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Preparation of $Ir_{0.3}Sn_{(0.7-x)}Ti_xO_2$ electrodes by the polymeric precursor method: Characterization and lifetime study

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Abstract

Thin film electrodes of nominal composition $Ir_{0.3}Sn_{(0.7-x)}Ti_xO_2$ ($0 \leq x \leq 0.7$) were prepared by decomposition of polymeric precursors. The solutions used to prepare the electrodes were obtained by mixing of the precursor salts with a mixture of ethylene glicol and citric acid. The films were burned at 400 °C and characterized by X-ray diffraction, scanning electronic microscopy, energy dispersive X-ray spectroscopy and cyclic voltammetry. The electrodes were submitted to high anodic current density in order to evaluate their lifetime in perchloric acid solution. Results show that the electrodes present compositions similar to that of the precursor solutions, suggesting that there is no loss of tin during the calcination step. The electrodes had large surface area and higher lifetime in comparison with electrodes of similar composition prepared by other methods. The possible mechanisms involved in deactivation of the electrodes are discussed.

1. Introduction

Electrodes formed with oxide layers have an important role in electrochemical industry, mainly when Dimensionally Stable Anodes (DSA®) are concerned, because of their application in the chlorine industry and in processes involving the oxygen evolution reaction [1]. Such electrodes consist basically of conductive layers of ruthenium or iridium oxides. Other components can also be added with the purpose of modulating the electrochemical properties of the active component, so as to increase the lifetime of these electrodes. The long-term performance of anodes is an important parameter for technological applications. Systems containing TiO_2 and SnO_2 as an additive for RuO_2 or IrO_2 electrodes have received special attention [2, 3]. Electrodes containing IrO_2 are highly stable at potentials where RuO_2-containing electrodes are not [4].

The main method of preparation of these electrodes consists in the thermal decomposition of metal chlorides. However, the volatility of the $SnCl_4$ precursor is a problem inherent to the preparation of electrodes containing SnO_2 [2], resulting in a composition different from the nominal one. Different alternatives have been proposed in order to simplify electrode preparation, to avoid the tin loss, and to obtain electrodes with controlled stoichiometry, as well as high surface area, chemical homogeneity, and higher lifetime in aggressive conditions. Among these methods are the spray pyrolysis [4] and the sol-gel methods [5].

An alternative method is the thermal decomposition of polymeric precursors, also known as the Pechini method, which has been previously employed in the preparation of SnO_2 [6] electrodes on ITO (Indium Tin Oxide), for use as counter electrode in electrochromic devices. This same method has also been used to produce Sb and Ce-doped tin oxide films [7–9]. Oliveira-Sousa et al. [10] prepared electrodes of pure IrO_2 on Ti plates and verified that this method produces electrodes with higher lifetime when compared with electrodes prepared by the thermal decomposition of chlorides and the sol-gel preparation method. In another study [11], electrodes with nominal composition $Ru_{0.3}Ti_{(0.7-x)}Sn_xO_2$ were prepared via the polymeric precursor method and it was found that the preparation method provides electrodes with good yield between nominal and experimental composition and good electrode stability. The maximum stability was obtained for electrodes with a $Ru_{0.3}Sn_{0.7}O_2$ composition, and the addition of Ti to the coating layer leads to decreased electrode lifetime [11].

In the present work we have prepared electrodes of composition $Ir_{0.3}Sn_{(0.7-x)}Ti_xO_2$, with $0 < x < 0.7$, starting from polymeric precursors and $IrCl_3$ as the iridium precursor salt. The main aim was to investigate the physical properties and the stability of these electrodes under high current density conditions in order to evaluate the real influence of Ti substitution by Sn atoms in the composition of DSA type electrodes.

