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ABSTRACT

Antimony–platinum doped tin dioxide electrodes supported on titanium have been prepared by thermal decomposition. The effect of the progressive replacement of Sb with Ru ($x = 0.00; 3.25; 6.50; 13.00 \text{ at.}\%$) on their electrochemical response in acid medium has been analysed by cyclic voltammetry. The morphology of the coatings was observed by scanning electron microscopy. $\text{Ti/SnO}_2\text{–Sb–Pt}$ electrodes without Ru presented a cracked-mud structure, typical of oxide electrodes prepared by thermal decomposition. The introduction of Ru in the oxide layer modified the coating morphology. The roughness increased and passed through a maximum with the increase of Ru content. A relation between the surface morphology, the roughness factor, voltammetric charge and the electrochemical activity has been established. The mechanism and electrocatalytic activity towards the oxygen evolution reaction has been studied from Tafel measurements. The progressive introduction of Ru in the electrodes increased their electrocatalytic activity for the oxygen evolution reaction with a change on the mechanism from non-active to active electrodes. The electrocatalytic activity mainly depends on electronic factors.

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1. Introduction

The metallic-oxide electrodes form an important and diverse family of materials which have been used in many fields of technological interest owing to their electronic, optical, magnetic and catalytic properties [1,2]. These electrodes consist of a titanium substrate covered with an oxide coating. The tetragonal rutile-like transition metal oxides (TMOs) containing noble metal cations have been successfully applied as anode (commonly known as dimensionally stable anodes, DSAs) in a number of important electrolytic processes, such as oxygen and chlorine evolution or the electrochemical oxidation of biorefractory organic pollutants in wastewaters [3–9]. The composition and the nature of the active component in the anode coating strongly affect the stability and electrochemical activity of these electrodes.

RuO_2 is a metallic-oxide which is of interest in a variety of technologies. The material shows very low resistivity, high thermal stability and high resistance to chemical corrosion [3]. As a result, RuO_2 -based electrodes have been widely used due to their good catalytic activity, even for the oxygen evolution reaction (OER) [3]. However, for applications such as electrochemical oxidation of organic compounds, the electrode material requires a minimal catalytic activity toward the OER [7,10]. Antimony-doped tin dioxide supported on titanium has emerged as an anode for the removal of

organic pollutant from aqueous wastes, allowing the attainment of efficiencies higher than those of more traditional materials [7,11,12]. In this way, coatings with properties of both RuO_2 and SnO_2 and high stability would be desirable.

Several $\text{Ti/SnO}_2\text{–Sb}$ electrodes were prepared and characterized from an electrochemical and physicochemical point of view [5,6,13–16]. The introduction of little amounts of platinum (around 3 at.%) in the layer produces an increase of the service life of the electrode of several orders of magnitude [5]. Then, the objective of this work has been the preparation and characterization of electrodes of nominal composition $\text{Ti/SnO}_2\text{–Sb}(13-x)\text{–Ru}(x)\text{–Pt}(3)$, with properties ranging from SnO_2 to RuO_2 . For such a purpose, a progressive replacement of Sb with Ru ($x = 0.00\%; 3.25\%; 6.50\%; 13.00\%$) has been carried out and the oxide coatings have been electrochemically characterized by cyclic voltammetry. The effect of the Ru content on the mechanism and electrocatalytic activity towards the oxygen evolution reaction has been studied from Tafel measurements.

2. Experimental

2.1. Preparation of the electrodes

Tin tetragonal rutile-like oxide electrodes of nominal composition $\text{SnO}_2\text{–Sb}(13-x)\text{–Ru}(x)\text{–Pt}(3)$ (with $0.00 \leq x \leq 13.0 \text{ at.}\%$) were prepared as thin films by thermal decomposition of proper salt precursors onto a Ti support. The salt precursors were made up of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (Aldrich), SbCl_3 (Fluka p.a.), H_2PtCl_6 (Aldrich) and

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RuCl₃·nH₂O (Aldrich) dissolved in absolute ethanol (J.T Baker) + HCl (Merck p.a.). The salts were mixed in stoichiometric amounts according to the desired nominal composition. The total metallic cation concentration was kept constant at 0.5 M. Prior to the decomposition process, Ti plates (1 cm × 1 cm × 0.05 cm, Goodfellow 99.6%) were degreased in acetone, etched in a boiling 10% oxalic acid solution for 1 h and finally rinsed with distilled water. The precursor solution was spread over the Ti surface with the aid of a brush. The solvent was dried at 70 °C and the electrode was subsequently calcined at 400 °C for 10 min, for the thermal decomposition of the salt and metal oxide formation to be accomplished. The Ti sheets were coated with successive layers of the oxides by repeating this procedure. A final annealing step was carried out for 1 h at 600 °C. The weight of the electrode was measured before and after the deposition processes in order to determine the oxide loading.

