

Preparation and Characterization of Ti/SnO₂-Sb Electrodes without or with a Platinum Interlayer Using the Polymeric Precursor Method and Thermal Decomposition

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SnO₂-Sb electrodes on a Ti substrate, prepared without (Ti/SnO₂-Sb) or with a Pt interlayer (Ti/Pt/SnO₂-Sb), were prepared using the polymeric precursor method followed by thermal decomposition. The platinum film on titanium (Ti/Pt) was prepared by thermal decomposition of an alcoholic solution of Pt. Scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), and elemental mapping were used to characterize the surfaces of Ti/Pt, Ti/SnO₂-Sb, and Ti/Pt/SnO₂-Sb. The electrochemical characterization of the electrodes was performed using cyclic voltammetry in a 0.5 M H₂SO₄ solution. The electroactive area of the electrodes was determined using measurements of the electrosorption hydrogen charge for Ti/Pt and the capacitance of the electric double layer for Ti/SnO₂-Sb and Ti/Pt/SnO₂-Sb. Tafel slopes for the oxygen evolution reaction (OER) were estimated from polarization curves. The SEM and EDS results obtained from the electrodes prepared with or without a platinum interlayer displayed distinct behaviors. In the absence of Pt, the SnO₂-Sb coating on titanium formed a compact layer with a good distribution of Sn, Sb, O, and a low Ti content. In the presence of the Pt coating, SnO₂-Sb was heterogeneously distributed. The heterogeneous character of the Ti/Pt/SnO₂-Sb film resulted from surface segregation during the calcination process. The voltammetric behaviors of the SnO₂-Sb electrodes prepared with or without a Pt interlayer displayed similar trends, although the presence of Pt produced a greater electroactive area and shifted the oxygen evolution potential toward less positive values; therefore, the electrocatalytic activity toward the OER was higher compared to the Ti/SnO₂-Sb electrode. The Tafel slope estimated for Ti/Pt/SnO₂-Sb is consistent with a mechanism in which OH[•] generation is the rate controlling step.

Keywords: Electrodes, Ti/Pt, Ti/SnO₂-Sb, Ti/Pt/SnO₂-Sb, Preparation, Characterization

1. INTRODUCTION

Tin dioxide anodes doped with antimony and supported on titanium are a promising material for the electrochemical oxidation of organic contaminants containing antibiotics [1-5]. The service life of these electrodes is relatively short; however, the material has several advantages, including a high overpotential for the oxygen evolution reaction, an excellent electrocatalytic performance, facile preparation, and low costs [6-10]. The instability of Ti/SnO₂-Sb anodes has been associated with the formation of a TiO₂ interlayer between the Ti substrate and the SnO₂-Sb film [10-14]. Eliminating or reducing the formation of the undesirable TiO₂ interlayer has been a topic of interest in efforts to obtain Ti/SnO₂-Sb anodes with a high mechanical and electrochemical stability [6,15-17]. The introduction of metal interlayers between the titanium substrate and the SnO₂-Sb film has favored electrode stability [18, 28]. Platinum-coated titanium is a common configuration used as an anode or cathode for different purposes [15, 19-23]. For Ti/SnO₂-Sb electrodes, platinum has been used as an interlayer or as a doping agent in the Sn-Sb system [9, 18, 27, 28]. The introduction of Pt into the SnO₂-Sb system changes the packing and increases the porosity of the coating, increases the electroactive area and electric current density, and favors the electrocatalytic activity towards the oxygen evolution reaction (OER). Santos et al. [15] reported the preparation of Ti/Pt/SnO₂-Sb₂O₃ electrodes and their application to the anodic oxidation of pharmaceutical drugs. Those electrodes were prepared by alternately applying Sn and Sb electrodeposited layers onto a platinized titanium foil followed by thermal oxidation to form the respective oxides. Their results showed that Ti platinization improved the service life of the Ti/Pt/SnO₂-Sb₂O₄ electrodes without losing their capacity for oxidizing organic compounds. In this work, we report the preparation of SnO₂-Sb electrodes on a titanium substrate prepared without or with a platinum interlayer using the polymer precursor method and thermal decomposition. The surface characterization results and the electrochemical properties of the Ti/SnO₂-Sb electrodes under the influence of the Pt interlayer are discussed.

2. EXPERIMENTAL

2.1. Materials and reagents

All chemical reagents used in experiments were of analytical grade. Titanium discs of diameter 11 mm and thickness 2 mm (99.7% Sigma-Aldrich,) were used as substrates. Sandpaper # 80, sodium hydroxide (Baker), hydrochloric acid (37%, Mallinckrodt Chemicals), oxalic acid (99.5%, Baker), acetone (99.5%, Baker), and ethyl alcohol (99.8%, Baker) were used to pretreat the titanium substrate. H₂SO₄ 0.5 M was used as an electrolyte in the electrochemical experiments and was prepared from concentrated sulfuric acid (97%, Merck) and deionized water (18 MΩ cm) from a Milli-Q system.

