solution at different rate of rotation frequency (100, 225, 400, 625, 900 and 1600 rpm).

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 0.8V for ORR and 1.55 V for OER of potential with alternate signal amplitude of 10 mV .

Chronoamperometry technique for OER were performed at a potential of 1.63 V for 8 hour.

3. RESULTS AND DISCUSSION

3.1 Evaluation of the supports by cyclic voltammetry

Figure 1 and 2 shows cyclic voltammograms obtained for IrO_2 and Pt supported on ATO, vulcan and ATO-Vulcan mixture respectively in N_2 saturated $0.5 \text{ M H}_2\text{SO}_4$ solution. The CV diagrams (Figure 1), reveal that the



electrochemical response for Pt present change with the use of different support, the Pt/Vulcan shows the known behavior of Pt, where the process adsorption and desorption of H_2 , the redox reaction of Pt and OER are present; on the other hand the Pt/ATO-Vulcan mixture have a similar behavior, however, the process adsorption and desorption of H_2 are not defined clearly, in the case of Pt/ATO the process mentioned are less evident, show an offset in the potential at which the Pt reduction process performed. Also is showed that the current density (j) attributed to Pt supported on vulcan and mixture are greater than the ATO, this enhancement may be considered evidence that the dispersion of Pt is improved with the use of these supports.

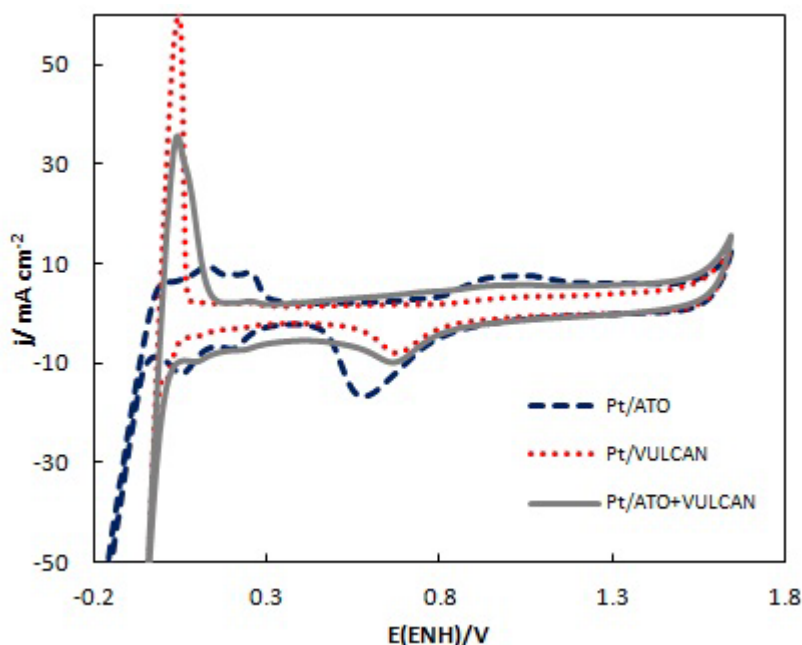


Figure 1 Cyclic voltammograms of GCEs coated with Pt support on different materials in 0.5 M H_2SO_4 at 50 mV s^{-1} with atmosphere: N_2 and room temperature.

Figure 2 shows cyclic voltammograms obtained for IrO_2 supported on vulcan, ATO-Vulcan mixture and ATO in N_2 saturated 0.5 M H_2SO_4 solution. The CV diagrams reveal that the electrochemical response for IrO_2 is practically unchanged with the use of different supports. Also is showed that the current density (j) attributed to IrO_2 supported on ATO-Vulcan mixture is greater than the rest of the supports; this enhancement may be considered evidence that the dispersion of IrO_2 is improved with the use of this supports. The off-peak potential for oxygen evolution on the different supports appears between 1.4 and 1.6 V, although this behavior is more evident in VL.