2. Experimental

Electrodes of nominal composition $Ir_{0.3}Sn_{(0.7-x)}Ti_xO_2$ ($0 \leq x \leq 0.7$) were prepared by thermal decomposition of polymeric precursors at 400 °C. A set of eight oxide layer compositions, in duplicate, were obtained with constant catalyst loading (IrO_2 30 mol%), while TiO_2 was replaced by SnO_2 in 10 mol% steps. Three precursor solutions of the three cations were prepared. The final solutions used to obtain the films were prepared by mixing the three precursor ones so as to obtain the desired compositions. Tin citrate prepared in our laboratory and titanium (IV) isopropoxide (Merck) dissolved in citric acid/ethylene glycol (1:4) were used as Sn and Ti precursors, respectively. The iridium precursor solution was prepared from $IrCl_3 \cdot xHCl \cdot yH_2O$ (Aldrich) dissolved in HCl 1:1 (v/v).

The appropriate mixture of the precursor solutions was spread by brushing on both sides of a $10 \times 10 \times 0.15$ mm Ti support. The Ti plates were pretreated by sandblasting and etched in boiling 10% oxalic acid solution. After each application, the electrode was heated at 140 °C for 5 min, followed by heating at 400 °C for 5 min, under a 5 L min^{-1} O_2 stream in a preheated oven. The procedure was repeated until the oxide mass reached the value necessary to obtain a 2 μm nominal thickness. When this condition was attained the electrodes were subjected to final annealing at 400 °C for 1 h. A diagram of a similar procedure for the preparation of oxide layers can be found elsewhere [8].

Scanning electronic microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) were used to investigate the surface morphologies and composition of the electrodes layers. These analyses were done with a Zeiss model DSM 940 microscope, coupled to a LINK ANALYTICAL model QX 2000 microanalyzer.

Investigation of the crystalline structure was carried out by X-ray diffraction analysis (XRD) as a function of the electrode composition. These analyses were performed using CuKα radiation (30 kV, 30 mA) on a SIEMENS D5005 diffractometer equipped with a grazing incident angle accessory. The analyses were done on freshly prepared films.

Surface features of the mixed oxides were characterized *in situ* by cyclic voltammetry at a 20 mV s^{-1} scan rate, in the potential range between 0.4 and 1.4 V/RHE, in 1.0 mol l^{-1} $HClO_4$ solutions. After the measurement of the open circuit potential, E_{oc}, (10 min after immersion), the electrodes were submitted to 50 cycle potential sweeps in order to evaluate their chemical stability and to reach a steady state condition of the surface. The double-layer capacity of the oxide/solution interface and electrode roughness were obtained from cyclic voltammograms recorded at several scan rates ranging from 5 to 200 mV s^{-1}. Tests of accelerated anodic deactivation were also carried out, with applied currents of 800 mA cm^{-2}, and the potential was monitored until a maximum value of 6 V was reached. The time necessary to reach this potential value was considered as the electrode lifetime.

Electrochemical measurements were performed using a four-compartment cell with two counter electrodes (platinized platinum wires) facing the working electrode from opposite sides. The reference electrode was a reversible hydrogen electrode in the same supporting electrolyte (RHE) in a Luggin capillary. In such experiments, a PAR model 273 potentiostat was used coupled to an IBM microcomputer.

All experiments were carried out in 1.0 mol dm^{-3} $HClO_4$ (Merck) solutions prepared using Milli-Q quality water. Solutions were deaerated and stirred by bubbling nitrogen. All the electrochemical experiments were carried out at room temperature, ca. 25 °C.

3. Results and discussions

SEM results show that our eletrodes have typical morphology, with a "cracked mud" aspect, similar to electrodes prepared by the thermal decomposition of chlorides [12]. Figure 1 depicts the micrographs obtained by SEM for electrodes with nominal compositions $Ir_{0.3}Sn_{0.7}O_2$ and $Ir_{0.3}Sn_{0.5}Ti_{0.2}O_2$. Structures obtained for the different compositions are very similar, differing only in the number of cracks, crack width and grain size. This structure type results in high roughness, so the electrodes should present high area.