2.2. Precursor solutions

The precursor solution based on Sn and Sb was prepared using the polymer precursor method (Pechini method) [24] using ethylene glycol (99%, Sigma Aldrich), citric acid (99.5%, Sigma Aldrich),

tin chloride pentahydrate IV ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, 98%, Sigma Aldrich), and antimony oxide III (Sb_2O_3 , 99.9%, Sigma Aldrich). The molar ratio of Sn:Sb was 95:5 mol%. The ratio among citric acid (CA), ethylene glycol (EG), and the metals (Sn and Sb) was CA:EG:Metals, 3:14:1, where Sn:Sb corresponds to 0.95:0.05. The platinum precursor solution was prepared using hexachloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, Sigma Aldrich) in ethyl alcohol.

2.3. Methodology

2.3.1. Substrate surface treatment.

The surfaces of the titanium discs were treated to remove fats, eliminate surface oxides, and promote the surface roughness of the substrate [9]. The sanded Ti discs were treated in a 20% NaOH solution at 80 °C for 3.5 hours. Subsequently, the discs were treated in 10% hydrochloric acid solution at 60 °C for one hour, and finally in 10% oxalic acid solution at 80 °C for 2.5 hours. The treated Ti discs were washed with acetone and stored in ethyl alcohol.

2.3.2. Formation of films on titanium: Ti/Pt, Ti/SnO₂-Sb y Ti/Pt/SnO₂-Sb.

In all cases, the precursor solution was applied to the substrate using a brush. Platinum films on titanium were prepared using the platinum precursor solution by applying the following heat treatment: drying on a grill at 35 °C for 10 min and later at 60 °C for 10 min in a tubular furnace (Thermoline Fisher). The temperature was then increased to 325 °C for 10 min, and the film was finally calcined at 400 °C for 30 min. This procedure was repeated for each layer applied to the substrate. The total number of layers applied was five. The SnO₂-Sb films on titanium were prepared using the Sn-Sb precursor solution. In this case, the thermal program was the following: Drying was carried out at room temperature, then the sample was placed in a tubular furnace and the temperature was increased to 160 °C for 60 min. The temperature was then increased to 400 °C for one hour to form the first layer. The number of precursor layers applied to the substrate was five. The last layer was applied by raising the final temperature to 600 °C for 3 hours. The SnO₂-Sb films were formed on the platinum film (Ti/Pt) using the same methodology as was used on the titanium substrate.

2.4. Physicochemical characterization of Ti/Pt, Ti/SnO₂-Sb, and Ti/Pt/SnO₂-Sb.

Ti/Pt, Ti/SnO₂-Sb, Ti/Pt/SnO₂-Sb electrodes were characterized using SEM, EDS, and elemental mapping using a JEOL JSM-7600F at 15 kV. The electrodes were electrochemically characterized using cyclic voltammetry conducted in a 0.5 M H₂SO₄ solution using a conventional three-electrode cell. Synthesized electrodes were used as working electrodes, the auxiliary electrode consisted of a graphite bar, and the reference electrode comprised saturated mercury sulfate (Hg/Hg₂SO₄/K₂SO₄ sat) attached to a Luggin capillary. Electrochemical experiments were carried out

using a potentiostat/galvanostat (Voltalab, Mod. PGZ402). The solutions in the electrochemical cell were purged with nitrogen for 10 minutes before each experiment to avoid interference with oxygen.

For Ti/Pt the electrochemically active electrode area was estimated using cyclic voltammetry in 0.5 M H₂SO₄, by integrating the charge due to hydrogen desorption in the anodic sweep between 0 and 300 mV/NHE after subtracting the double layer charge. A theoretical charge of $Q_H = 210 \mu\text{C}/\text{cm}^2$ for hydrogen adsorption over polycrystalline platinum was used [31]. For the Ti/SnO₂-Sb electrodes with and without a Pt interlayer, the electroactive area was determined from capacitance measurements of the double layer on the voltammograms recorded between 20 and 100 mV s⁻¹, using a specific capacitance of 8 μF cm⁻² [29]. Linear sweep voltammetry at 1 mVs⁻¹ in 0.5 M H₂SO₄ was used to determine Tafel slopes.

3. RESULTS AND DISCUSSION

3.1. Characterization of the film–substrate constructs using scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), and elemental mapping.

