

# Morphological and Electrochemical Characterization of $\text{Ti}/\text{M}_x\text{Ti}_y\text{Sn}_z\text{O}_2$ (M = Ir or Ru) Electrodes Prepared by the Polymeric Precursor Method

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## Abstract

This paper describes the effect of the composition of the oxide films on the properties of electrodes  $\text{Ti}/\text{M}_x\text{Ti}_y\text{Sn}_z\text{O}_2$  (M = Ir or Ru) prepared by the polymeric precursor method. XRD studies showed that the anodes are formed by solid solutions. The electrodes containing  $\text{IrO}_2$  exhibit lower activity for the oxygen evolution reaction. The doping of the electrode surface with  $\text{SnO}_2$  improves the catalytic properties of the anodes. However, it should be held in appropriate compositions, because the change in the atomic ratio of this element shows a marked effect on the stability of the oxides. Electrode  $\text{Ti}/\text{Ir}_{0.2}\text{Ti}_{0.3}\text{Sn}_{0.5}\text{O}_2$  has lower lifetime, *i.e.* 6 hours. The 20% decrease in the stoichiometric amount of  $\text{SnO}_2$  increases the time to a value above 70 hours, as observed for  $\text{Ti}/\text{Ir}_{0.3}\text{Ti}_{0.4}\text{Sn}_{0.3}\text{O}_2$ . Electrode  $\text{Ti}/\text{Ru}_{0.3}\text{Ti}_{0.4}\text{Sn}_{0.3}\text{O}_2$  shows lifetime of 11 hours; therefore  $\text{IrO}_2$  is more stable than  $\text{RuO}_2$  under the conditions investigated. These results suggest that electrode  $\text{Ti}/\text{Ir}_{0.3}\text{Ti}_{0.4}\text{Sn}_{0.3}\text{O}_2$  is promising for different applications, such as water electrolysis, capacitors and organic electrosynthesis.

## Keywords

Dimensionally Stable Anodes (DSA), Oxide Films, Electrochemical Properties, Polymeric Precursor Method

## 1. Introduction

Oxide electrodes have been technologically important since the discovery of dimensio-

nally stable anodes (DSA<sup>®</sup>) by Beer [1] and their applications in chlor-alkali industries. These electrodes constitute a mixture of oxides frequently prepared by standard thermal decomposition (SD) of metallic precursor salts in aqueous or alcohol solution, supported by metallic titanium [2].

The electro-catalytic properties of metal oxides are associated with electronic and geometric factors [3]. The electronic factor is related to the chemical composition of the film, hence the physico-chemical properties of the constituent oxides, affecting the adhesion strength surface/intermediate. The geometric factor is directly related to the morphology of the film.

Research has been conducted to find new materials and procedures to improve the performance of DSA, for example, thermal decomposition of iridium and/or ruthenium precursor salts [4] [5], thermal decomposition of hydroxo-aceto-chloro-based precursors [6], Ti/TiO<sub>2</sub> nanotubes prepared by anodization method [7] spin coating deposition technique [8]. The total or partial deactivation of thin films prepared by SD can be observed when they operate under drastic conditions and in a short period of time [4] [9] [10]. Electrodes as Ti/RuO<sub>2</sub> and Ti/IrO<sub>2</sub>, prepared by the decomposition of polymeric precursors (Pechini method) [11], have shown better electrochemical activity, *i.e.* longer life and higher active area than those prepared by the method of chlorides [12]-[14]. Moreover, the chemical or mechanical stability of oxide electrodes can be enhanced by incorporating/doping other metal ions into the films [3].

The polymeric precursor method consists in the formation of chelates between metal cations and carboxylic acid and subsequent polymerization by a polyesterification reaction with polyalcohol [15]. The central idea is to distribute the cations throughout the polymeric structure. Heat treatment causes the release of organic matter and the formation of crystallites duly ordained [16]. This result is particularly interesting when the aims are to obtain materials with high crystallinity and controlled distribution of the constituents in the crystalline lattice.

This study investigates the morphological and electrochemical properties of oxide electrodes Ti/Ir<sub>0.3</sub>Ti<sub>0.4</sub>Sn<sub>0.3</sub>O<sub>2</sub>; Ti/Ir<sub>0.2</sub>Ti<sub>0.3</sub>Sn<sub>0.5</sub>O<sub>2</sub> and Ti/Ru<sub>0.3</sub>Ti<sub>0.4</sub>Sn<sub>0.3</sub>O<sub>2</sub> prepared by the thermal decomposition of polymeric precursors.

## 2. Experimental

### 2.1. Preparation of Electrodes

Thin film electrodes of nominal compositions Ir<sub>0.3</sub>Ti<sub>0.4</sub>Sn<sub>0.3</sub>O<sub>2</sub>, Ir<sub>0.2</sub>Ti<sub>0.3</sub>Sn<sub>0.5</sub>O<sub>2</sub> and Ru<sub>0.3</sub>Ti<sub>0.4</sub>Sn<sub>0.3</sub>O<sub>2</sub> were prepared by the thermal decomposition of a polymeric precursor solution (DPP) [11]. This method consists in synthesizing resins of metallic precursors by mixing citric acid (CA) in ethylene glycol (EG). The Ru, Ir, Sn, and Ti resins were prepared separately. First, 8 g of citric acid (Merk) were dissolved in 9 mL ethylene glycol (Merk) at 60°C - 65°C. After the dissolution of the acid, a solution of the precursor metal in isopropanol with 0.1 mol·L<sup>-1</sup> concentration (RuCl<sub>3</sub>·xH<sub>2</sub>O, IrCl<sub>3</sub>·xH<sub>2</sub>O, TiCl<sub>2</sub>·6H<sub>2</sub>O all purchased from Aldrich and C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>Sn<sub>2</sub> synthesized from SnCl<sub>2</sub> (Aldrich), as described in [17]), was added to the CA/EG solution. The temperature was

then raised up to 85°C - 90°C and the solution under was kept under rigorous stirring (300 rpm) for 1 - 2 hours for esterification and total isopropanol evaporation.

The precursor solutions were deposited on both sides of the pretreated metallic titanium (2.5 × 2.5 cm) by brushing, as described in the literature [12]. After the application of the coating, the electrodes were dried at 130°C for 5 minutes and then calcined at 450°C for 5 minutes. This procedure was repeated until the desired mass (125 mg·cm<sup>-2</sup>) had been achieved. The layers were finally annealed at 450°C for 1 hour under air flow.

## 2.2. Morphological and Electrochemical Characterizations

This measurement and others are deliberate, using specifications that anticipate your paper as one part of the entire journals, and not as an independent document. Please do not revise any of the current designations. The crystalline structures were physically characterized by X-ray diffraction (XRD) using an XRD-6000 diffractometer (Shimadzu) with a CuK $\alpha$  radiation source ( $\lambda = 1.5406 \text{ \AA}$ ) operating in the continuous scan mode (4° min<sup>-1</sup>) from 10° to 90°.

The surface morphology and microstructure of the deposited oxide films were analyzed through optical microscopy and scanning electron microscopy (SEM). Photomicrographs were obtained by a Zeiss LEO model 440 SEM coupled to an OXFORD operating with electron beam of 15 kV. The average composition was analyzed by PGT PRISM energy dispersive X-ray spectrometer (EDX) coupled to the SEM instrument.