The composition of the oxide layers was analyzed by EDX on 0.81 mm^2 surface area in order to verify the possibility of tin loss during the calcination process. In these experiments, the obtained titanium concentration was always higher then the nominal one. This behavior was attributed to the influence of the titanium substrate, since the radiation falls mainly on the cracked region. Therefore the determined tin concentration was divided by the iridium concentration value, which was maintained constant in all electrodes, in order to normalize the results, thus avoiding the influence of the substrate. The results presented in Figure 2 show that the concentrations approach the nominal very closely, indicating that tin loss did not occur during the calcination step.

The structures of the electrodes were analyzed by X-ray diffraction using a grazing incident angle attachment. Figure 3 presents typical XRD patterns obtained for $Ir_{0.3}Sn_{(0.7-x)}Ti_xO_2$ films. Besides the peaks corresponding to the oxides present in the film, the contribution of metallic titanium present in the substrate can also be observed. This result is similar for other compositions, but in the films containing higher titanium concentrations, there is formation of TiO_2 with rutile structure. This phase disappears when the amount of titanium in the sample decreases, and the presence of SnO_2 with cassiterite structure is observed. IrO_2 should

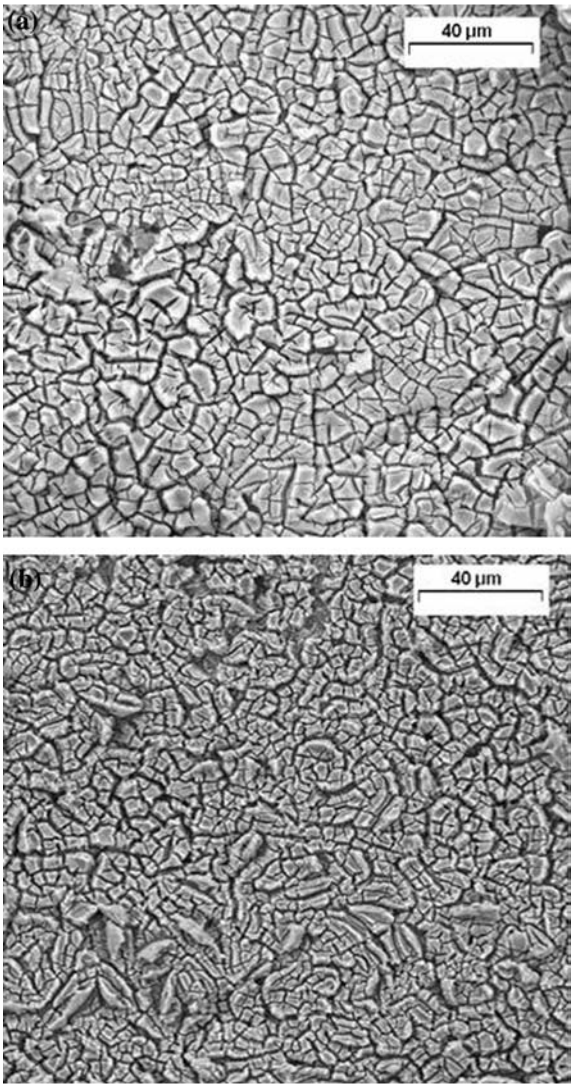

Fig. 1. SEM micrographs of electrodes prepared by the decomposition of polymeric precursors. Composition of the films: (a) $\mathrm{Ir_{0.3}Sn_{0.7}O_2}$ and (b) $\mathrm{Ir_{0.3}Sn_{0.5}Ti_{0.2}O_2}$.