3.1.a. Ti/SnO₂-Sb electrodes

Figures 1a–1b show SEM images of the Ti/SnO₂-Sb film. The SnO₂-Sb film on the titanium substrate was formed using five layers of the precursor (Sn-Sb) and a final calcination temperature of 600 °C applied over 3 hours. The SEM micrograph (Fig. 1a) revealed a homogeneous surface with compact and cracked areas produced during the film forming process. A high-magnification photo (Fig. 1b) revealed the presence of cracks produced during the thermal decomposition of the polymeric resin. Surface cracks may arise from the contraction of the polymer resin during the calcination process and/or by mechanical stress caused by differences in the thermal expansion coefficients of the film and substrate [25, 26]. Figure 1c shows the EDS spectrum of the SnO₂-Sb film prepared on titanium. The energy lines corresponding to the elements O(Kα = 0.52 keV), Sn(Lα = 3.44 keV), Sb(Lα = 3.60 keV) confirmed the presence of these elements in the film. The energy line corresponding to Ti(Kα = 4.50 keV) was also observed, suggesting that the electron beam reached the surface of the substrate through the cracks or crossed the SnO₂-Sb film to detect the substrate. C and Fe, observed in the spectrum, may correspond to trace contaminants present during the preparation of the electrodes. The elementary mapping of the SnO₂-Sb film on titanium (Fig. 1d–1g) revealed a favorable distribution of Sn (Fig. 1d), Sb (Fig. 1e), and O (Fig. 1f) elements on the surface of the substrate, and some points suggested the presence of titanium in the surface cracks. Zhi et al. [2], reported the preparation of Ti/SnO₂-Sb anodes using the sol-gel technique and thermal decomposition at 500 °C. They observed that the conditions used to prepare these electrodes favored highly porous morphologies. By contrast, our results did not produce Ti/SnO₂-Sb electrodes with a high porosity. The applied calcining temperature (600 °C) may have been responsible for the low surface porosity.

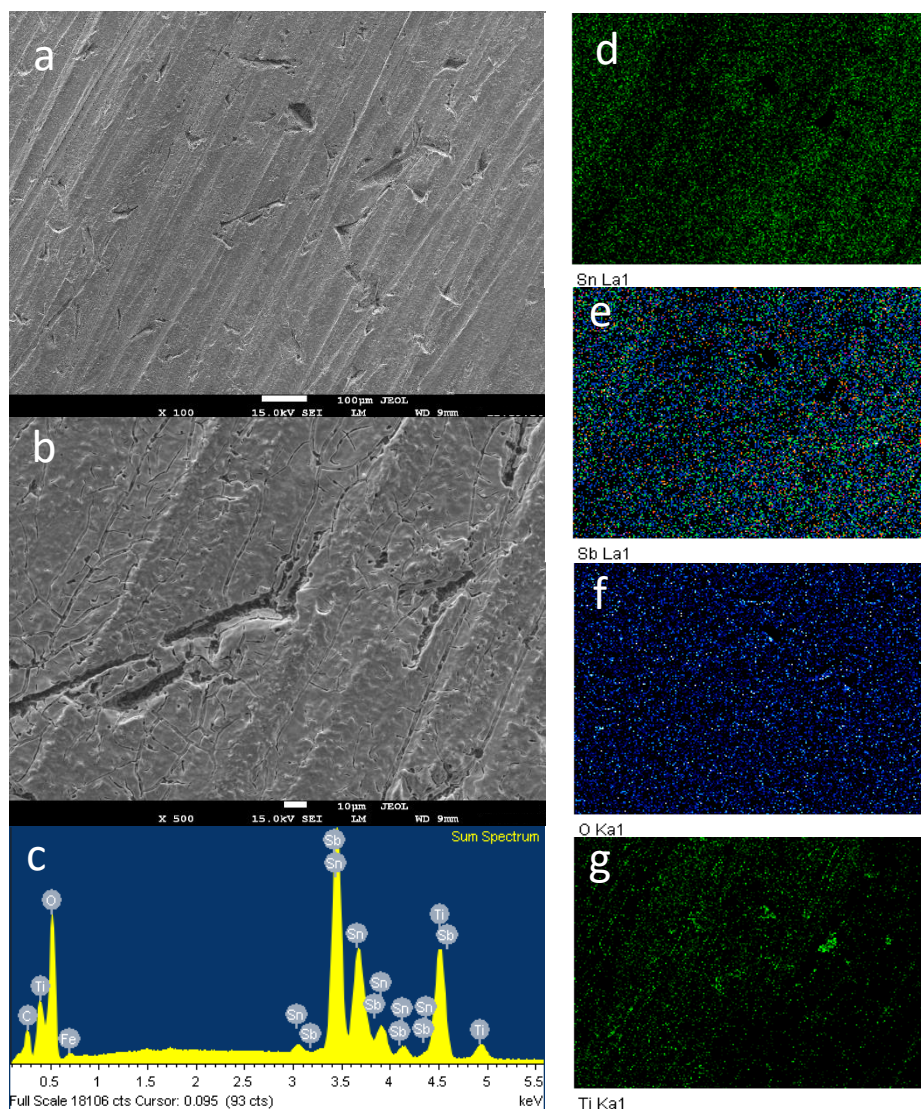


Figure 1. $\text{SnO}_2\text{-Sb}$ films prepared on titanium ($\text{Ti/SnO}_2\text{-Sb}$). SEM images: a) 100x and b) 500x magnification; c) EDS spectrum; d–g) elementary mapping. Five layers of the precursor and a final calcination temperature of 600 °C over 3 hours.