2.2. Electrochemical measurements and characterization of the electrodes

All electrochemical measurements were carried out in a conventional three-electrode cell. The counter electrode was a platinum wire electrode and the potentials are referred to a reversible hydrogen electrode (RHE) immersed in the same solution. The aqueous 0.5 M H₂SO₄ solutions were de-oxygenated by N₂ bubbling and were prepared from the Merck Suprapur concentrated acid and ultrapure water (Purelab Ultra from Elga-Vivendi, 18.2 MΩ cm).

An Autolab PGSTAT 30 system, controlled by GPES EcoChimie software, has been employed for all the electrochemical studies carried out at different scan rates. In these studies cyclic voltammetry (CV) measurements were performed between different potential limits at a scan rate between 1 and 5000 mV s^{−1}, using a Solartron 1470E multistat system. The current densities have been calculated using the apparent geometric area of the electrodes (2 cm²). The voltammetric charges (*q*^{*}) corresponding to active surface areas were determined by integrating the area of the cyclic voltammograms. The electrocatalytic activity towards OER was investigated in aqueous 0.5 M H₂SO₄ solution by quasi-steady galvanostatic curves at current densities lower than 5 mA cm^{−2} at a scan rate of 3 μA s^{−1}.

The surface texture of the electrodes was studied by scanning electron microscopy (SEM Hitachi S-3000N), which was coupled to a Rontec X-ray detector for energy dispersive X-ray (EDX) microanalysis.

3. Results and discussion

3.1. SEM and EDX characterization

Fig. 1 shows the SEM micrographs of the SnO₂-Sb(13 − *x*)-Ru(*x*)-Pt(3%) coatings prepared by thermal decomposition onto a Ti support. The Ti substrates were uniformly covered by the oxide layers. In the absence of Ru (Fig. 1a), the oxide layer presents a cracked-mud structure, typical of metal oxide coatings obtained by thermal decomposition [3,17–20]. These cracks are produced on the surface during the cooling of the electrode to room temperature [5,15] and/or during the solvent evaporation stage [19]. However, and due to its compacting effect, the presence of platinum makes these coatings less cracked than usual, as it has been previously observed [5,21].

Significant morphologic changes are observed upon substituting Sb with Ru in the doped SnO₂ electrodes. With small amounts of Ru (Fig. 1b) cracks disappear and porosity strongly increases. Further increase of Ru in the oxide layer reduces gradually the porosity (Fig. 1c and d) until a cracked-mud structure is reached again at *x* = 13.00 (Fig. 1e). Apart from SnO₂-based coatings, this cracked

Table 1

Nominal and experimental atomic ratios for Ti/SnO₂-Sb(13 − *x*)-Ru(*x*)-Pt(3%) electrodes obtained by EDX and XPS techniques.

Electrode (<i>x</i>)	Sb/Sn		Ru/Sn		Ru/Sb	
	Nom.	EDX	Nom.	EDX	Nom.	EDX
0.00	0.15	0.14	–	–	–	–
3.25	0.12	0.35	0.04	0.04	0.33	0.11
6.50	0.08	0.27	0.08	0.10	1.00	0.35
9.75	0.04	0.15	0.12	0.16	3.00	1.12
13.00	–	–	0.15	0.20	–	–

morphology has been also widely observed on RuO₂ oxides prepared by this method (Fig. 1f) [3,22], although with larger cracks and a much more smooth surface. Morphologic changes were also observed by other authors when Ru was introduced in SnO₂ electrodes, but the absence of platinum on these electrodes makes difficult any comparison [22,23].

The bulk composition of the SnO₂-Sb(13 − *x*)-Ru(*x*)-Pt(3%) coatings was determined by EDX microanalysis. EDX results indicated a homogeneous distribution of the components and a negligible signal of the underlying Ti (<1%), pointing out that a good coverage of the substrate was achieved. It has been previously reported that well-covered substrates are obtained with coatings of at least 2 μm thick [24]. In this work, oxides loadings were around 1.5–2.0 mg cm^{−2} and, considering the density for SnO₂ (cassiterite), $\rho = 6.95 \text{ g cm}^{-3}$, the nominal thickness of the deposited layers would be 2.2–2.9 μm.