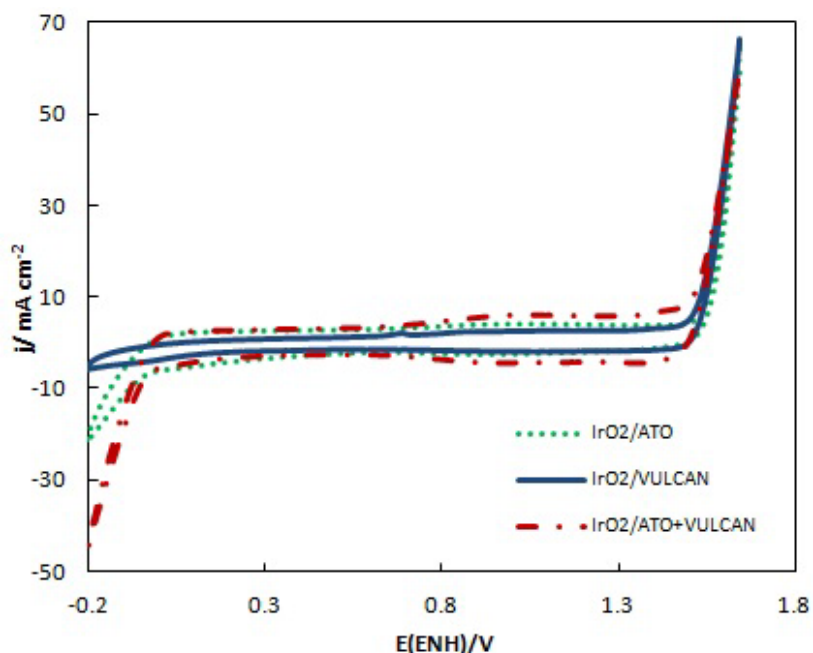


Figure 2 Cyclic voltammograms of GCEs coated with IrO_2 support on different materials in 0.5 M H_2SO_4 at 50 mV s^{-1} with atmosphere: N_2 and room temperature.

3.2 OER activity of the IrO_2 support on vulcan, ATO and Vulcan-ATO mixture

The Figure 3 shows linear scan voltammograms for OER with IrO_2 support on vulcan, ATO and Vulcan-ATO mixture in 0.5 M H_2SO_4 at a scan rate of 5 mVs^{-1} . Since the 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 support used in the electrodes. It is observed that the OER begins in a potential near to 1.45 V when the IrO_2 is supported on Vulcan, while that for the IrO_2 supported on ATO-Vulcan mixture the EOR onset occurs near to 1.5 V and finally the IrO_2 supported on ATO the OER begins in a potential near to 1.57 V. It can be observed that the oxygen evolution occurs in a potential about 50 mV lees anodic when the IrO_2 is supported on the mixture respect to the onset OER potential obtained with the IrO_2 /Vulcan electrode, this is argument show that ATO-Vulcan is feasible option for OER.

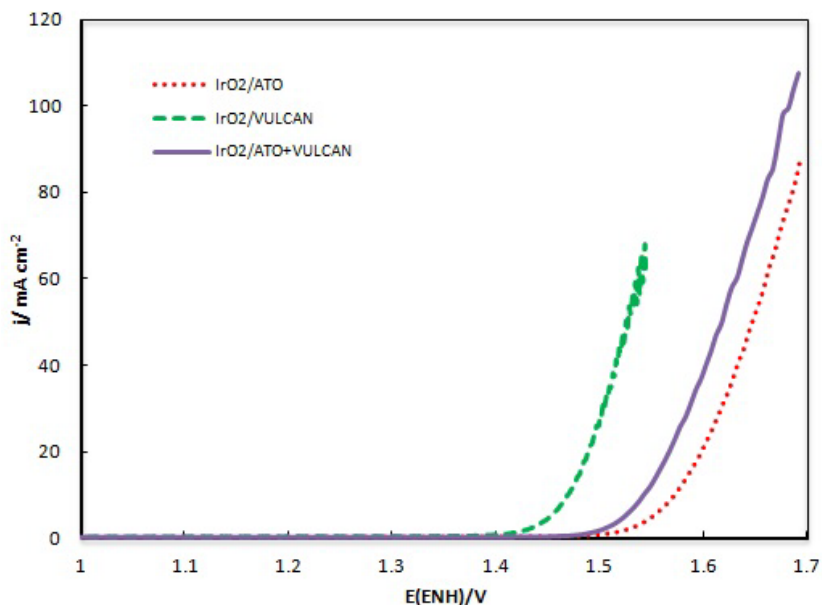


Figure 3 Linear voltammograms for OER IrO_2 support on Vulcan, ATO and Vulcan-ATO electrodes in N_2 saturated 0.5 M H_2SO_4 , at $v=5 \text{ mVs}^{-1}$.