3.1.b. *Ti/Pt electrodes*

Figures 2a–2b show SEM micrographs of a platinum film on the titanium substrate with different magnifications (100x and 500x). The film consisted of five precursor layers. The morphology of the platinum film was continuous and apparently compact and homogeneous; however, some cracks were present in the surface, as shown in Fig. 2b. The EDS spectrum in Fig. 2.c shows the energy line of $\text{Pt(L}\alpha = 2.048 \text{ keV)}$, confirming the presence of Pt on the titanium surface. The low intensity of the energy lines of $\text{O(K}\alpha = 0.52 \text{ keV)}$, $\text{Ti(L}\alpha = 0.452 \text{ keV)}$, and $\text{C(K}\alpha = 0.277 \text{ keV)}$ indicated that the content of these elements was low in relation to Pt.

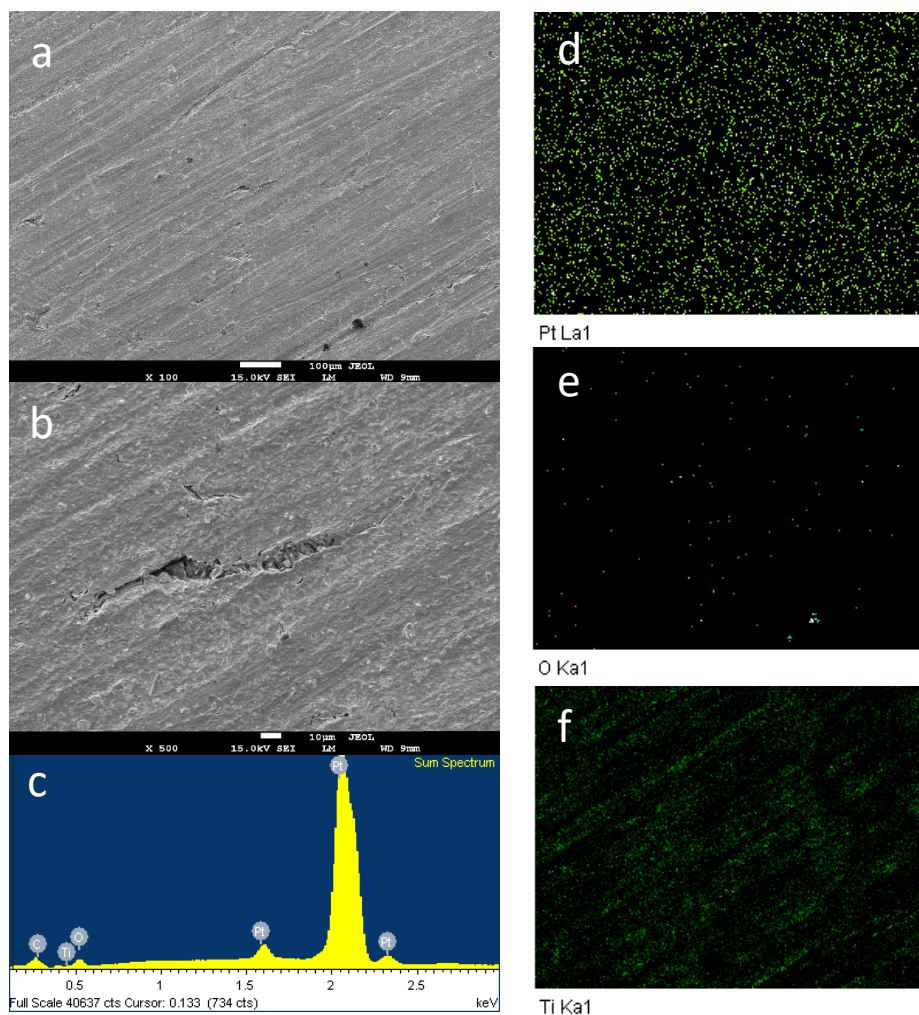


Figure 2. Pt films on titanium (Ti/Pt). SEM images: a) 100x and b) 500x; c) EDS spectrum; d–f) elementary mapping. Five layers of the precursor and final calcination temperature 400 °C over 30 min.

The elementary mapping (Fig. 2d–2f) revealed an excellent distribution of Pt (Fig. 2.d). The presence of oxygen was scarce (Fig. 2e) compared to titanium (Fig. 2f). It is possible that the electron beam reached the surface of the substrate through cracks or passed through the Pt film and detected the underlying metal substrate. Similar morphological characteristics of Ti/Pt thin films prepared using the Pechini method were observed by Freitas et al. [21], whereas platinum films obtained by potentiostatic or galvanostatic electrodeposition revealed different observed morphologies [19].