Table 1 summarizes the nominal ratios of Sb/Sn, Ru/Sn and Ru/Sb together with the experimental ratios as determined by EDX. A fairly good correlation exists between the nominal and EDX Sb/Sn values at *x* = 0.00. When Ru is introduced in the oxide layer an increase in the Sb/Sn ratio is observed that can be attributed to bulk enrichments with Sb. This could be due to either some effect of Ru and/or loss of Sn by evaporation of the salt precursor during preparation [25,26]. The Sb enrichment is also observed in the low Ru/Sb ratios obtained by EDX with respect to the nominal values. On the other hand, Ru/Sn ratios show a good correlation between nominal and EDX results at low Ru contents, although a slight Ru enrichment is observed at compositions above *x* = 6.50, pointing out again to some bulk Sn depletion.

3.2. Cyclic voltammetry characterization

Fig. 2 shows the cyclic voltammograms of Ti/SnO₂-Sb(13 − *x*)-Ru(*x*)-Pt(3%) and Ti/RuO₂ electrodes in a 0.5 M H₂SO₄ solution. In the case of the electrode without Ru (Fig. 2a), an oxidation current at potentials more positive than 0.8 V is observed due to the oxidation of the platinum surface (A₁) [5,27]. The anodic current rises at potentials more positive than 1.6 V due to the OER. The cathodic peak (C₁) between 0.6 and 0.7 V corresponds to the reduction of the platinum oxides formed in the positive scan [5,27]. The absence of electrochemical features belonging to SnO₂ and Sb₂O₅ is characteristic of these “non-active” oxides [5,28,29]. A cathodic current appears at potentials less positive than 0.3 V due to the irreversible reduction of the tin oxide, which produces electrode damage. For this reason, the lower potential limit must not be fixed below 0.3 V [13,16,30].

The voltammogram for the active RuO₂ sample (Fig. 2f) shows clearly its characteristic and highly reversible surface redox processes [31,32]. The peaks observed at a half-wave potential of ca. 0.6 and 0.8 V have been attributed to Ru(II) ↔ Ru(III) (A₁/C₁) and Ru(III) ↔ Ru(IV) (A₂/C₂) surface transitions, respectively, whereas that at ca. 1.25 V corresponds to the couple Ru(IV) ↔ Ru(VI) (A₃/C₃). During the voltammetric cycle the electrode surface is oxidised and

Fig. 1. SEM images of Ti/SnO₂-Sb(13-x)-Ru(x)-Pt(3%) electrodes: (a) x = 0.00, (b) x = 3.25, (c) x = 6.50, (d) x = 9.75, (e) x = 13.00, (f) Ti/RuO₂.

reduced reversibly through several solid-state surface redox transitions of oxyruthenium species according to the following reversible mechanism [31,33–35]:

The sharp current rise occurring at potentials above the A₃' peak corresponds to the oxygen evolution reaction and appears 0.2 V earlier than in the case of the Ti/SnO₂-Sb(13)-Pt(3%) electrode (Fig. 2a), pointing out the higher electrocatalytic activity towards oxygen evolution for RuO₂ electrodes. The cathodic peak at ca. 1.4 V (C₄) could be attributed to the reduction of higher oxidised oxyruthenium species (Ru(VII)) probably formed and hidden during OER and masked by the Faradaic process. This peak is rarely observed in cyclic voltammograms for RuO₂-coated electrodes prepared by thermal decomposition, being more commonly seen in single crystal RuO₂ (1 1 0), (0 0 1) and (1 0 0) voltammograms [31,32]. On the other hand, it appears as a prominent reversible peak in alkaline medium, where higher oxidation states of Ru are more stable [31].

When the “non-active” Sb is progressively substituted by Ru into the tin oxide (Fig. 2b–e) the voltammetric features of RuO₂ progressively appear. As the amount of Ru increases, (i) an anodic oxidation peak at around 1.20–1.25 V becomes more prominent, what may be due to the sum of platinum (A₁) and Ru (A₃) oxidation currents; (ii) the cathodic peaks C₃ and C₄, corresponding the reduction of the higher oxidised Ru species, appear; (iii) the cathodic peak C₁ strongly broadens and shifts slightly to more positive potentials due to the contribution of the reduction of the less oxidised Ru species (C₂ and C₁) and (iv) the OER shifts to less positive potentials, what could be associated with an electrocatalytic effect in the OER by the ruthenium in the electrode composition. However, better defined

peaks and changes in voltammograms are not more evident owing to the coincidence of the ruthenium and platinum electrochemical features. Therefore, any estimation of the surface composition from CV cannot be derived.