3.3 ORR activity of the Pt supported on Vulcan, ATO and Vulcan-ATO mixture

For the ORR used RDE for meet the behavior of Pt support on Vulcan, ATO and Vulcan-ATO, obtained a typical diagram j - V depend on the rotating speed of RDE, the j increases when the speed of rotation also done [25-27]. The ORR curves have the zone mixed, kinetic and diffusion control, the reaction in the potential region between 1 V and 0.4 V, followed by a region where the diffusion limiting current ($\sim 2 \text{ mA cm}^{-2}$ for Pt/ATO, $\sim 2.6 \text{ mA cm}^{-2}$ for Pt/Vulcan-ATO and $\sim 4.6 \text{ mA cm}^{-2}$ for Pt/vulcan) was observed (Figure 4). The difference in the limiting currents for different support may be attributed the surface coverage of the catalyst and the physical properties such as the porosity of the thin catalyst layer and nature the supports deposited on the glassy carbon electrode.

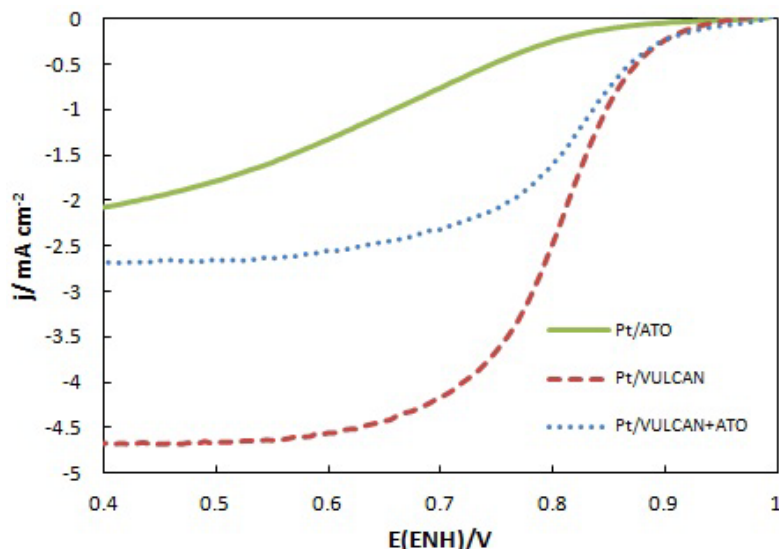


Figure 4 RDE for ORR of Pt support on Vulcan, ATO and Vulcan-ATO mixture electrodes in O_2 saturated 0.5 M H_2SO_4 , at $v=5 \text{ mVs}^{-1}$.

3.4 Electrochemical impedance spectroscopy performance for OER and ORR

EIS measurements for oxygen evolution was carried out on IrO_2 on Vulcan, ATO-Vulcan and ATO in O_2 -free 0.5 M H_2SO_4 solution, in the potentiostatic mode at an anodic potential of 1.55 V. Figure 5 shows the Nyquist plots for OER that in consistency with the LV results, the plots show that OER is faster when the IrO_2 is supported on vulcan (with $R_s=3.5 \Omega$ and $R_{tc}=93 \Omega$ @ 1.51 V), followed by supporting on mixture (with $R_s=3.5 \Omega$ and $R_{tc}=77 \Omega$ @ 1.55 V), and finally on ATO (with $R_s= \Omega$ and $R_{tc}=103 \Omega$ @ 1.55 V) as can be seen by their smaller semicircles in the complex impedance plane.