3.1.c. Ti/Pt/SnO₂-Sb electrodes

Figures 3a–3b show an SEM image and EDS spectrum of the SnO₂-Sb film on Ti/Pt, respectively. The SnO₂-Sb film on Ti/Pt was prepared using the methodology applied to prepare Ti/SnO₂-Sb, that is, five layers of the precursor were deposited and a final heating temperature of 600 °C was applied over 3 hours. The SEM micrograph shows a heterogeneous surface with dark and light areas, indicating that the SnO₂-Sb film on Ti/Pt was not distributed homogeneously. The EDS

spectrum (Fig. 3b) confirmed the heterogeneous characteristics of the surface, with energy lines corresponding to the elements Sn(L α = 3.44 keV), Sb(L α = 3.60 keV), Pt(L α = 2.048 keV), Ti(K α = 4.50 keV), and O(K α = 0.52 keV). The heterogeneous character of Ti/Pt/SnO₂-Sb surface was evident in the elementary mapping (Figs. 3c–3g), which revealed the presence of uncovered areas of the Ti substrate.

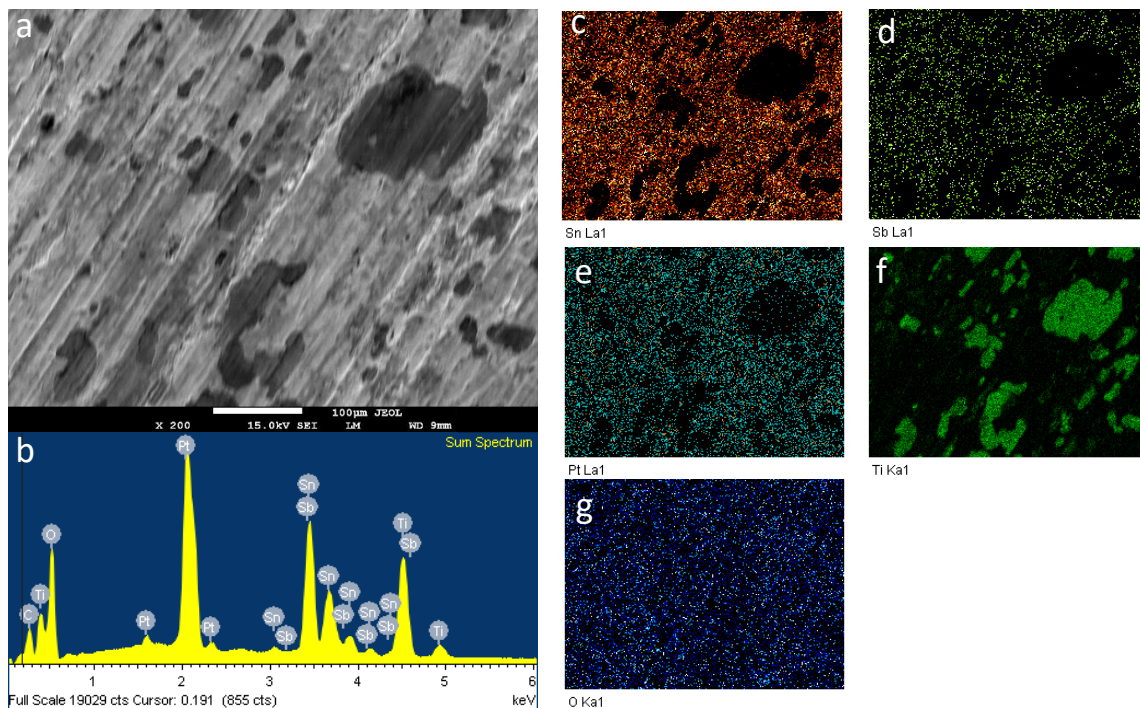


Figure 3. SnO₂-Sb films on titanium/platinum (Ti/Pt). a) SEM images; b) EDS spectrum; c–g) elementary mapping. Five layers of the precursor solution and a final calcination temperature of 600 °C over 30 min.

Table 1. Elemental analysis (weight%) of the Ti, Ti/Pt, Ti/SnO₂-Sb, and Ti/Pt/SnO₂-Sb surfaces, as determined from the EDS spectra.