Cyclic voltammograms with features belonging to both Pt and Ru were also obtained by Lassali et al. [36], but in this case these active components were mixed in a ternary oxide with Ti, no immersed in a SnO₂ matrix. Therefore, to our knowledge, there are no works studying the effect of Pt on mixed Sn–Ru oxides.

Studies of the influence of the Ru on the onset of the OER in SnO₂-based electrodes are lacking in the literature. Alves et al. [37] found that the substitution of TiO₂ by SnO₂ promotes ~60 mV shifts of the overpotential towards less positive values, although the effect of the Ru content was not analysed. Gaudet et al. [29] remarked that the shape of the voltammetric curves with a Ru surface content >28 at.% is similar to that of pure RuO₂ and observed very large distortions of the voltammetric curves at Ru surface contents >28 at.%, although the preparation method was completely different. Our results show that the onset of the OER at x = 9.75 is shifted respect to the pure RuO₂ coating only ~50 mV to more positive potentials, pointing out that very good electrocatalytic properties towards the OER can be achieved with low Ru contents in SnO₂-based electrodes.

3.2.1. Capacitive measurements

Capacitance measurements have been performed in order to analyse and determine the capacitance and the roughness factor (Rf) of the different electrodes. The roughness factor of the electrodes can be determined from the value of the double-layer capacitance (C_{dl}) and constitutes a measure of the real surface area

Fig. 2. Stabilized cyclic voltammograms of the $\text{Ti/SnO}_2\text{-Sb}(13-x)\text{-Ru}(x)\text{-Pt}(3\%)$ electrodes in a 0.5 M H_2SO_4 solution: (a) $x=0.00$, (b) $x=3.25$, (c) $x=6.50$, (d) $x=9.75$, (e) $x=13.00$, (f) Ti/RuO_2 , $\nu=20\text{ mV s}^{-1}$.

of the electrodes, which is one of their electrocatalytic activity determining factors.

It is well known that the capacitance of “non-active” metallic-oxides electrodes corresponds with the non-Faradaic double layer capacitance, since the absence of electrochemically active species involves the charge accumulation in the electrode-solution interface as the unique charge storage mechanism. However, when

electrochemically active species are present in the oxide coating the total capacitance has contribution of non-Faradaic capacitance component (the electric double-layer charge) and the Faradaic components due to electrochemical reactions. In this case the total capacitance is known as pseudocapacitance.

Fig. 3a and b show the cyclic voltammograms of $\text{Ti/SnO}_2\text{-Sb}(13\%)\text{-Pt}(3\%)$ ($x=0$) and Ti/RuO_2 at a scan rate of

Fig. 3. Cyclic voltammograms of (a) Ti/SnO₂-Sb(13%)-Pt(3%) ($x=0.00$) and (b) RuO₂ electrodes in a 0.5 M H₂SO₄ solution between 0.3 and 1.1 V (CV) and in five shorter ranges of potential (DV). $v = 100 \text{ mV s}^{-1}$. Evolution of the current density at different potentials against the potential scan rate for (c) Ti/SnO₂-Sb(13%)-Pt(3%) ($x=0.00$) and (d) Ti/RuO₂ electrodes in a 0.5 M H₂SO₄ solution.

100 mV s⁻¹ (complete voltammogram, CV) and the voltammograms obtained at the same scan rate but in five narrower potential ranges with $\Delta E = 0.1 \text{ V}$ (differential voltammogram, DV) [5,39]. The differences between currents measured in the complete, CV, and the differential, DV, voltammograms could be mainly associated to some hysteresis in the pseudo-capacitance phenomena caused by the oxidation and reduction of the platinum and ruthenium species. Thus, capacitance obtained from the differential (DV) voltammograms corresponds mainly to the electric-double-layer capacitance.

The values of capacitance have been measured in the DV from the cathodic and anodic current densities in the midpoint of the potential range (0.55, 0.75, 0.95, 1.15 and 1.35 V) for several scan rates. Fig. 3c and d show the plot of the cathodic and anodic current densities obtained at the different potentials vs. the scan rate for both electrodes. The linear relationship between current density and scan rate confirms the non-Faradic character of the current in these DV potential regions. The capacitance at each potential is obtained from the absolute value of the slopes of the linear plots.