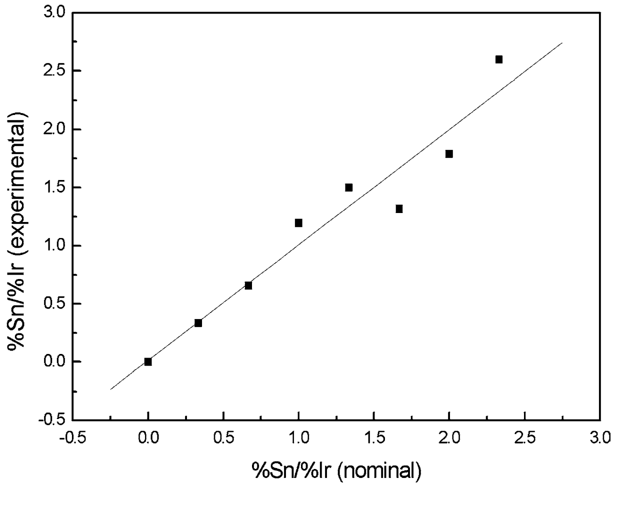

Fig. 2. Relationship between the nominal concentrations and the concentrations obtained by EDX.

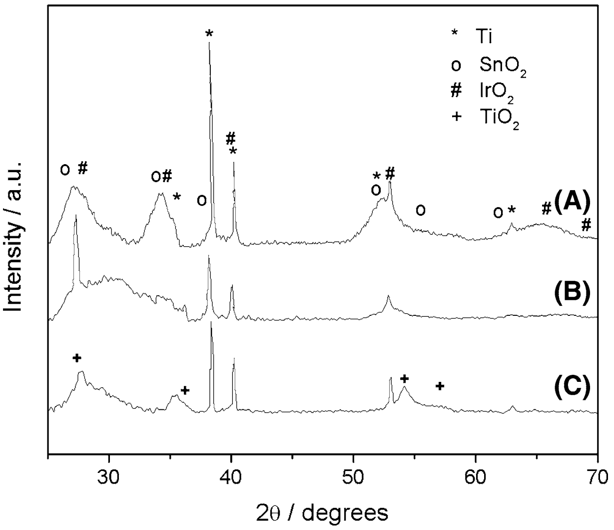

Fig. 3. X-ray pattern of the electrode with nominal composition (a) $\mathrm{Ir_{0.3}Sn_{0.7}O_2}$, (b) $\mathrm{Ir_{0.3}Sn_{0.3}Ti_{0.4}O_2}$ and (c) $\mathrm{Ir_{0.3}Ti_{0.7}O_2}$.

be present in all the samples, but its identification is hindered due to the proximity of its peaks with the peaks of the other phases. The formation of solid solutions could not be determined since the films presented low crystallinity and low intensity due to their small thickness. Nevertheless, the formation of a solid solution cannot be dismissed since $\mathrm{IrO_2}$, $\mathrm{SnO_2}$ and $\mathrm{TiO_2}$ present tetragonal structure, and the radii of the metallic ions do not differ very much, providing the conditions for the formation of a solid solution.

Cyclic voltammetry experiments were carried out in $\mathrm{HClO_4}$ solution to characterize the electrochemical processes occurring in these electrodes. Figure 4 presents a typical result obtained with an $\mathrm{Ir_{0.3}Sn_{0.2}Ti_{0.5}O_2}$ electrode. Results show an oxidation peak at ca. 0.88 V (vs. RHE) due to Ir(III)/Ir(IV) transition, and a cathodic peak due to the reverse process at ca. 0.78 V (vs. RHE). This process was identified in all electrodes, independent of the $\mathrm{TiO_2}$ and $\mathrm{SnO_2}$ content. The observed voltammetric profile is compatible with those

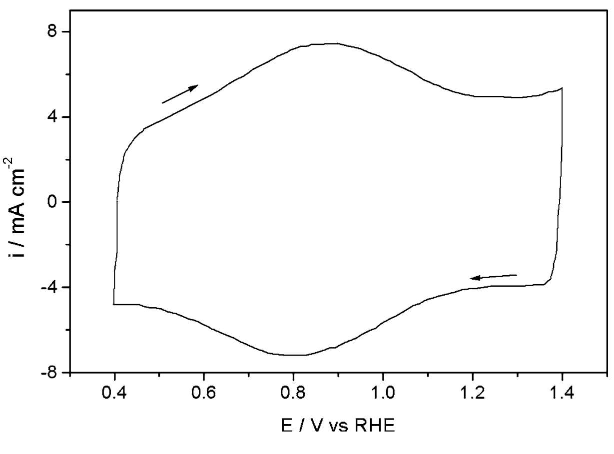

Fig. 4. Cyclic voltammogram of the electrode with nominal composition $\mathrm{Ir_{0.3}Sn_{0.2}Ti_{0.5}O_2}$. $v = 50\ \mathrm{mV\ s^{-1}}$; $\mathrm{HClO_4}$ 1.0 mol $\mathrm{l^{-1}}$ solution.