Elemental composition	Samples			
	Ti	Ti/Pt	Ti/SnO ₂ -Sb	Ti/Pt/SnO ₂ -Sb
	Weight%			
C(K)	1.83	4.83	2.28	3.46
Ti(K)	98.13	9.30	15.10	18.47
O(K)	-	4.02	34.84	24.11
Pt(M)	-	81.85	-	25.11
Sn(L)	-	-	44.64	26.53
Sb(L)	-	-	2.63	2.32
Fe(K)	-	-	0.52	-

Table 1 lists the elemental analysis (weight%) of the Ti, Ti/Pt, Ti/SnO₂-Sb and Ti/Pt/SnO₂-Sb surfaces based on the EDS measurements. In the Ti/Pt surface, Pt enrichment (81.85%) and a low

oxygen content (4.02%) were observed, suggesting that the platinum film could have a more metallic character. Freitas et al. [21] concluded from the X-ray and electrochemical results that platinum thin film electrodes prepared using the Pechini method behaved like metallic platinum. A comparison of Ti/SnO₂-Sb and Ti/Pt/SnO₂-Sb showed that in the absence of the Pt layer, the contents of Sn (44.64%) and O (34.84%) were higher than they were in the presence of the Pt layer, which featured considerably lower Sn (26.53%) and O (24.11%) contents. The Sb and Ti content was low and practically independent of the presence of Pt. Therefore, the platinum film modified the surface composition by modulating the content of Sn and O on the Ti substrate.

SEM and EDS results revealed that it was possible to obtain homogeneous films of SnO₂-Sb or Pt on the titanium substrate by thermal decomposition of the precursor solution (Sn-Sb or Pt); however, heterogeneous films of SnO₂-Sb were obtained on Ti/Pt under the operating conditions applied in this work. The formation of a SnO₂-Sb film on Ti/Pt evidently occurred in conjunction with surface segregation between Sn (and/or Sn-Sb) and Pt. In this case, the Pt film was dispersed, leaving uncovered regions of titanium and regions enriched with tin. The segregation of Sn and Pt could be induced by the calcination temperature (600 °C) applied to form the SnO₂-Sb film on Ti/Pt, i.e., the calcining temperature applied may have promoted the surface heterogeneity observed in the Ti/Pt/SnO₂-Sb system.

3.2. Cyclic voltammetry of Ti/Pt, Ti/SnO₂-Sb, Ti/Pt/SnO₂-Sb electrodes.

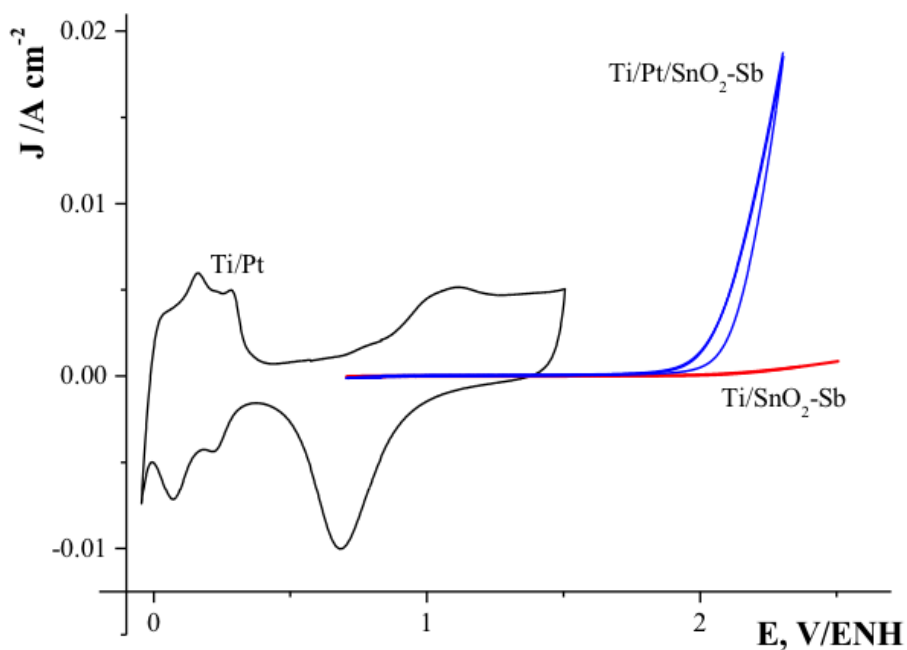


Figure 4. Voltammograms of (a) Ti/Pt, (b) Ti/SnO₂-Sb, and (c) Ti/Pt/SnO₂-Sb electrodes in H₂SO₄ 0.5 M. $v = 50$ mV/s.

Figure 4 shows the cyclic voltammograms of the (a) Ti/Pt, (b) Ti/SnO₂-Sb, and (c) Ti/Pt/SnO₂-Sb electrodes in H₂SO₄ 0.5 M. The Ti/Pt voltammogram shows the current–potential characteristics of a polycrystalline platinum electrode in the same support electrolyte and under the potential limits of 0 to 1.5 V/NHE [19, 21]. The electroadsorption and electrodesorption of hydrogen was characterized by the cathodic and anodic peaks over the interval 0 to 0.3 V/NHE. The electroadsorption of oxygen correspond a sudden increase in the anodic current between 0.5 and 1.5 V/NHE, and oxygen electrodesorption corresponded to a cathodic peak at 0.64 V/NHE. The two processes, hydrogen and oxygen electroadsorption, are separated by the double layer region. This behavior indicated that the platinum layer covered the titanium surface.