Table 2 shows the values of capacitance obtained for the different Ti/SnO₂-Sb(13-x)-Ru(x)-Pt(3%) and Ti/RuO₂ electrodes at different potentials. For a fixed potential, the capacitance increases when a small amount of Ru is introduced ($x=3.25$) and then decreases with a further increase of the Ru content. It can also be observed in Table 2, that the capacitance for the Ti/SnO₂-Sb-Pt electrode ($x=0$) decreases as the potential increases. This trend was previously observed for this kind of electrodes [5] and it was

related with the Mott-Schottky relationship for n-type semiconductors [40,41]. The same trend is also observed for the electrodes with a Ru content lower than 9.75. However, for Ru content of 9.75 and higher the capacitance increases with the increase of potential.

Table 2 summarizes the roughness factor (Rf) defined as real surface area per geometric area of electrode (2 cm²) at 1.15 V. The values of Rf has been calculated according to Wu et al. using a specific capacitance of 8 $\mu\text{F cm}^{-2}$ [37] for the SnO₂-based electrodes and 80 $\mu\text{F cm}^{-2}$ for the RuO₂ one, according to Sugimoto et al. [38] A maximum in the Rf when $x=3.25$ is observed and when the Ru content increases the Rf decreases, what is in close agreement with

Table 2

Capacitance and specific capacitance at various potentials and roughness factor calculated at 0.55 V for Ti/SnO₂-Sb(13-x)-Ru(x)-Pt(3%) electrodes obtained from the differential voltammetric measurements in a 0.5 M H₂SO₄ solution.

Potential (V vs. RHE)	Capacitance (mF cm^{-2})					
	Electrode (x)					
	0.00	3.25	6.50	9.75	13.00	RuO ₂
0.55	6.5	11.3	8.7	7.7	5.4	3.7
0.75	5.2	9.5	7.5	7.6	5.6	4.0
0.95	3.9	9.2	6.9	8.0	5.5	4.0
1.15	3.3	8.9	7.1	8.5	5.5	4.5
1.35	2.8	7.2	6.0	8.0	6.4	6.5
Rf	816	1413	1088	968	672	92
$q_{\text{IN}}^*/q_{\text{TOT}}$	0.29	0.19	0.20	0.21	0.22	0.20

Fig. 4. (a) Extrapolation of the total charge (q_{TOT}) for $\text{Ti/SnO}_2\text{-Sb}(13-x)\text{-Ru}(x)\text{-Pt}(3\%)$ electrodes from the representation of the reciprocal voltammetric charge (q^*)⁻¹ vs. the square root of the voltammetric scan rate ($v^{1/2}$). (b) Extrapolation of the outer charge (q_{OUT}^*) for the electrodes of different composition from the representation of the voltammetric charge (q^*) vs. the reciprocal square root of the voltammetric scan rate ($v^{-1/2}$). Data obtained from the cyclic voltammograms obtained between 0.4 and 1.3 V vs. RHE at various scan rates in a 0.5 M H_2SO_4 solution. (c) Total, outer and inner charges for $\text{Ti/SnO}_2\text{-Sb}(13-x)\text{-Ru}(x)\text{-Pt}(3\%)$ electrodes as a function of the nominal Ru content.

the previous SEM results. Maxima in R_f values at low contents of the active component were also observed by Nanni et al. [35] for the Sn–Ru system and by Lassali et al. [20] for the Sn–Ir system and have been attributed to characteristic morphologies produced by the segregation of one of the components at a given composition.

3.2.2. Voltammetric charge analysis

The total voltammetric charge (q_{TOT}^*) is related to the real surface area but is also affected by the specific electroactivity of the sites, which depends on the chemical composition of the layers [34,36]. Therefore the voltammetric charge of an electrode is a measure of its active surface area. During potential cycling, an increase in the scan rate has a direct effect on the diffusion of the electrolyte ions into the electrode coating. At higher scan rates the ions only approach to the outer surface of the electrode and hence the oxide film that is accessible only through the deep pores does not actively contribute to the charge. Then, the total voltammetric charges have been studied as function of the scan rate and presented in Fig. 4. The voltammetric charge q^* decreases with increasing the potential scan rate for all of the investigated electrode materials. These results can be due to the slow diffusion of electrolyte ions within the pores of the electrode material that means that the accessibility of ions to the inner regions of the electrode material is hindered [5,19,29,34]. At very low scan rates, the total electrochemically active surface takes part in the charging process. Then, the extrapolation of q^* to $v=0$ from $1/q^*$ vs. $v^{1/2}$ (Fig. 4a) gives the total voltammetric charge (q_{TOT}^*) which is the charge related to the entire electroactive sur-

face of the oxide coating. The extrapolation of q^* to $v=\infty$ ($v^{-1/2}=0$) from the q^* vs. $v^{-1/2}$ (Fig. 4b) gives the outer voltammetric charge (q_{OUT}^*), which is the charge due to the most accessible electroactive surface [5,19,29,34]. The inner voltammetric charge (q_{IN}^*), that corresponds to the less accessible surface sites of the oxide layer, can be calculated from the total charge and outer charge by subtraction.