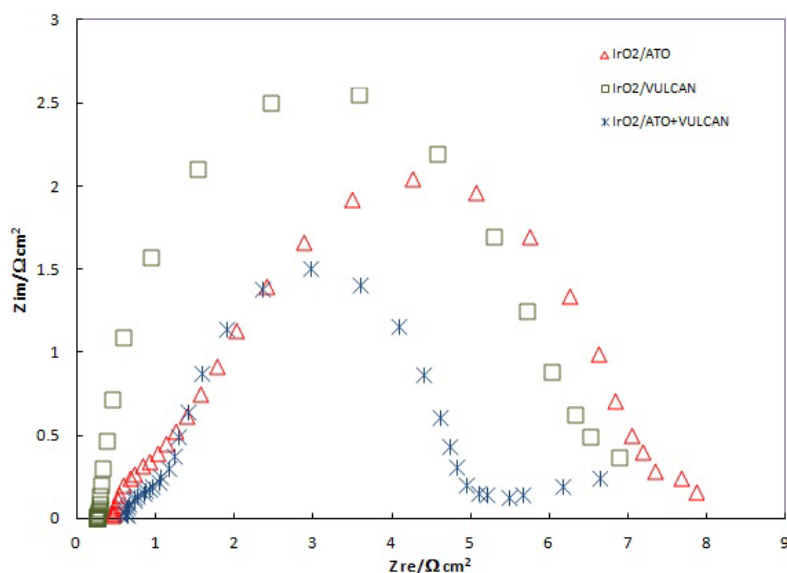


Figure 5 Nyquist plots for OER on IrO₂ support on Vulcan, ATO and Vulcan-ATO electrodes at anodic potential value of 1.55 V, in O₂-free 0.5 M H₂SO₄ solutions

EIS measurements for oxygen reduction was carried out on Pt on Vulcan, ATO-Vulcan and ATO in O₂ saturade 0.5 M H₂SO₄ solution, in the potentiostatic mode at an catodic potential of 0.8 V. Figure 6 shows the Nyquist plots for ORR that in consistency with the RDE, the plots show that ORR is faster when the Pt is supported on vulcan, followed by supporting on mixture, and finally on ATO as can be seen by their smaller semicircles in the complex impedance plane.

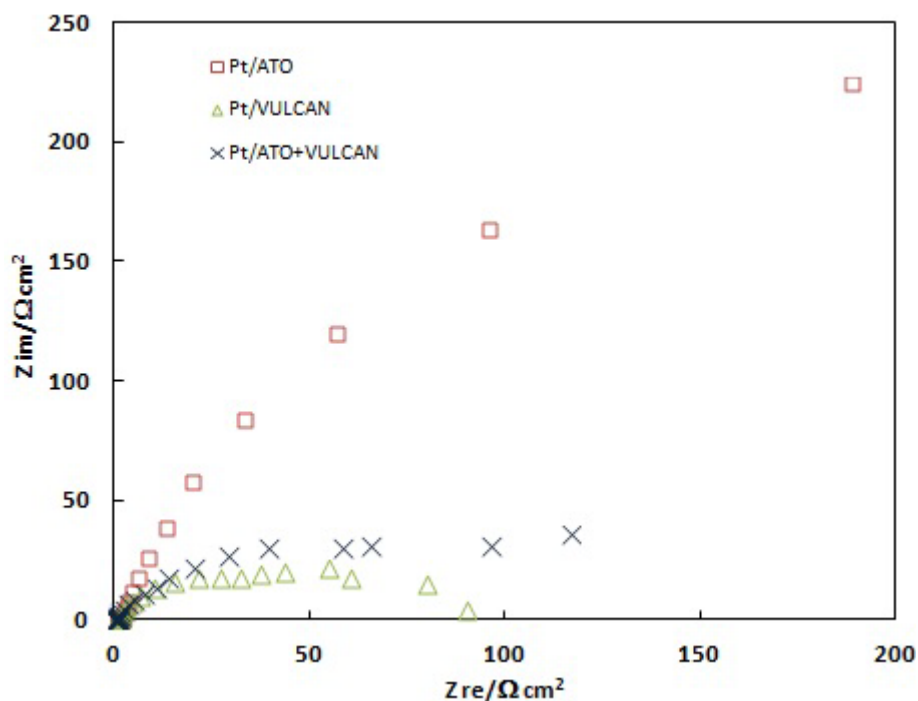


Figure 6 Nyquist plots for ORR on Pt support on Vulcan, ATO and Vulcan-ATO electrodes at anodic potential value of 0.8 V, in O₂, 0.5 M H₂SO₄ solutions