## 2.3. Electrochemical Measurements

Electrochemical experiments were conducted with AUTOLAB model PGSTAT30 instrumentation. Voltammetric curves were recorded at scan rate of 50 mV·s<sup>-1</sup> using 0.5 mol·dm<sup>-3</sup> of H<sub>2</sub>SO<sub>4</sub> as the supporting electrolyte. A platinum foil served as the auxiliary electrode and the KCl saturated calomel electrode (SCE) was used as the reference. The cell was thermostated at 25°C.

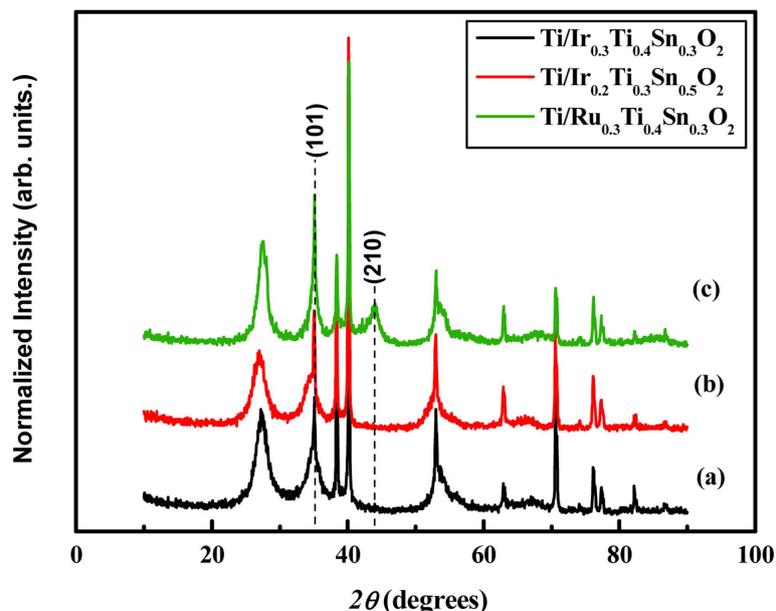
Impedance spectra were recorded at constant potential between 0.3 and 1.4 V vs Ag/AgCl. Electrochemical impedance spectroscopy (EIS) measurements were obtained in the 5 mHz - 10 kHz frequency interval using the "single sine" method and a sine wave amplitude of 5 mV (p/p). An AUTOLAB software program (FRA analyzer) was used for the analysis of the impedance data.

The stability of the electrodes was assessed based on their lifetime (LT) under galvanostatic conditions at a high current density (400 mA·cm<sup>-2</sup>) in 0.5 mol·dm<sup>-3</sup> of H<sub>2</sub>SO<sub>4</sub>. The electrode lifetime was considered the time necessary for the electrode potential to achieve a value of 8.0 V.

## 3. Results and Discussion

### 3.1. Morphological and Chemical Characterizations

**Figure 1** shows the XRD patterns for different compositions of electrodes prepared at 450°C. In the electrodes containing iridium, characteristic diffraction peaks were



**Figure 1.** XRD patterns obtained for the oxide electrodes with different nominal compositions (a)  $\text{Ti/Ir}_{0.3}\text{Ti}_{0.4}\text{Sn}_{0.3}\text{O}_2$ ; (b)  $\text{Ti/Ir}_{0.2}\text{Ti}_{0.3}\text{Sn}_{0.5}\text{O}_2$ ; (c)  $\text{Ti/Ru}_{0.3}\text{Ti}_{0.4}\text{Sn}_{0.3}\text{O}_2$ .

observed and attributed to  $\text{IrO}_2$ , according to JCPDS PDF #15-0870.  $\text{Ti/Ru}_{0.3}\text{Ti}_{0.4}\text{Sn}_{0.3}\text{O}_2$  showed two peaks, one at  $2\theta = 43.7^\circ$  and another at  $2\theta = 53.6^\circ$ , which correspond to  $\text{RuO}_2$  JCPDS PDF #40-1290. However, by comparing the positions of the peaks in the XRD obtained with the respective pure oxide, it is possible to observe that Sn-rich electrode composition displays peaks shifted toward the pure  $\text{SnO}_2$  pattern JCPDS PDF #46-1088, indicating that Ir and/or Ti atoms may be incorporated into the  $\text{SnO}_2$  crystalline reticule. The opposite trend is observed for Ru-electrode composition, which have their peaks shifted toward the pure  $\text{RuO}_2$  pattern due to the incorporation of Sn and/or Ti atoms into the  $\text{RuO}_2$  crystalline reticule. All samples displayed typical crystalline characteristics of tetragonal, with space group P42/nm. All those evidences suggesting the formation of a saturated solid solution for all the compositions investigated, one for Ir/Ti/Sn and other for Ru/Ti/Sn compositions. The XRD patterns show that all materials synthesized contained the Ti phase attributed to the Ti metallic substrate.

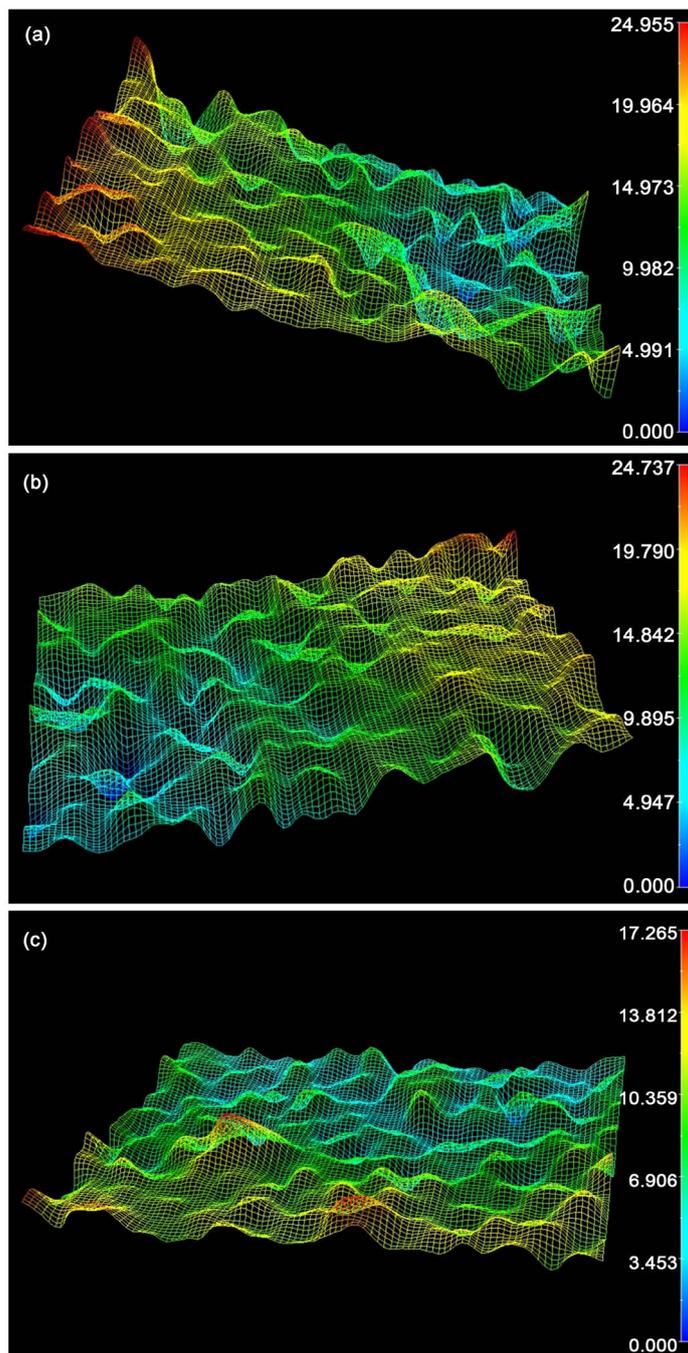
The average crystallite sizes of the oxide particles were estimated by the Debye-Scherrer equation [18] at crystalline planes ((210):  $2\theta = 43.7^\circ$ ) for  $\text{Ti/Ru}_{0.3}\text{Ti}_{0.4}\text{Sn}_{0.3}\text{O}_2$ , and ((101):  $2\theta = 34.5^\circ$ ) for  $\text{Ti/Ir}_{0.2}\text{Ti}_{0.3}\text{Sn}_{0.5}\text{O}_2$  and  $\text{Ti/Ir}_{0.3}\text{Ti}_{0.4}\text{Sn}_{0.3}\text{O}_2$ . The values obtained were approximately 4 and 5 nm, respectively.