The electrochemically active electrode area was estimated by integrating the charge due to hydrogen electrodesorption in the anodic sweep between 0 and 0.3 V/NHE after subtracting the double layer charge. A theoretical charge of $Q_H = 210 \mu\text{C}/\text{cm}^2$ for hydrogen adsorption over platinum was used [31]. The estimated value of the electrochemically active electrode area was 50.3 cm², with a roughness factor of 64.0 [32, 33].

The voltammograms of the SnO₂-Sb electrodes prepared without or with a Pt interlayer (Fig.4) showed a similar trend: A large region of potential associated with the capacitive current preceded the sudden increase in current to positive potentials caused by the oxidation of water to produce molecular oxygen.

The i-E behavior of the Ti/SnO₂-Sb electrodes with and without a Pt interlayer (Fig. 4) is consistent with that reported by other authors under the same experimental conditions [18]. The current magnitude as a function of potential was considerably higher at the Ti/Pt/SnO₂-Sb electrode compared to the Ti/SnO₂-Sb electrode. The electroactive areas of the Ti/SnO₂-Sb and Ti/Pt/SnO₂-Sb electrodes, determined by capacitance measurements, were 25.5 and 42.6 cm², respectively. Similar behavior was observed on Ti/Pt/SnO₂-Sb electrodes prepared by electrodeposition de Sn y Sb [15, 18].

Figure 5 shows the i-E curves of the linear potential sweep (1 mV s⁻¹) of the Ti/SnO₂-Sb and Ti/Pt/SnO₂-Sb electrodes in 0.5 M H₂SO₄ at a highly sensitive current scale. As observed in Fig. 5, the onset potential for H₂O oxidation is different on the distinct electrodes, with Ti/Pt/SnO₂-Sb displaying the lowest potential with respect to Ti/SnO₂-Sb. Therefore, the Pt interlayer shifted the oxygen evolution potential toward less positive values and favored high currents for the evolution of oxygen. These results indicated a substantial increase in the electroactive area and conductivity of the electrode caused by the presence of Pt.

Figure 6 shows the Tafel graphs (η vs Log (J)), where $\eta = E - E_{eq}$ is the overpotential and J is current density, for the OER at the Ti/SnO₂-Sb and Ti/Pt/SnO₂-Sb electrodes. The Tafel slopes estimated from the graphs were 179 and 119 mV/dec, respectively. These values are consistent with slopes estimated in the literature for similar electrodes [18, 34]. In previous studies of Ti/SnO₂-Sb electrodes without a Pt interlayer, the Tafel slope observed in acid medium was between 110 and 270 mV/dec [9, 34], while for SnO₂ electrodes doped with antimony and platinum, the Tafel slope recorded in acid medium was 120 mV/dec [18]. The value obtained for the Tafel slope in the present work (119 mV/dec) for the Ti/Pt/SnO₂-Sb electrode suggests kinetic control by the adsorption of OH[•] according to the proposed OER mechanism [30]. Therefore, the presence of Pt as an interlayer in the Ti/SnO₂-Sb electrode induces a similar OER mechanism with that SnO₂ electrode doped with Sb and Pt [18].

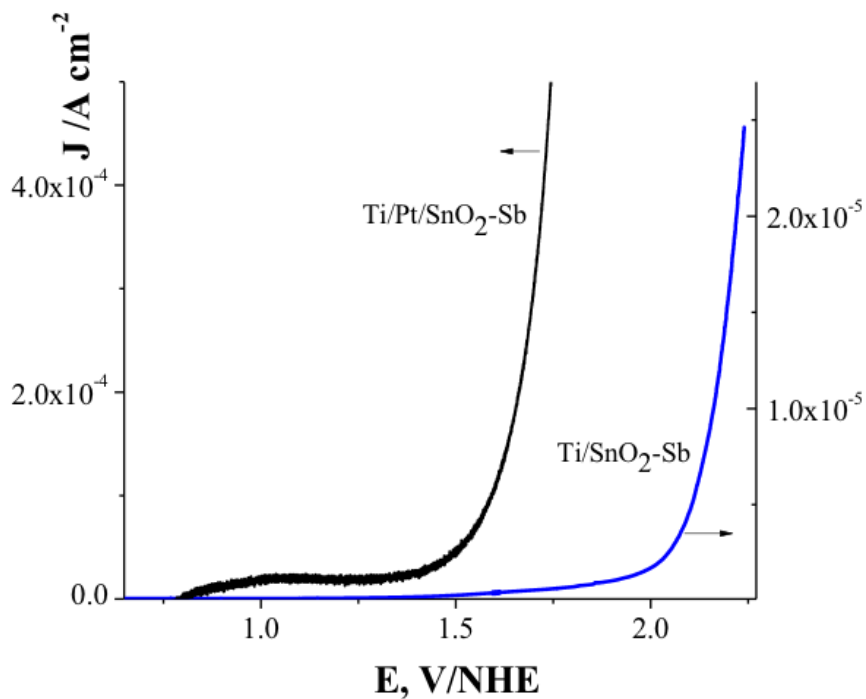


Figure 5. Linear sweep voltammograms for Ti/SnO₂-Sb y Ti/Pt/SnO₂-Sb in 0.5 M H₂SO₄ electrolytes at 1mV s⁻¹.

