Preparation of Ir$_{0.3}$Sn$_{(0.7-x)}$Ti$_x$O$_2$ 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$_x$O$_2$ (0 ≤ x ≤ 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$_x$O$_2$ 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$_x$O$_2$, 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 \( \text{Ir}_x\text{Sn}_{0.7-x}\text{Ti}_1\text{O}_2 \) (\( 0 \leq x \leq 0.7 \)) 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 (\( \text{IrO}_2 \) 30 mol%), while \( \text{TiO}_2 \) was replaced by \( \text{SnO}_2 \) 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 \( \text{IrCl}_3 \cdot x\text{HCl} \cdot y\text{H}_2\text{O} \) (Aldrich) dissolved in \( \text{HCl} \) 1:1 (v/v).

The appropriate mixture of the precursor solutions was spread by brushing on both sides of a 10 × 10 × 0.15 mm Ti support. The Ti plates were pre-treated by sandblasting and etching 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 \( \text{O}_2 \) 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 \textit{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 \( \text{HClO}_4 \) 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 \( \text{HClO}_4 \) (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 electrodes 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 \( \text{Ir}_x\text{Sn}_{0.7-x}\text{Ti}_1\text{O}_2 \) and \( \text{Ir}_x\text{Sn}_{0.7}\text{Ti}_{0.5}\text{O}_3 \). 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 mm² 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 than 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 \( \text{Ir}_x\text{Sn}_{0.7-x}\text{Ti}_1\text{O}_2 \) 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 \( \text{TiO}_2 \) with rutile structure. This phase disappears when the amount of titanium in the sample decreases, and the presence of \( \text{SnO}_2 \) with cassiterite structure is observed. \( \text{IrO}_2 \) should