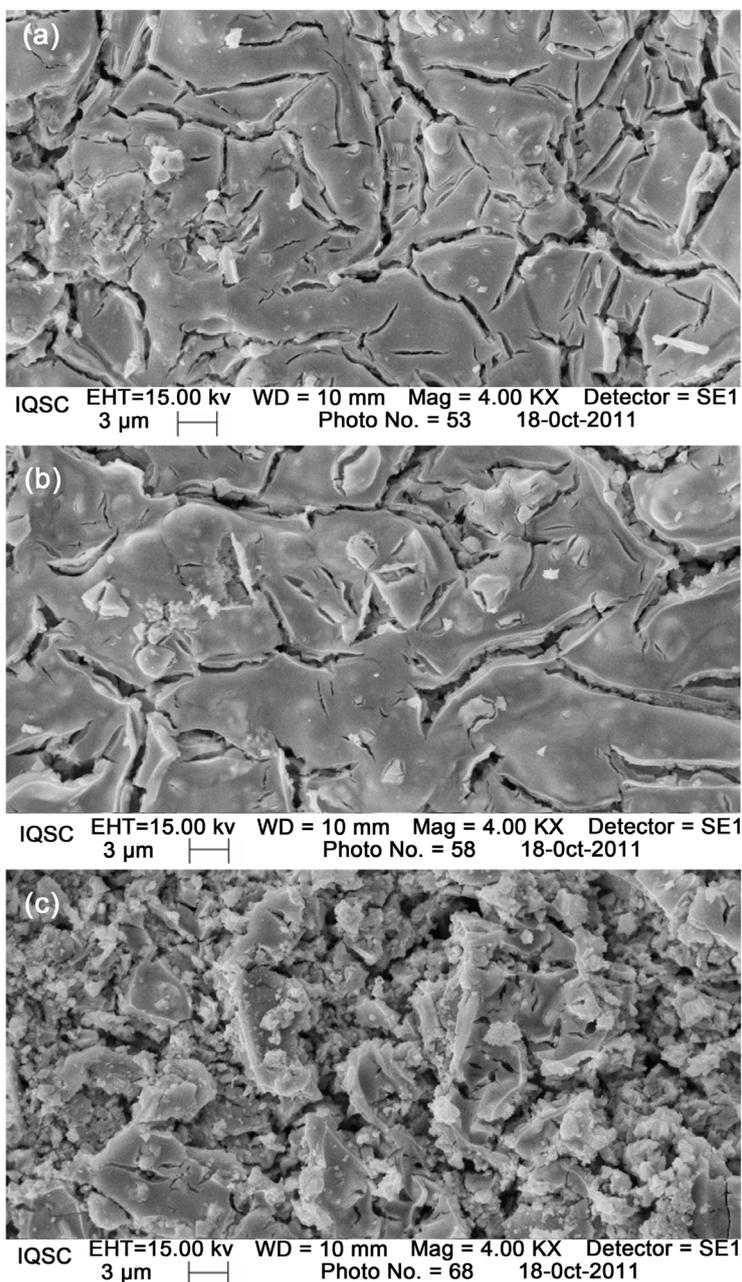
The roughness of the oxides **Table 1** was estimated from the optical microscopy analyses **Figure 2** performed in random areas of the film (average of five analyses). The electrode with nominal composition of  $\text{Ti/Ru}_{0.3}\text{Ti}_{0.4}\text{Sn}_{0.3}\text{O}_2$  showed the lowest roughness, which suggests that the morphology of the oxide layers is highly dependent on the physicochemical properties of the oxides and the nature of the precursors.

**Figure 3** shows some representative SEM images of the oxide films. Films containing

**Table 1.** Roughness estimated for the oxide films prepared by the polymeric precursor method.

	Roughness estimated ( $\mu\text{m}$ )
$\text{Ti}/\text{Ir}_{0.3}\text{Ti}_{0.4}\text{Sn}_{0.3}\text{O}_2$	13.9
$\text{Ti}/\text{Ir}_{0.2}\text{Ti}_{0.3}\text{Sn}_{0.5}\text{O}_2$	12.6
$\text{Ti}/\text{Ru}_{0.3}\text{Ti}_{0.4}\text{Sn}_{0.3}\text{O}_2$	8.3

**Figure 2.** Optical microscopy of the oxide electrodes, original magnification 350 $\times$  (a)  $\text{Ti}/\text{Ir}_{0.3}\text{Ti}_{0.4}\text{Sn}_{0.3}\text{O}_2$ ; (b)  $\text{Ti}/\text{Ir}_{0.2}\text{Ti}_{0.3}\text{Sn}_{0.5}\text{O}_2$ ; (c)  $\text{Ti}/\text{Ru}_{0.3}\text{Ti}_{0.4}\text{Sn}_{0.3}\text{O}_2$ . Beside each picture is displayed the scale in  $\mu\text{m}$ .



**Figure 3.** SEM surface image of the oxide electrodes, original magnification 4000 $\times$  (a)  $\text{Ti/Ir}_{0.3}\text{Ti}_{0.4}\text{Sn}_{0.3}\text{O}_2$ ; (b)  $\text{Ti/Ir}_{0.2}\text{Ti}_{0.3}\text{Sn}_{0.5}\text{O}_2$ ; (c)  $\text{Ti/Ru}_{0.3}\text{Ti}_{0.4}\text{Sn}_{0.3}\text{O}_2$ .

$\text{IrO}_2$  (a, b) show uniform and continuous structures with cracks, *i.e.*, mud-cracked-type morphology which are typical of thermally prepared oxide layers [10] [12]. Moreover, one observe that due to the increase in the amount of  $\text{SnO}_2$  in the electrode composition, cracks become larger (b), however the surface becomes less rough (see **Table 1**). However, the SEM image of the films containing  $\text{RuO}_2$  (c) indicate a distinct morphology, and in this case, the morphology change severally where the amount of fissures and cracks increase. The oxide surface morphology shows a clear relationship with the

coating compositions investigated.