observed for electrodes prepared by decomposition of chlorides [12, 13] and sol-gel [5].

Results of cyclic voltammetry at different scan rates (v) were used to determine the surface roughness factor (RF) through determination of the pseudo capacitance of the double layer (CDL) obtained from the angular coefficient of the i vs. v curves. RF values were obtained by dividing CDL average values for each composition by 60 μF cm^{-2}. Table 1 shows RF results in relation to electrodes composition.

Results show that these electrodes have a mean roughness factor value of about 33% of that obtained by thermal decomposition of chlorides [12]. This observation implies that, although the morphologies observed by SEM are the same in both cases, the electrodes obtained by the decomposition polymeric precursors present a more compact structure. Nevertheless, the determined RF values are up to 3 times higher than that obtained for Ti/ $Ru_{0.3}Sn_{(0.7-x)}Ti_xO_2$ also prepared by the polymeric precursor method [11].

Previous accelerated anodic deactivation experiments had been carried out at 400 mA cm^{-2} in order to compare values obtained with Ti/ $Ru_{0.3}Sn_{(0.7-x)}Ti_xO_2$ [11], but the obtained lifetimes were too high, making the performance of tests impossible. So tests were accomplished by application of constant current values of 800 mA cm^{-2}. The potential vs. time curves registered during the lifetime tests are presented in Figure 5a. Figure 5b shows the lifetime for the different electrode compositions. The tests of accelerated anodic deactivation showed that electrodes containing IrO_2 and TiO_2 have a lifetime of 48 h, which is larger than the lifetime electrodes containing IrO_2 and SnO_2 only; i.e., approximately 14 h. This type of behavior can be explained by analyzing the surface by SEM after the deactivation experiment, which is shown in Figure 6. While electrodes containing Sn in their composition show a strong breakup of the active layer, electrodes that do not contain Sn, have a lot of particles rich in Ir after the deactivation test. In the case of electrodes containing SnO_2 (Figure 6a), some areas containing IrO_2 can be observed, while for electrodes containing TiO_2, a distribution of particles containing IrO_2 can be seen over the whole surface. This suggests that the mechanism for the formation of a passive film of TiO_2 at the interface between Ti and the oxide layer is the main mechanism involved in the deactivation of the $Ir_{0.3}Ti_{0.7}O_2$ electrode while in the case of the $Ir_{0.3}Sn_{0.7}O_2$ electrode, the breakup of the layer is the most important factor, probably leading to an increase in the speed of formation of the TiO_2 passive film and causing electrode deactivation. Electrodes with intermediate compositions generally had a much higher lifetime than the binary oxides; i.e., the lifetime values ranged from 170 to 220 h (Figure 5b). A comparison of the lifetime of the films prepared by the Pechini method with that of films prepared by thermal decomposition of chlorides [13] shows that the long-term performance of the former is superior for all compositions. The gratest difference is observed for the electrode containing 40 mol% of Ti, which had a lifetime of 6 h when prepared by the thermal decomposition of chlorides [13] and a lifetime of 220 h when prepared by the decomposition of polymeric precursors.These values show that the introduction of tin oxide in the DSA type electrode enhances electrode lifetime, and the preparation method gives reliable performance.