Fig. 4a and b show these plots for the different $\text{Ti/SnO}_2\text{-Sb}(13-x)\text{-Ru}(x)\text{-Pt}(3\%)$ and Ti/RuO_2 electrodes. Fig. 4c plots the values of total charge, outer charge and inner charge as function of the nominal Ru content in the oxide layer. It can be observed a larger contribution of the outer charge to the total charge and that the outer charge increases with the amount of Ru in the oxide layer until $x=9.75$ and then decreases to values lower than the limit cases ($x=0$ and RuO_2). A maximum in the charge at low contents of the more active material was also observed for the Sn–Ru system [35,42], for the Sn–Ir system [19,20] and for the Ir–Ru system [31,43]. This maximum has been attributed to several factors like a higher degree of non-stoichiometry, a higher segregation of the active component or a finer particle size at a given composition, which can produce higher conductivities, higher concentration of surface active species or higher exposed surface areas. The decrease in the charge at high active component concentrations could be due to a significant decrease in the surface area, what is in close agreement with the SEM and capacitance results found in this work. However, the highest surface area observed by SEM and capacitance measurements at $x=3.25$ does not agree with the highest charge value, i.e., the highest electro-

chemically active surface area, found at $x = 9.75$, indicating that the effect of the Ru content dominates and prevails over that of the exposed surface area.

Fig. 4c also shows that while q_{OUT}^* is seen to increase almost proportionally with q_{TOT}^* , the inner charge remains low and does not increase appreciably as the total charge increases. These results were also observed by other authors [19,44] and indicate that, despite the differences observed by SEM, the morphology of the inner layer seems not to change substantially with composition and only the outer surface seems to be affected by the introduction of Ru. This is corroborated from the electrochemical porosity values, defined as the relation between the inner and the total charges ($q_{\text{IN}}^*/q_{\text{TOT}}^*$), as a function of the nominal Ru content in the oxide layer presented in Table 2. It can be observed that the electrochemical porosity does not change considerably with the amount of Ru in the oxide layer, being in all cases of the same order of magnitude than the RuO_2 electrode and lower than the value obtained for the $\text{Ti/SnO}_2\text{-Sb-Pt}$ ($x = 0$).

A larger contribution of the outer charge to the total charge and an electrochemical porosity independent of the Ru content were also observed by Gaudet et al. [29], although they did not observed any maximum in the charge with the composition. However, any comparison with these results cannot be carried out due to the different technique employed in the preparation of the mixed oxides.

3.3. Oxygen evolution reaction (OER). Tafel slope measurements

The study of the oxygen evolution reaction in 0.5 M H_2SO_4 solution on doped SnO_2 electrodes has been performed by quasi-steady galvanostatic curves at current densities lower than 5 mA cm^{-2} . Tafel plots are useful for evaluating the electrocatalytic activity of the electrodes towards the OER. Fig. 5 shows the Tafel plots obtained from the polarization curves (j - E curves) for the $\text{Ti/SnO}_2\text{-Sb}(13-x)\text{-Ru}(x)\text{-Pt}(3\%)$ and Ti/RuO_2 electrodes. Tafel plots exhibit a sufficiently extended linear region at low current densities while deviations from linearity occur at high current densities probably due to uncompensated ohmic drops. However, a larger deviation involving two linear regions in the case of the Ti/RuO_2 electrode can be observed and will be explained in more detail below.

The electrocatalytic activity of the various oxide materials is best compared by following the potential at constant current density. As it can be seen, this comparison can be easily carried out because of the substantial parallelism of the Tafel plots and shows that small additions of Ru in the SnO_2 -based coatings sharply decrease the

potential values at constant current density, increasing their electrocatalytic activity towards the OER. This electrocatalytic effect of Ru on SnO_2 anodes was also observed by other authors [22,29].