**Table 2** shows the EDX analyses of the micrographs **Figure 3**. The EDX analysis of the electrodes indicated a good correlation between experimental and nominal compositions. The control of the composition of the films can be explained by the method used, since this polymer is formed before the calcination and the metal atoms are trapped in the matrix, which hinders its evaporation and consequent loss. All electrodes exhibited a homogenous distribution of particles on the electrode surface.

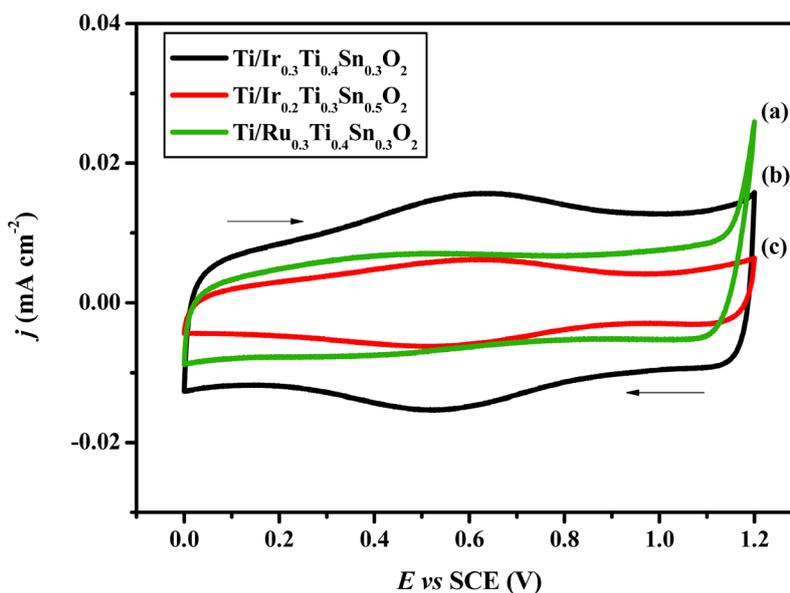
### 3.2. Electrochemical Characterizations

**Figure 4** shows the  $j/E$  curve obtained in the cyclic voltammetric experiments. This profile is typical of thermally prepared oxide layer electrodes [19] [20] and characteristic of DSA® electrodes [21]. The figure also shows a blurred peak at around 0.5 V associated with the Ru (III)/Ru(IV) redox transition [22] for the Ti/Ru<sub>0.3</sub>Ti<sub>0.4</sub>Sn<sub>0.3</sub>O<sub>2</sub> electrode. The voltammograms of the electrodes containing IrO<sub>2</sub> showed a peak typical of the Ir(III)/Ir (IV) transition in the region between 0.4 and 0.8 V [6].

The oxygen evolution reaction occurs at a more positive potential for the electrode containing the largest amount of SnO<sub>2</sub>. According to Fukunaga *et al.* [23], the doping of the electrode surface with SnO<sub>2</sub> is an effective strategy to improve performance even in

**Table 2.** Atomic ratios (%) of the oxide films with different nominal compositions.

	Ti	Ir	Ru	Sn
Ti/Ir <sub>0.3</sub> Ti <sub>0.4</sub> Sn <sub>0.3</sub> O <sub>2</sub>	50.8	25.1	-	24.1
Ti/Ir <sub>0.2</sub> Ti <sub>0.3</sub> Sn <sub>0.5</sub> O <sub>2</sub>	39.8	11.5	-	48.7
Ti/Ru <sub>0.3</sub> Ti <sub>0.4</sub> Sn <sub>0.3</sub> O <sub>2</sub>	40.6	-	36.7	22.7



**Figure 4.** Cyclic voltammograms at 50 mV·s<sup>-1</sup> in 0.5 mol·dm<sup>-3</sup> of H<sub>2</sub>SO<sub>4</sub> of the oxide electrodes vs. SCE (a) Ti/Ir<sub>0.3</sub>Ti<sub>0.4</sub>Sn<sub>0.3</sub>O<sub>2</sub>; (b) Ti/Ir<sub>0.2</sub>Ti<sub>0.3</sub>Sn<sub>0.5</sub>O<sub>2</sub>; (c) Ti/Ru<sub>0.3</sub>Ti<sub>0.4</sub>Sn<sub>0.3</sub>O<sub>2</sub>.

the treatment of degradation of organic compounds thus our results are in agreement with previous report.

The comparison between the electrode containing IrO<sub>2</sub> and those containing RuO<sub>2</sub> shows the IrO<sub>2</sub> exhibits lower activity for the oxygen evolution reaction.

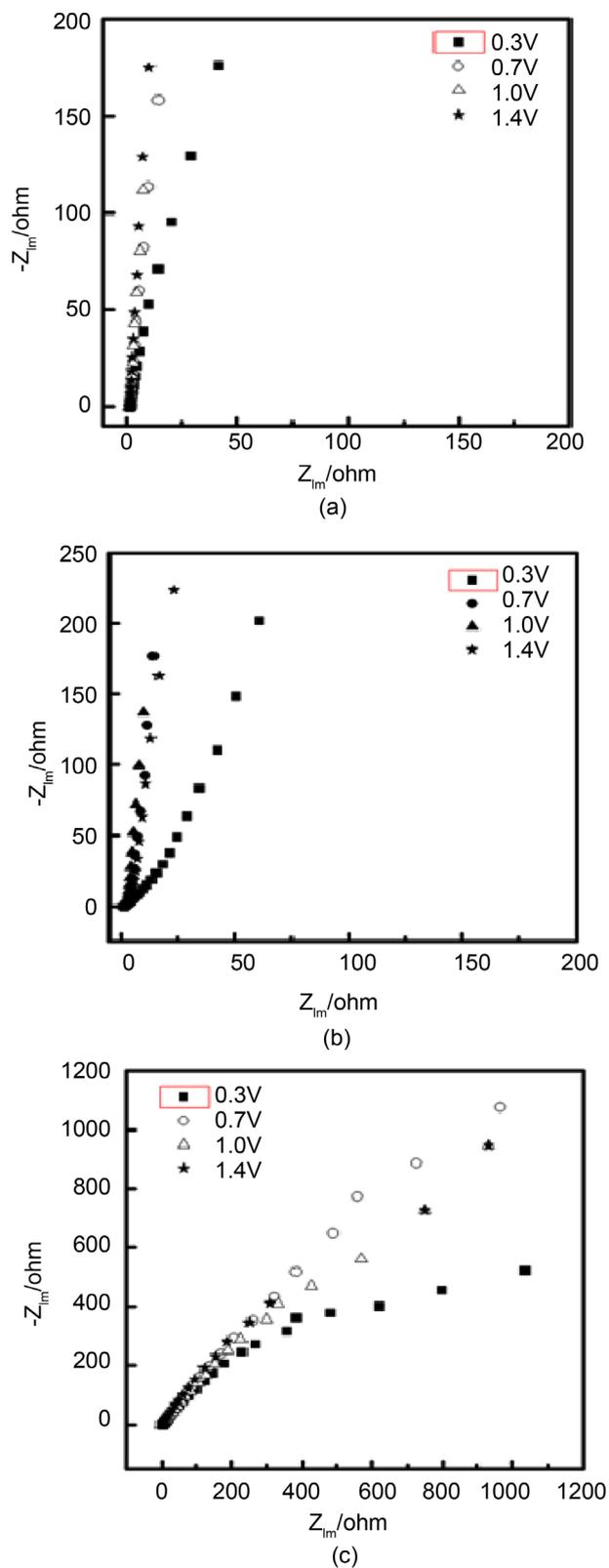
The impedance behavior of the electrodes was investigated to further characterize the different Ti/Ir<sub>0.3</sub>Ti<sub>0.4</sub>Sn<sub>0.3</sub>O<sub>2</sub>; Ti/Ir<sub>0.2</sub>Ti<sub>0.3</sub>Sn<sub>0.5</sub>O<sub>2</sub> and Ti/Ru<sub>0.3</sub>Ti<sub>0.4</sub>Sn<sub>0.3</sub>O<sub>2</sub> systems. The Nyquist diagram ( $Z'$  vs  $Z''$ ) of the electrodes obtained between 0.3 and 1.4 V vs Ag/AgCl is shown in **Figure 5**. In the low frequency domain, electrodes Ti/Ir<sub>0.3</sub>Ti<sub>0.4</sub>Sn<sub>0.3</sub>O<sub>2</sub> and Ti/Ir<sub>0.2</sub>Ti<sub>0.3</sub>Sn<sub>0.5</sub>O<sub>2</sub> formed a straight line parallel to  $Z''$ , characteristic of an ideally polarizable electrode, and a slight deviation from the straight line along  $Z''$ , suggesting a non-ideally polarizable electrode [24] [25]. The shift from the ideal capacitor behavior is a consequence of the material's porosity [24] [26]. In the low-frequency domain region a decrease in impedance was found when the applied potentials were positively shifted. This result suggests that the EIS responses in this domain region indicate a faradaic process of the bulk redox transitions of the oxide material. The difference observed between the Ir-based electrodes and Ru-based electrodes maybe could be explained due to the higher electronic conductivity in the Ru-Ti-Sn/solution than in the Ir-Ti-Sn/solution interfaces.