Table 1. Values of roughness factor for the different electrodes

% Ti	70	60	50	40	30	20	10	0
RF	1328	1149	1810	1895	1666	1641	1002	1164

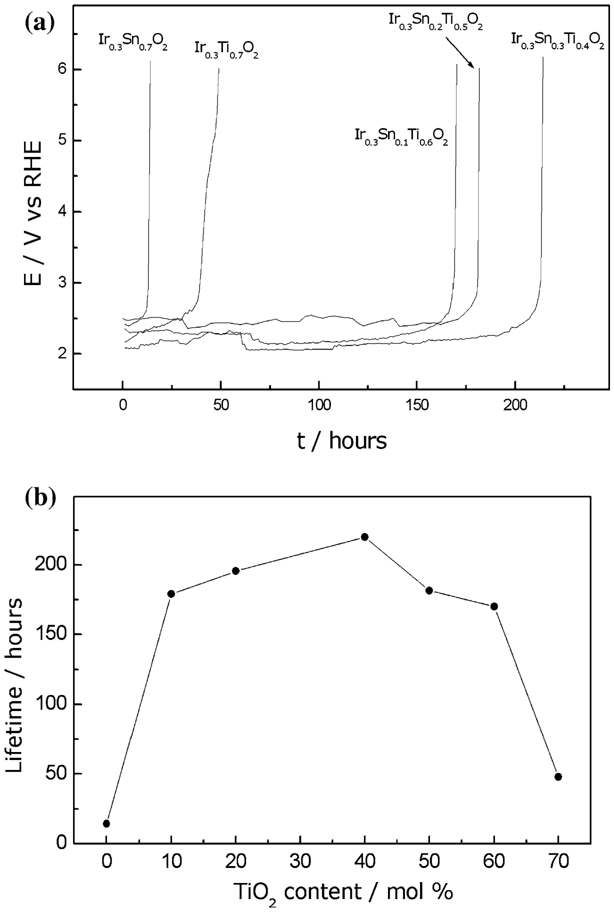

Fig. 5. Potential-time curves (a) and lifetime (b) as a function of the nominal composition of $Ir_{0.3}Sn_{(0.7-x)}Ti_xO_2$ electrodes, in 1.0 mol l^{-1} $HClO_4$, at 800 mA cm^{-2}.

Another observation is that higher lifetime values were obtained for electrodes with higher RF values (see Table 1). However, electrodes containing 60 mol% of Ti and 10 mol% of Ti, which present RF values lower than the electrodes containing 70 mol% and 0 mol% of Ti, showed higher lifetime values than the latter electrodes. This implies that the enhancement in lifetime is not only due to an increase in surface area, but to an interaction between Ir, Sn, and Ti, which must lead to a more resistant structure. During the lifetime tests, cyclic voltammetry was performed in order to verify the