From the linear part of the Tafel plots (see Fig. 5), kinetic parameters for the OER can be evaluated. From a fundamental point of view, the activity of an electrocatalyst is expressed by the Tafel slope, which can reflect materials-specific reaction mechanisms and/or, indirectly, the conditions of adsorption of reaction intermediates. The Tafel slope (a) for a multi-electron process, such as the oxygen evolution reaction, is $\beta F/2.3RT$ [45]. On the other hand, from the y-intercept of the Tafel plot (b), the j_0 value can be derived, which measures the intrinsic ability of the solid surface to catalyze the reaction at $\eta = 0$. In general, the best electrocatalysts are those with lower Tafel slopes and lower b values (higher j_0).

The values of the Tafel slopes, determined in the linear region close to the reversible oxygen potential (in the low current density region), and b constants are depicted against the nominal Ru content in Fig. 6. As it can be seen, the Tafel slope for the $\text{Ti/SnO}_2\text{-Sb}(13\%)\text{-Pt}(3\%)$ electrode is close to 120 mV/dec, which corresponds to a single electron transfer suggesting a kinetic control by the adsorption of OH from water according to the generally proposed mechanism in the oxygen evolution reaction [3] (see below Eq. (1)). This high Tafel slope value is in close agreement with those found in the literature for SnO_2 -based electrodes [5,29] and reflects their poor electrocatalytic activity towards the OER.

The Tafel slope of 40 mV observed for the Ti/RuO_2 electrode is a typical value for OER on this type of anodes [3,31,46] and involves the electrooxidation of the intermediate surface complex as the rate-determining step (see below Eq. (3)). Moreover, as it has been previously mentioned, the Tafel slope for the Ti/RuO_2 electrode increases at higher current densities, where a value close to 120 mV is reached. This change (or break) in the Tafel slope at a “critical” potential of about 1.45 V vs. RHE is typical of these electrodes and is attributable to a combination of three reasons [3,31]: (i) gas bubble formation and pore closure effects; (ii) the saturation of higher oxidation state active surface oxyanions, e.g., Ru(VII) , which results in a new rate-determining step predominating in the region of high current density; and (iii) a change in the reaction mechanism involving corrosion of the material. The absence of this Tafel slope break on Ru-doped SnO_2 electrodes reflects the fact that tin serves as a stabiliser of the ruthenium oxide against dissolution.

The gradual substitution of Sb by Ru produces a decrease in both the Tafel slope and the Tafel line y-intercept (b) value, indicating a clear electrocatalytic effect of Ru on the response towards the OER. The Tafel slope is decreased from 120 to 100 mV/dec when the Ru concentration is increased from 0 to 13 at.%, and, as it was found by other authors [29], a further decrease of the Tafel slope, until a

Fig. 5. Tafel plots for the oxygen evolution reaction in a 0.5 M H_2SO_4 solution for $\text{Ti/SnO}_2\text{-Sb}(13-x)\text{-Ru}(x)\text{-Pt}(3\%)$ electrodes.

Fig. 6. Tafel slope and Tafel line y-intercept (b) for $\text{Ti/SnO}_2\text{-Sb}(13-x)\text{-Ru}(x)\text{-Pt}(3\%)$ electrodes as a function of the nominal Ru content.

limit value of 40 mV, with higher amounts of Ru in the mixed oxide would be expected. However, it can be stressed the very similar results obtained between the $x = 9.75$ and $x = 13.00$ electrodes, what seems to indicate the presence of a composition range with slight influence of the Ru content on the electrocatalytic activity.

The variation observed with the composition suggests a modification of the mechanism or of its **rate-determining** step [29,46]. A complete kinetic study of oxygen evolution (including the determination of the reaction order) was not carried out, so it is not possible to establish a precise mechanism for this family of electrodes. However, an explanation for the variation of the Tafel slope with the composition can be attempted, considering the proposed generalized mechanism for oxygen evolution on oxide electrodes [3,29] and that the catalytic activity of an oxide material is related to the metal–**oxygen** bond strength on the surface [29].

According to this generalized mechanism, the first step of the oxygen evolution reaction comprises a primary discharge of water molecules (acid medium) with the oxidation of a surface active site

and then, the intermediate surface complex formed is converted to another more suitable intermediate

followed by its oxidation

and finally O_2 is liberated from decomposition of the higher intermediate oxide

The Tafel slope for each step are presented next to their respective equations, and the rate determining step for a certain oxide material is determined by the strength of interaction between the oxide surface and the oxygenated intermediates. On the basis of this mechanism it can be proposed that the variation of Tafel slope from 120 mV for sample without Ru, to 100 mV for $x = 13.00$ sample is due to a decreased difficulty of the oxide electrode to proceed with the discharge of the first water molecule occurring with the oxidation of a surface active site. This may be due to the fact the substitution of Sb for Ru into the SnO_2 –**Sb** phase, which is an electronic semiconductor with no marked redox behavior in the studied potential range, introduces a higher redox activity and produces a carrier transport mechanism change (from n-type to p-type transport) and an increase in its electrical conductivity [29].