The Bode plot ( $\theta$  vs.  $\log f$ ) obtained at 0.3 V vs Ag/AgCl for electrodes is shown in **Figure 6**. An analysis of this figure indicates that the main feature of these electrodes is the appearance of a well-defined time constant ( $\tau$ ) for the Ti/Ru<sub>0.3</sub>Ti<sub>0.4</sub>Sn<sub>0.3</sub>O<sub>2</sub> electrode, which is characterized by a maximum phase angle ranging from 1 to 100 Hz. This behavior can be ascribed to the large number of RuO<sub>2</sub> transition states contributing to the charging system [27]. This results corroborated with the Nyquist plot interpretation above because the Ru-based electrode shows more pseudo capacitive behavior than the Ir-based electrode [10] [24].

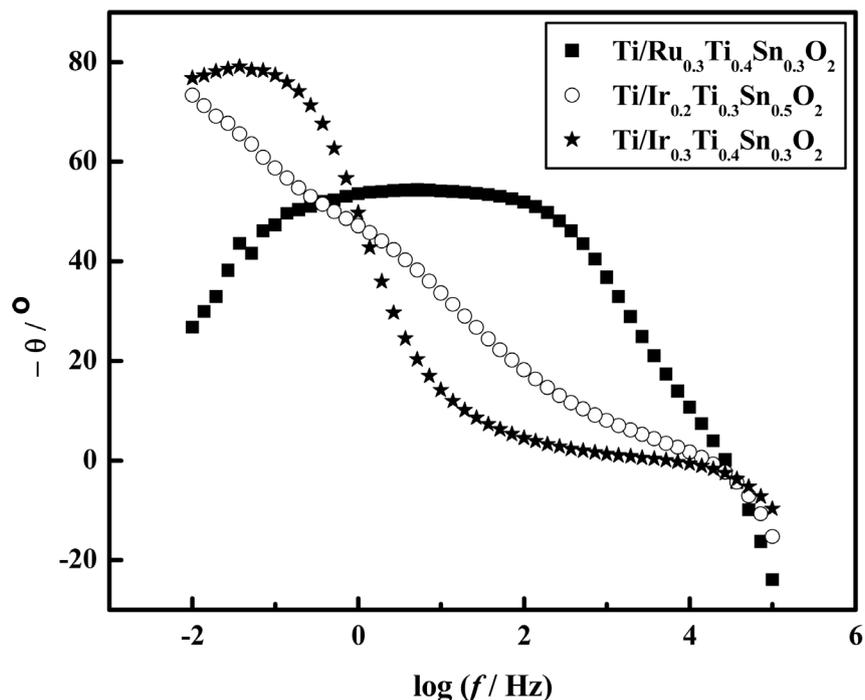
The stability of the electrodes was assessed based on their lifetime, considering the time necessary for the electrode potential to reach 8.0 V. The electrode containing larger amounts of SnO<sub>2</sub> (Ti/Ir<sub>0.2</sub>Ti<sub>0.3</sub>Sn<sub>0.5</sub>O<sub>2</sub>) has a shorter lifetime. The 20% decrease in the stoichiometric amount of this oxide as well as the high amount (10%) of IrO<sub>2</sub> (Ti/Ir<sub>0.3</sub>Ti<sub>0.4</sub>Sn<sub>0.3</sub>O<sub>2</sub>) increase the time to a value above 70 hours. Comparing the electrode Ti/Ir<sub>0.3</sub>Ti<sub>0.4</sub>Sn<sub>0.3</sub>O<sub>2</sub> with Ti/Ru<sub>0.3</sub>Ti<sub>0.4</sub>Sn<sub>0.3</sub>O<sub>2</sub>, IrO<sub>2</sub> has higher stability under drastic conditions of electrolysis than RuO<sub>2</sub> (**Table 3**).

The lifetime of oxide electrodes is directly correlated with two factors: passivation and dissolution of the coating [21]. The first factor is due to the penetration of the electrolyte through the pores or cracks towards the substrate, resulting in the oxidation of the metallic support and forming a non-conductive layer between the substrate and the oxide coating [28]-[30]. The second factor involves the loss of electroactive material (erosion or dissolution), resulting in a gradual reduction of the voltammetric charge. This may occur due to the pores in the layer and the rapid evolution of gas on the surface, inducing the separation of weakly bound parts of the active layer [28] [31] [32].

Morphological changes of the electrode surface after the lifetime test can be observed



**Figure 5.** Nyquist diagrams of the oxide electrodes as a function of the applied potential (0.3, 0.7, 1.0 and 1.4 V) vs. Ag/AgCl (a)  $\text{Ti}/\text{Ir}_{0.3}\text{Ti}_{0.4}\text{Sn}_{0.3}\text{O}_2$ ; (b)  $\text{Ti}/\text{Ir}_{0.2}\text{Ti}_{0.3}\text{Sn}_{0.5}\text{O}_2$ ; (c)  $\text{Ti}/\text{Ru}_{0.3}\text{Ti}_{0.4}\text{Sn}_{0.3}\text{O}_2$ .



**Figure 6.** Bode plot at 0.3 V vs. Ag/AgCl as a function of the oxide electrodes. (—○—)  $\text{Ti/Ir}_{0.2}\text{Ti}_{0.3}\text{Sn}_{0.5}\text{O}_2$ ; (—■—)  $\text{Ti/Ir}_{0.3}\text{Ti}_{0.4}\text{Sn}_{0.3}\text{O}_2$  (—★—)  $\text{Ti/Ru}_{0.3}\text{Ti}_{0.4}\text{Sn}_{0.3}\text{O}_2$ .