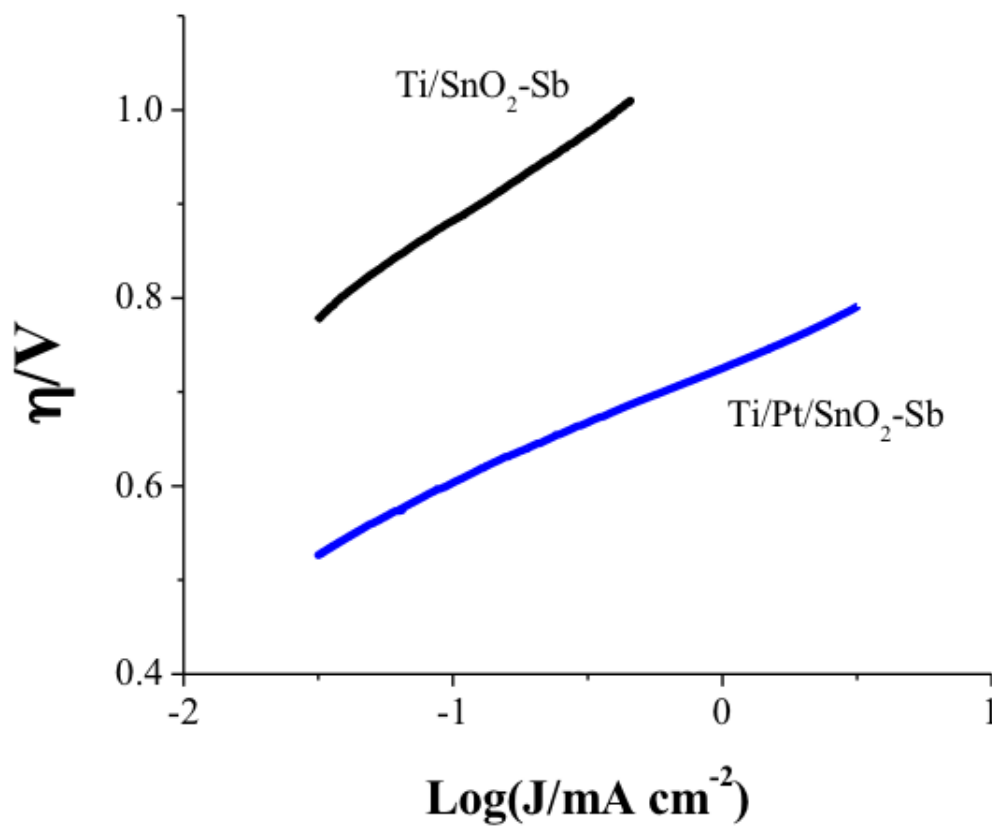


Figure 6. Tafel plots for Ti/SnO₂-Sb and Ti/Pt/SnO₂-Sb recorded in 0.5 M H₂SO₄ electrolyte solution at 1 mV s⁻¹.

4. CONCLUSIONS

SnO₂-Sb electrodes on a Ti substrate without or with a Pt interlayer were prepared using the polymer precursor method followed by thermal decomposition. The Ti/Pt, Ti/SnO₂-Sb, and Ti/Pt/SnO₂-Sb electrodes were characterized by SEM, EDS, elemental mapping, and cyclic voltammetry, revealing that the experimental conditions used to form the platinum or SnO₂-Sb films on a titanium substrate produced compact films with a favorable distribution. For the Ti/Pt electrode, the voltammetric behavior in 0.5 M H₂SO₄ was characteristic of a polycrystalline platinum electrode. The SnO₂-Sb coatings prepared on Ti substrates without or with a platinum interlayer exhibited distinct behaviors. In the absence of Pt, the SnO₂-Sb coating formed a compact layer with a good distribution of Sn, Sb, and O. In the presence of Pt, the SnO₂-Sb layer was heterogeneous. The heterogeneous nature of the SnO₂-Sb coating on Ti/Pt (Ti/Pt/SnO₂-Sb) apparently resulted from surface segregation. The voltammetric behaviors of the SnO₂-Sb electrodes prepared without or with a Pt interlayer showed similar trends; however, the presence of Pt produced a greater electroactive area and shifted the oxygen evolution potential to less positive values compared to those observed at the Ti/SnO₂-Sb electrode. The slope of the Tafel graph for the Ti/Pt/SnO₂-Sb electrode (119 mV/dec) is consistent with a mechanism in which OH[•] generation is the rate controlling step.

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