The electrocatalytic activity of an electrode depends on both electronic (structure and surface chemistry composition) and geometric (extension of the surface area) factors and the knowledge of the real surface area is important to disentangle truly electrocatalytic (electronic) factors from mere surface area (geometric) effects. The results of the previous section have shown that the effective electrochemical area (total voltammetric charge) of the coatings changes drastically with composition. Therefore, true electrocatalytic effects will be mixed with roughness factors. To overcome this problem, the currents densities measured in the polarisation experiments for the different compositions, calculated as usual using the geometric surface area of the electrodes, were divided by the corresponding total voltammetric charge (q_{TOT}^*) [46]. This correction produces a shift of the curves in the x-direction without altering the corresponding shapes. The resulting “normalised” Tafel plots are presented in Fig. 7 for electrodes of different compositions. In this figure, the “normalised” Tafel plots are better distinguished (see $x = 9.75$ and 13.00) and show the same sequence of electrocatalytic activity as the non-corrected Tafel plots, corroborating the existence of true electrocatalytic (electronic) factors.

Fig. 7. “Normalised” Tafel plots for the oxygen evolution reaction in a 0.5 M H_2SO_4 solution for Ti/SnO_2 –**Sb**(13– x)–**Ru**(x)–**Pt**(3%) electrodes.

As it would be expected, the increased electrocatalytic activity with the Ru content observed from Tafel slope measurements is in close agreement with the highest voltammetric charge obtained at higher Ru contents, and indicates that the performance of Ti/SnO_2 –**Sb**(13– x)–**Ru**(x)–**Pt**(3%) electrodes towards the OER is governed by true electrocatalytic (electronic) factors, which prevail over the higher surface areas found at lower Ru contents (geometrical factors). However, the decrease in the voltammetric charge with the Ru content above $x = 9.75$ does not agree with the higher electrocatalytic activity towards the OER observed for Ti/RuO_2 and predicted for higher Ru contents. This could be a consequence of a gradual change towards a more favoured mechanism of the OER as the Ru content increases, as it has been proposed and discussed in this section.

4. Conclusions

Ti/SnO_2 –**Sb**(13– x)–**Ru**(x)–**Pt**(3%) electrodes with different values of x between 0 and 13 were prepared by thermal decomposition. These electrodes were characterized by SEM and cyclic voltammetry. The progressive substitution of Sb by Ru in the doped- SnO_2 electrodes produces significant morphologic changes. The surface roughness firstly increases with small amounts of Ru and it gradually decreases at higher Ru content reaching a cracked-mud structure again. The EDX results point out that the presence of Ru in these electrodes results in a bulk Sb enrichment and some Sn depletion.

As the “non-active” Sb is progressively substituted by Ru into the doped- SnO_2 layer, the RuO_2 electrochemical features are progressively distinguished in the cyclic voltammograms. The OER shifts to less positive potentials, indicating an electrocatalytic effect by the Ru. The capacitance and R_f values reached a maximum at the lowest Ru content ($x = 3.25$) what is in agreement with the SEM results. As the Ru content increases in the oxide layer, the behaviour of the SnO_2 –based coating changes progressively from the n-type to that of p-type semiconductor, characteristic of the RuO_2 .

The voltammetric charge analysis shows that the outer charge and the total charge increase until the Ru content is $x = 9.75$ and reveals a larger contribution of the outer charge to the total charge.

Tafel analysis indicates that small additions of Ru in the SnO_2 –based coatings sharply decrease the potential values at constant current density, increasing their electrocatalytic activity towards the OER as it was obtained with voltammetric analysis. The presence of Ru seems to favour the discharge of the first water molecule occurring with the oxidation of a surface active site,

as deduced from the decrease in the Tafel slope. These results are in agreement with the highest voltammetric charge obtained at higher Ru contents, and indicates that the performance of Ti/SnO₂-Sb(13-x)-Ru(x)-Pt(3%) electrodes towards the OER is governed by true electrocatalytic (electronic) factors, which prevail over the higher surface areas found at lower Ru contents (geometrical factors).

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