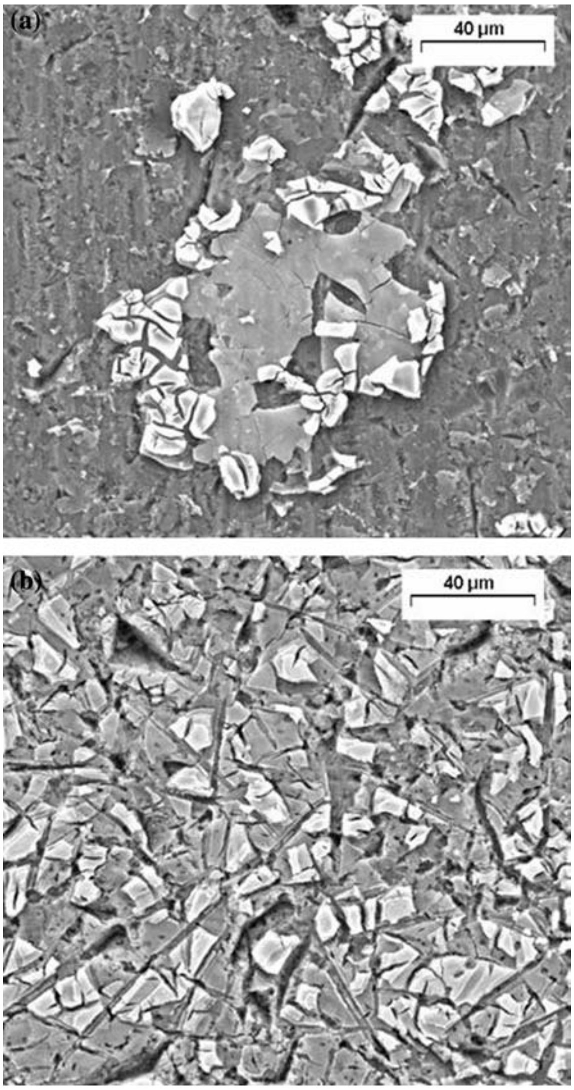

Fig. 6. SEM micrographs of electrodes after accelerated life test. Nominal electrode composition (a) $Ir_{0.3}Sn_{0.7}O_2$ and (b) $Ir_{0.3}Ti_{0.7}O_2$. Detection by backscattering electrons.

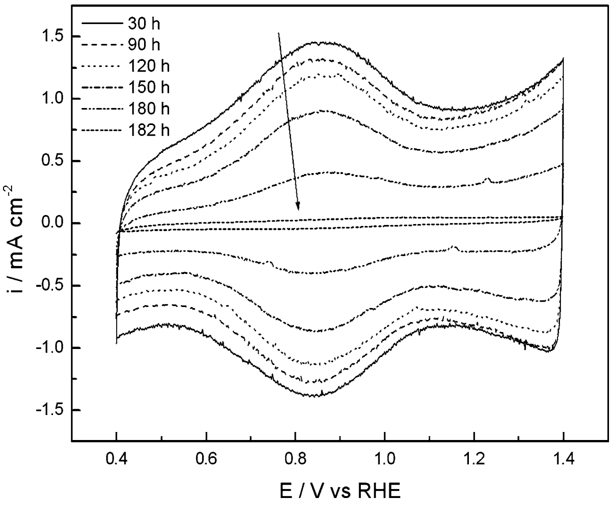

Fig. 7. Cyclic voltammograms of the electrode with nominal composition $Ir_{0.3}Sn_{0.2}Ti_{0.5}O_2$ during lifetime experiments. v = 20 mV s^{-1}; $HClO_4$ 1.0 mol l^{-1} solution.

possible mechanisms of electrode deactivation. Typical voltammetric curves are presented in Figure 7. The voltammograms showed that there is a decrease in charge during the tests, which may be associated to loss of catalytic material. This material loss may be attributed to two different factors; i.e., dissolution of the catalytic layer and mechanical erosion caused by the intense generation of oxygen bubbles. SEM of the electrode surface after the deactivation tests are similar to that depicted in Figure 6a; i.e., a surface containing only small "islands" of the original catalytic layer. Analyses of the electrode surface after deactivation by X-ray mapping using the EDX system (Figure 8) show also that the catalytic layer is practically destroyed during the deactivation tests. However, even if this behavior is compatible with deactivation by erosion, the dissolution of the catalytic layer is the only explanation for the increase in lifetime observed for electrodes containing both Ti and Sn. In this case, soluble species containing iridium in higher oxidation states can be formed [14]. Besides the dissolution of the catalytic layer, there is growth of a titanium oxide layer between the catalytic layer and the substrate metallic titanium due to metal oxidation. The rapid increase in the electrode potential is a characteristic of TiO_2 layer growth. This oxide layer is inactive and has high electrical resistance, leading to a rapid increase in the electrode potential. This potential behavior is very pronounced and can be observed for all the electrode compositions. Some of the potential vs. time curves are presented in Figure 5a. The same behavior was observed by Alves et al. [15] in accelerated anodic deactivation testing of IrO_2-based electrodes with the substitution of TiO_2 by CeO_2. These authors presented a detailed representation of this deactivation mechanism in which the state of the electrode after deactivation corresponds to the result obtained by us and is shown in Figures 6 and 8. It is interesting to note that the addition of CeO_2 to the IrO_2–TiO_2 system causes a decrease in the lifetime, which was 6 h. A detailed discussion about the deactivation mechanism involved in DSA® type electrodes was presented by Da Silva et al. [16] and they also found that the electrodes may be deactivated without total consumption of the active layer. In that case, the electrode deactivation was attributed to the growth of a passive layer on the Ti support. Our results agree with that proposition, i.e., there is incomplete consumption of the active layer in the electrodes and the passivation of the Ti substrate must be the main cause of electrode deactivation.