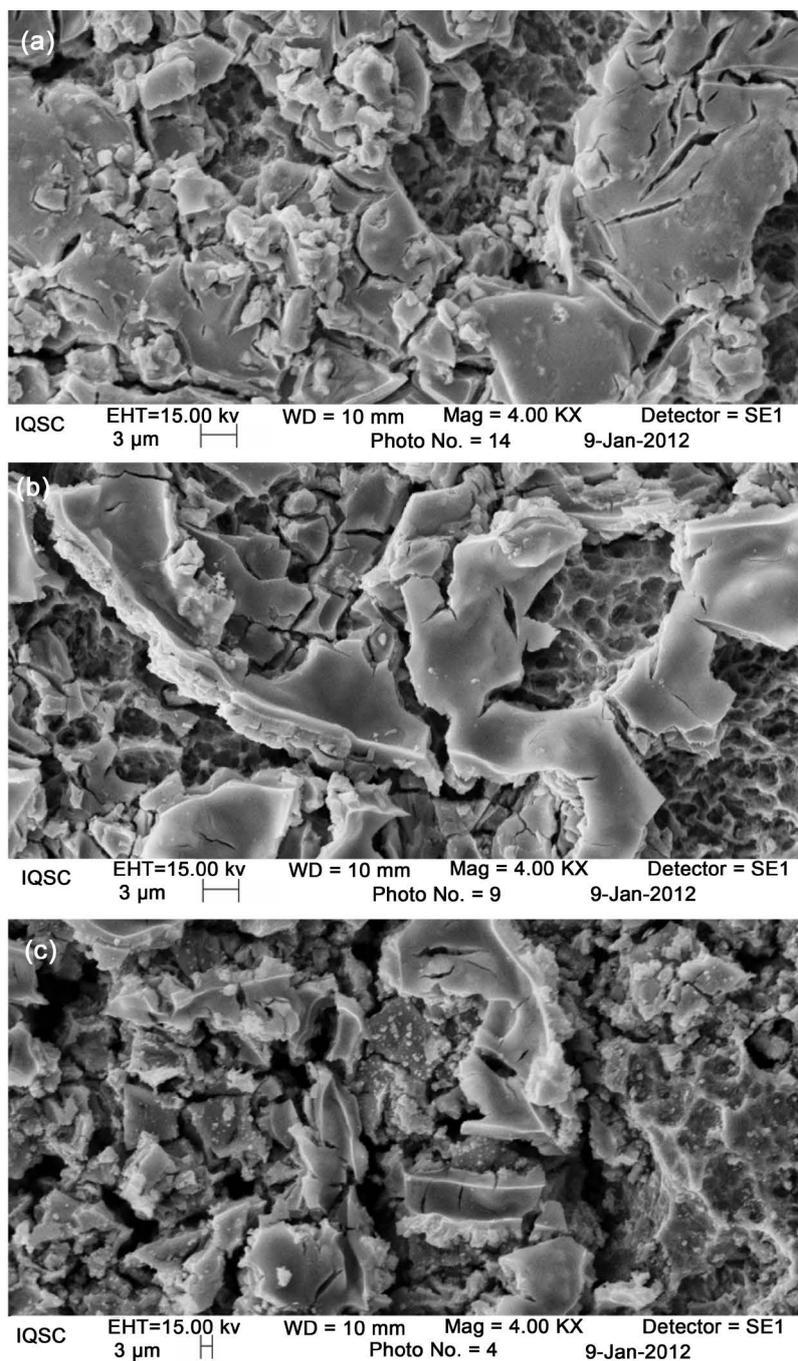
**Table 3.** Lifetime values obtained for the oxide electrodes under galvanostatic conditions at a high current density ( $400 \text{ mA}\cdot\text{cm}^{-2}$ ) in  $0.5 \text{ mol}\cdot\text{dm}^{-3}$  of  $\text{H}_2\text{SO}_4$ .

	Lifetime (h)
$\text{Ti/Ir}_{0.3}\text{Ti}_{0.4}\text{Sn}_{0.3}\text{O}_2$	>70
$\text{Ti/Ir}_{0.2}\text{Ti}_{0.3}\text{Sn}_{0.5}\text{O}_2$	6.16
$\text{Ti/Ru}_{0.3}\text{Ti}_{0.4}\text{Sn}_{0.3}\text{O}_2$	11.65

through microstructural analysis (**Figure 7**), which shows worn structures with erosion of the active layer. The EDX analysis revealed a decrease in the quantity of Ir and Ru, confirming the loss of the electroactive material, well as a decrease of Sn (**Table 4**).

The curves obtained for the lifetime showed a slow increase in the potential followed by an abrupt increase at the end of the experiment for all compositions investigated. This behavior indicates a rise in the electrode structure resistance. Such an increase may have resulted from the loss of Ir or Ru in the top layers of the electrode and/or the formation and growth of a non-conductive oxide film between the metallic substrate and the conductive oxide [9] [31].

EDX analysis after lifetime revealed a considerable increase in the titanium signal. These results suggest that besides the process of erosion, there is also a process of anodic passivation of the metallic base due to the formation of an insulating film composed primarily of  $\text{TiO}_x$ .



**Figure 7.** SEM surface image of the oxide electrodes after the lifetime test, original magnification 4000×. (a)  $\text{Ti/Ir}_{0.3}\text{Ti}_{0.4}\text{Sn}_{0.3}\text{O}_2$ ; (b)  $\text{Ti/Ir}_{0.2}\text{Ti}_{0.3}\text{Sn}_{0.5}\text{O}_2$ ; (c)  $\text{Ti/Ru}_{0.3}\text{Ti}_{0.4}\text{Sn}_{0.3}\text{O}_2$ .

**Table 4.** Variation in the atomic ratios (%) of the oxide films after the lifetime test.

	$\Delta\text{Ir}$ (%)	$\Delta\text{Ru}$ (%)	$\Delta\text{Sn}$ (%)
$\text{Ti/Ir}_{0.3}\text{Ti}_{0.4}\text{Sn}_{0.3}\text{O}_2$	-10.7	-	-20.3
$\text{Ti/Ir}_{0.2}\text{Ti}_{0.3}\text{Sn}_{0.5}\text{O}_2$	-58.3	-	-61.2
$\text{Ti/Ru}_{0.3}\text{Ti}_{0.4}\text{Sn}_{0.3}\text{O}_2$	-	-72.7	-54.2

## 4. Conclusion

This study has demonstrated the effect of the composition of oxide films on the properties of DSA prepared by the thermal decomposition of polymeric precursors. IrO<sub>2</sub>-based electrodes are more stable than RuO<sub>2</sub>-based electrode under the conditions investigated and show lower activity for the oxygen evolution reaction, which makes it attractive in the oxidation of organic substances. The introduction of tin oxide in the composition film enhances the catalytic properties of the anodes. However, it should be held in appropriate compositions, because the change in the atomic ratio of this element produces marked effects on the stability of the oxides. The thin films formed are composed of a solid solution among the various oxides constituents of the film. The procedure employed for the preparation of the anodes is a good alternative to SD, minimizing the volatilization of the metal.