3.5 Chronoamperometry

The electrochemical stability is one important parameter for OER is necessary to apply a potential proximate to 1.6 V vs. ENH for splitting the water into H₂ and O₂ by this reason was evaluated only IrO₂ on different supports at room temperature as shown in Figure 7. The potential was 1.63 V for 8 h. The decay rate more faster was of IrO₂ support on Vulcan follow of IrO₂ support on mixture although this present one higher current respect at IrO₂ /Vulcan, but both electrodes present attenuates of current at 4.5 h approximate and finally the IrO₂ /ATO presents greater stability along 8 h, although the current density is lower with respect to other supports.

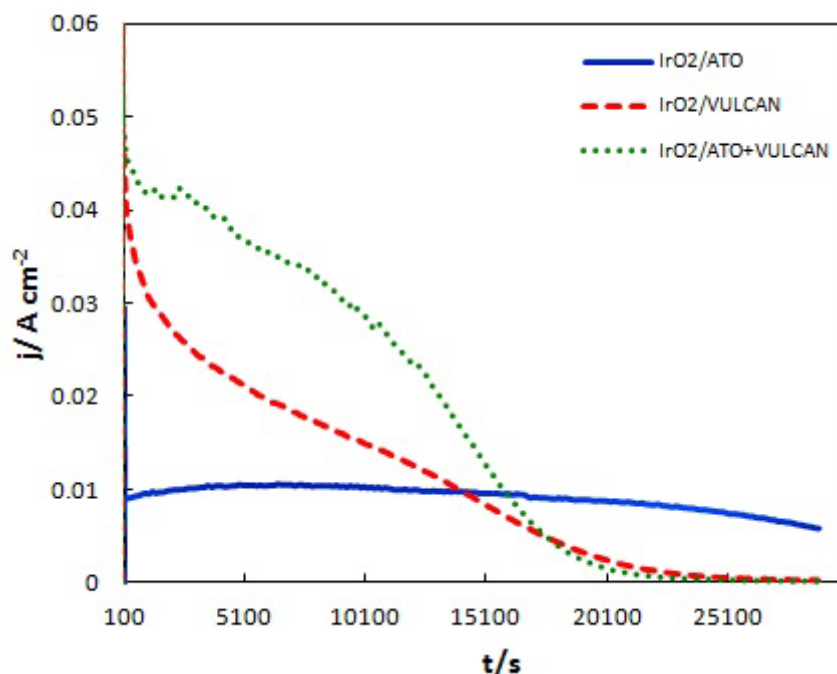


Figure 7 Chronoamperograms of IrO₂ on different supports for OER in 0.5 M H₂SO₄, at 1.63 V, at room temperature.

4. CONCLUSIONS

Electrochemical studies were performed for the OER and ORR IrO₂ or Pt on ATO, Vulcan and ATO-Vulcan electrodes. The OER was evaluated using the IrO₂ on ATO, Vulcan and ATO-Vulcan as supports. The results show that the catalytic activity of the electrocatalyst depend the support used, in this case the support mixture is option for are used in WE. The ORR was evaluated using the Pt on ATO, Vulcan and ATO-Vulcan as supports. The results show that the catalytic activity of the electrocatalyst depend the support used, in this case the vulcan is la option more workable for ORR, however, the support mixture is option for are used in this reaction too. Further improvements in synthesis of ATO are necessary to increase the electrochemical properties of support mixture. The study has showed that the ATO-Vulcan mixture is a promising supports for WE and FC. The electrochemical response for OER and ORR is similar to observed when Vulcan is used, this could mean that the electronic conductivity and catalyzer dispersion properties are similar in this support materials.

5. ACKNOWLEDGMENTS

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