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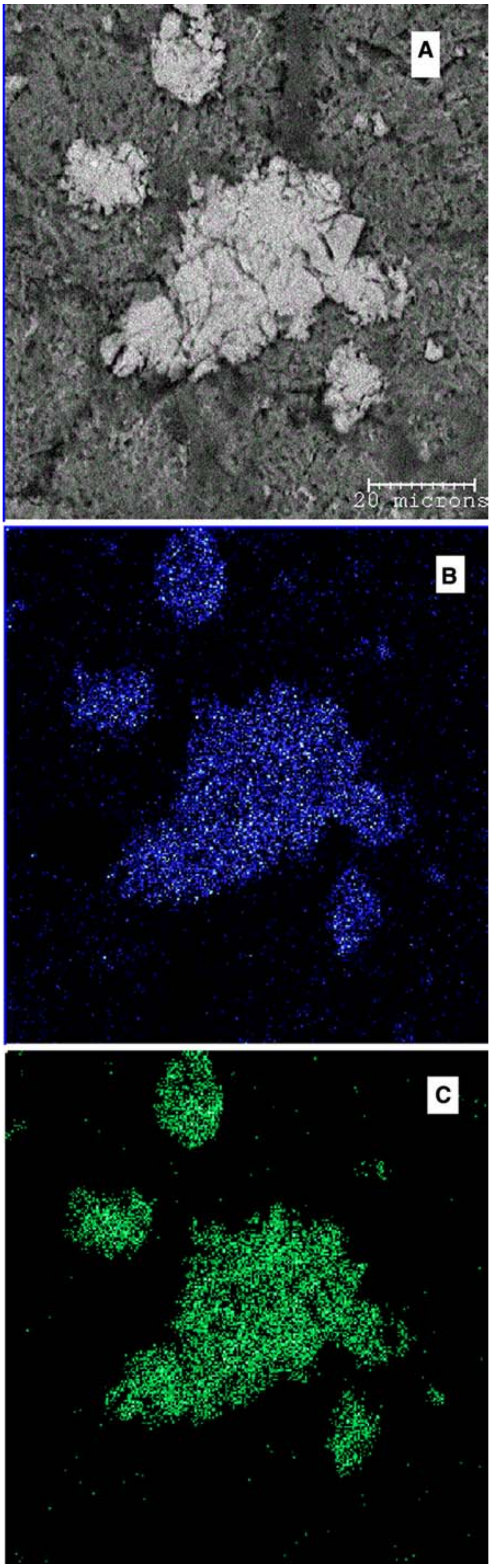
Fig. 8. SEM micrographs of a $Ir_{0.3}Sn_{0.3}Ti_{0.4}O_2$ electrode after accelerated life test (A) and X-ray mapping image obtained by EDX of the electrode showing the presence of Sn (B) and Ir (C).



4. Conclusions

The preparation method employed here results in electrodes with characteristics similar to those of electrodes obtained by traditional methods, being superior in some aspects, with the advantage of obtaining oxides with composition quite close to the nominal one. The electrodes presented "cracked-mud" type morphology, responsible for high roughness, and voltammetric behavior identical to that observed for electrodes obtained by other preparation methods. Results of accelerated anodic deactivation tests demonstrated that the electrodes prepared by the present method have lifetimes higher than those observed with electrodes of the same composition prepared by thermal decomposition of chlorides and submitted to the same experimental conditions. This preparation method is an important potential alternative to methods currently in use for the preparation of DSAs.

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