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## References

- [1] Beer, H.B. (1980) The Invention and Industrial Development of Metal Anodes. *Journal of the Electrochemical Society*, **127**, 303-307. <http://jes.ecsdl.org/content/127/8/303C.abstract>  
<http://dx.doi.org/10.1149/1.2130021>
- [2] Varela, H., Câmara Júnior, G.A.H.S. and Gonzalez, E.R. (2000) Oxygen Evolution Reaction on Mn<sub>2</sub>O<sub>3</sub> Electrodes Supported on Stainless Steel. *Química Nova*, **23**, 721-726. [http://www.scielo.br/scielo.php?script=sci\\_arttext&pid=S0100-4042200000600002](http://www.scielo.br/scielo.php?script=sci_arttext&pid=S0100-4042200000600002)  
<http://dx.doi.org/10.1590/S0100-4042200000600002>
- [3] Klink, M.J., Makgae, M.E. and Crouch, A.M. (2010) Physico-Chemical and Electrochemical Characterization of Ti/RhO<sub>x</sub>-IrO<sub>2</sub> Electrodes Using Sol-Gel Technology. *Materials Chemistry and Physics*, **124**, 73-77. <http://www.sciencedirect.com/science/article/pii/S0254058410003846>  
<http://dx.doi.org/10.1016/j.matchemphys.2010.05.016>
- [4] Trasatti, S. (1991) Physical Electrochemistry of Ceramic Oxides. *Electrochimica Acta*, **36**, 225-228. <http://www.sciencedirect.com/science/article/pii/0013468691852442>  
[http://dx.doi.org/10.1016/0013-4686\(91\)85244-2](http://dx.doi.org/10.1016/0013-4686(91)85244-2)
- [5] Lipkowski, J. and Ross, P.N. (1994) The Electrochemistry of Novel Materials. VCH, University of Michigan.
- [6] Ferro, S., Rosestolato, D., Martínez-Huitle, C.A. and DeBattisti, A. (2014) Charge-Storage Process in IrO<sub>2</sub>-SnO<sub>2</sub> Mixed-Oxide Electrodes. Role of Coating Composition, Solution pH and Temperature. *Electrochimica Acta*, **148**, 85-90. <http://www.sciencedirect.com/science/article/pii/S0013468614020490>  
<http://dx.doi.org/10.1016/j.electacta.2014.10.045>
- [7] Kruthika, N.L., Karthika, S., Raju, G.B. and Prabhakar, S. (2013) Efficacy of Electrocoagulation and Electrooxidation for the Purification of Wastewater Generated from Gelatin Pro-

- duction Plant. *Journal of Environmental Chemical Engineering*, **1**, 183-188.  
<http://www.sciencedirect.com/science/article/pii/S2213343713000298>  
<http://dx.doi.org/10.1016/j.jece.2013.04.017>
- [8] Fierro, C. and Comninellis, C. (2010) Kinetic Study of Formic Acid Oxidation on Ti/IrO<sub>2</sub> Electrodes Prepared Using the Spin Coating Deposition Technique. *Electrochimica Acta*, **55**, 7067-7071. <http://www.sciencedirect.com/science/article/pii/S0013468610008820>  
<http://dx.doi.org/10.1016/j.electacta.2010.06.066>
- [9] Ribeiro, J. and de Andrade, A.R. (2004) Characterization of RuO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub> Coated Titanium Electrode Microstructure, Morphology, and Electrochemical Investigation. *Journal of the Electrochemical Society*, **151**, D106-D111. <http://jes.ecsdl.org/content/151/10/D106.abstract>  
<http://dx.doi.org/10.1149/1.1787174>
- [10] Tilak, B.V., Birss, V.I., Wang, J., Chen, C.P. and Rangarajan, S.K. (2001) Deactivation of Thermally Formed Ru/Ti Oxide Electrodes: An AC Impedance Characterization Study. *Journal of the Electrochemical Society*, **148**, 112-116.  
<http://jes.ecsdl.org/content/148/9/D112.short>  
<http://dx.doi.org/10.1149/1.1388630>
- [11] Pechini, M.P. (1967) Method of Preparing Lead and Alkaline Earth Titanates and Niobates and Coating Method Using the Same to Form a Capacitor. US Patent No. 3330697.
- [12] Forti, J.C., Olivi, P. and de Andrade, A.R. (2001) Characterisation of DSA<sup>®</sup>-Type Coatings with Nominal Composition Ti/Ru<sub>0.3</sub>Ti<sub>(0.7-x)</sub>Sn<sub>x</sub>O<sub>2</sub> Prepared via a Polymeric Precursor. *Electrochimica Acta*, **47**, 913-917.  
<http://www.sciencedirect.com/science/article/pii/S0013468601007915>  
[http://dx.doi.org/10.1016/S0013-4686\(01\)00791-5](http://dx.doi.org/10.1016/S0013-4686(01)00791-5)
- [13] Terezo, A.J. and Pereira, E.C. (1999) Preparation and Characterization of Ti/RuO<sub>2</sub>-Nb<sub>2</sub>O<sub>5</sub> Electrodes Obtained by Polymeric Precursor Method. *Electrochimica Acta*, **44**, 4507-4511.  
<http://www.sciencedirect.com/science/article/pii/S0013468699001826>  
[http://dx.doi.org/10.1016/S0013-4686\(99\)00182-6](http://dx.doi.org/10.1016/S0013-4686(99)00182-6)
- [14] Lassali, T.A.F., Boodts, J.F.C. and Bulhoes, L.O.S. (2000) Effect of Sn-Precursor on the Morphology and Composition of Ir<sub>0.3</sub>Sn<sub>0.7</sub>O<sub>2</sub> Oxide Films Prepared by Sol-Gel Process. *Journal of Non-Crystalline Solids*, **273**, 129-133.  
<http://www.sciencedirect.com/science/article/pii/S0022309300001526>  
[http://dx.doi.org/10.1016/S0022-3093\(00\)00152-6](http://dx.doi.org/10.1016/S0022-3093(00)00152-6)
- [15] Marciel, A.P., Longo, E. and Leite, E.R. (2003) Nanostructured Tin Dioxide: Synthesis and Growth of Nanocrystals and Nanoribbons. *Química Nova*, **26**, 855-861.  
[http://quimicanova.sbq.org.br/imagebank/pdf/Vol26No6\\_855\\_13-RV02099.pdf](http://quimicanova.sbq.org.br/imagebank/pdf/Vol26No6_855_13-RV02099.pdf)
- [16] Mourão, H.A.J.L., de Mendonça, V.R., Malagutti, A.R. and Ribeiro, C. (2009) Nanostructures in Photocatalysis: A Review about Synthesis Strategies of Photocatalysts in Nanometric Size. *Química Nova*, **32**, 2181-2186.  
[http://www.scielo.br/scielo.php?pid=S0100-40422009000800032&script=sci\\_arttext&tlng=pt](http://www.scielo.br/scielo.php?pid=S0100-40422009000800032&script=sci_arttext&tlng=pt)  
<http://dx.doi.org/10.1590/S0100-40422009000800032>
- [17] Besso, M.M. (1965) Tin Salts of Citric Acid and Method of Preparation. US Patent No. 3213120.
- [18] Klung, H.P. and Alexander, L.E. (1975) X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials. *Journal of Applied Crystallography*, **8**, 573-580.  
<http://scripts.iucr.org/cgi-bin/paper?S0021889875011399>  
<http://dx.doi.org/10.1107/S0021889875011399>
- [19] Malpass, G.R.P., Miwa, D.W., Machado, S.A.S., Olivi, P. and Motheo, A.J. (2006) Oxidation of the Pesticide Atrazine at DSA<sup>®</sup> Electrodes. *Journal of Hazardous Materials*, **137**, 565-572.

- <http://www.sciencedirect.com/science/article/pii/S0304389406002160>  
<http://dx.doi.org/10.1016/j.jhazmat.2006.02.045>
- [20] Motheo, A.J., Gonzalez, E.R., Tremiliosi, G., Olivi, P., de Andrade, A.R., Kokoh, B., Leger, J.M., Belgsir, E.M. and Lamy, C. (2000) The Oxidation of Formaldehyde on High Overvoltage DSA Type Electrodes. *Journal of the Brazilian Chemical Society*, **11**, 16-21.  
[http://www.scielo.br/scielo.php?pid=S0103-50532000000100004&script=sci\\_arttext](http://www.scielo.br/scielo.php?pid=S0103-50532000000100004&script=sci_arttext)  
<http://dx.doi.org/10.1590/S0103-50532000000100004>
- [21] Forti, J. F., Ribeiro, J., Lanza M.R.V., de Andrade, A.R. and Bertazzoli, R. (2010) Electrochemical Characterization of DSA<sup>®</sup>-Type Electrodes Using Niobium Substrate. *Electrocatalysis*, **1**, 129-138. <http://link.springer.com/article/10.1007%2Fs12678-010-0020-3>
- [22] Ardizzone, S., Fregonara, G. and Trasatti, S. (1990) "Inner" and "Outer" Active Surface of RuO<sub>2</sub> Electrodes. *Electrochimica Acta*, **35**, 263-267.  
<http://www.sciencedirect.com/science/article/pii/001346869085068X>  
[http://dx.doi.org/10.1016/0013-4686\(90\)85068-X](http://dx.doi.org/10.1016/0013-4686(90)85068-X)
- [23] Fukunaga, M.T., Guimarães, J.R. and Bertazzoli, R. (2008) Kinetics of the Oxidation of Formaldehyde in a Flow Electrochemical Reactor with TiO<sub>2</sub>/RuO<sub>2</sub> Anode. *Chemical Engineering Journal*, **136**, 236-241.  
<http://www.sciencedirect.com/science/article/pii/S1385894707002495>  
<http://dx.doi.org/10.1016/j.cej.2007.04.006>
- [24] Sugimoto, W., Iwata, H., Yokoshima, K., Murakami, Y. and Takasu, Y. (2005) Proton and Electron Conductivity in Hydrous Ruthenium Oxides Evaluated by Electrochemical Impedance Spectroscopy: the Origin of Large Capacitance. *The Journal of Physical Chemistry B*, **109**, 7330-7338. <http://pubs.acs.org/doi/abs/10.1021/jp044252o>  
<http://dx.doi.org/10.1021/jp044252o>
- [25] De Carvalho, L.A., de Andrade A.R. and Bueno, P.R. (2006) Electrochemical Impedance Spectroscopy Applied in the Study of Heterogeneous Reactions at Dimensionally Stable Anodes. *Química Nova*, **29**, 796-804.  
[http://quimicanova.sbq.org.br/imagebank/pdf/Vol29No4\\_796\\_28-RV05188.pdf](http://quimicanova.sbq.org.br/imagebank/pdf/Vol29No4_796_28-RV05188.pdf)  
<http://dx.doi.org/10.1590/S0100-40422006000400029>
- [26] Terezo, A.J., Bisquert, J., Pereira, E.C. and Garcia-Belmonte, G. (2001) Separation of Transport, Charge Storage and Reaction Processes of Porous Electrocatalytic IrO<sub>2</sub> and IrO<sub>2</sub>/Nb<sub>2</sub>O<sub>5</sub> Electrodes. *Journal of Electroanalytical Chemistry*, **508**, 59-69.  
<http://www.sciencedirect.com/science/article/pii/S0022072801005228>  
[http://dx.doi.org/10.1016/S0022-0728\(01\)00522-8](http://dx.doi.org/10.1016/S0022-0728(01)00522-8)
- [27] Horvat-Radosevic, V., Kvastek, K., Vukovic, M. and Marijan, D. (1999) Impedance of Ruthenium Electrodes in Sulphuric Acid Solution. *Journal of Electroanalytical Chemistry*, **463**, 29-44. <http://www.sciencedirect.com/science/article/pii/S0022072898004306>  
[http://dx.doi.org/10.1016/S0022-0728\(98\)00430-6](http://dx.doi.org/10.1016/S0022-0728(98)00430-6)
- [28] Martelli, G.N., Ornelas, R. and Fanta, G. (1994) Deactivation Mechanisms of Oxygen Evolving Anodes at High Current Densities. *Electrochimica Acta*, **39**, 1551-1558.  
<http://www.sciencedirect.com/science/article/pii/0013468694851344>  
[http://dx.doi.org/10.1016/0013-4686\(94\)85134-4](http://dx.doi.org/10.1016/0013-4686(94)85134-4)
- [29] Jovanovic, V.M., Dekanski, A., Despotov, P., Nikolic, B. and Atanasoski, R.T. (1992) The Roles of the Ruthenium Concentration Profile, the Stabilizing Component and the Substrate on the Stability of Oxide Coatings. *Journal of Electroanalytical Chemistry*, **339**, 147-165. <http://www.sciencedirect.com/science/article/pii/002207289280449E>  
[http://dx.doi.org/10.1016/0022-0728\(92\)80449-E](http://dx.doi.org/10.1016/0022-0728(92)80449-E)
- [30] Panic, V.V., Dekanski, A., Milonjic, S.K., Atanasoski, R.T. and Nilolic, B.Z. (1999)

RuO<sub>2</sub>-TiO<sub>2</sub> Coated Titanium Anodes Obtained by the Sol-Gel Procedure and Their Electrochemical Behaviour in the Chlorine Evolution Reaction. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **157**, 269-274.

<http://www.sciencedirect.com/science/article/pii/S0927775799000941>

[http://dx.doi.org/10.1016/S0927-7757\(99\)00094-1](http://dx.doi.org/10.1016/S0927-7757(99)00094-1)

- [31] Loucka, T. (1977) The Reason for the Loss of Activity of Titanium Anodes Coated with a Layer of RuO<sub>2</sub> and TiO<sub>2</sub>. *Journal of Applied Electrochemistry*, **7**, 211-214.

<http://link.springer.com/article/10.1007%2FBF00618987#page-1>

<http://dx.doi.org/10.1007/BF00618987>

- [32] Iwakura, C. and Sakamoto, K. (1985) Effect of Active Layer Composition on the Service Life of (SnO<sub>2</sub> and RuO<sub>2</sub>)-Coated Ti Electrodes in Sulfuric Acid Solution. *Journal of the Electrochemical Society*, **132**, 2420-2423. <http://jes.ecsdl.org/content/132/10/2420.short>

<http://dx.doi.org/10.1149/1.2113590>



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