Electrochemical characterization of SnO₂ electrodes doped with Ru and Pt

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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 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. Ti/SnO₂–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 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 electrochemical processes, such as oxygen and chlorine evolution or the decomposition. The effect of the progressive replacement of Sb with Ru (x = 0.00; 3.25; 6.50; 13.00 at.%) on their electrocatalytic activity mainly depends on electronic factors. This work has been the preparation and characterization of electrodes of nominal composition Ti/SnO₂–Sb(13 − x)–Ru(x)–Pt(3), with properties ranging from SnO₂ to RuO₂. For such a purpose, a progressive replacement of Sb with Ru (x = 0.00; 3.25; 6.50; 13.00 at.%) 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.
RuCl₃. nH₂O (Aldrich) dissolved in absolute ethanol (J.T Baker)+ HCl (Merk p.a.). The salts were mixed in stoichiometric amounts according to the desired nominal composition. The total metal-cation concentration was kept constant at 0.5 M. Prior to the decomposition process, Ti plates (1 cm x 1 cm x 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 - 450 °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 prior to the measurements. The solvent was dried at 70 °C and the electrode was subsequently calcined at 400 - 450 °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.

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

\[
\text{RuO}_x(\text{OH})_y + \delta \text{H}^+ + \delta \text{e}^- \rightarrow \text{RuO}_{x-\delta}(\text{OH})_{y+\delta} \quad (1)
\]

The sharp current rise occurring at potentials above the A'3 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(VIII)) 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 (A'3) oxidation currents; (ii) the cathodic peaks C₁ and C₄, corresponding the reduction of the higher oxidised Ru species, appear; (iii) the cathodic peak C₄ 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 (Cdl) and constitutes a measure of the real surface area.
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 Ti/SnO$_2$–Sb(13%)–Pt(3%) ($x=0$) and Ti/RuO$_2$ at a scan rate of...

Fig. 3. Cyclic voltammograms of (a) Ti/SnO$_2$–Sb(13%)–Pt(3%) ($x=0.00$) and (b) RuO$_2$ electrodes in a 0.5 M H$_2$SO$_4$ solution between 0.3 and 1.1 V (CV) and in five shorter ranges of potential (DV), $v=100$ mVs$^{-1}$. Evolution of the current density at different potentials against the potential scan rate for (c) Ti/SnO$_2$–Sb(13%)–Pt(3%) ($x=0.00$) and (d) Ti/RuO$_2$ electrodes in a 0.5 M H$_2$SO$_4$ solution.

100 mV s$^{-1}$ (complete voltammogram, CV) and the voltammograms obtained at the same scan rate but in five narrower potential ranges with $\Delta E=0.1$ 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 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/SnO$_2$–Sb(13–$x$)–Ru($x$)–Pt(3%) and Ti/RuO$_2$ 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/SnO$_2$–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 cm$^2$) at 1.15 V. The values of Rf has been calculated according to Wu et al. using a specific capacitance of 8 F cm$^{-2}$ [37] for the SnO$_2$-based electrodes and 80 F cm$^{-2}$ for the RuO$_2$ 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

<table>
<thead>
<tr>
<th>Capacitance (mF cm$^{-2}$)</th>
<th>Electrode ($x$)</th>
<th>RuO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potential (V vs. RHE)</td>
<td>0.00</td>
<td>3.25</td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>5.20</td>
</tr>
<tr>
<td></td>
<td>0.95</td>
<td>3.95</td>
</tr>
<tr>
<td></td>
<td>1.15</td>
<td>3.35</td>
</tr>
<tr>
<td></td>
<td>1.35</td>
<td>2.85</td>
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<tr>
<td></td>
<td>0.85</td>
<td>1.35</td>
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<td></td>
<td>0.95</td>
<td>0.55</td>
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</table>

the previous SEM results. Maxima in RF 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. A 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 $\nu = 0$ from $1/q^* \approx \nu^{1/2}$ (Fig. 4a) gives the total voltammetric charge ($q_{TOT}$) which is the charge related to the entire electroactive surface of the oxide coating. The extrapolation of $q^*$ to $\nu = \infty$ ($\nu^{1/2} = 0$) from the $q^* \sim \nu^{1/2}$ (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 Ti/SnO$_2$–Sn(13–x)–Ru(x)–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 $q_{\text{OUT}}^x$ is seen to increase almost
proportionally with $q_{\text{TOT}}^x$, 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 val-
ues, defined as the relation between the inner and the total charges
($q_{\text{IN}}^x/q_{\text{TOT}}^x$), as a function of the nominal Ru content in the oxide
layer presented in Table 2. It can be observed that the electrochem-
ical 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
Ti/SnO$_2$–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 observe
any maximum in the charge with the composition. However, any
comparison with these results cannot be carried out due to the dif-
ferent technique employed in the preparation of the mixed oxides.

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

The study of the oxygen evolution reaction in 0.5 M H$_2$SO$_4$
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 active-
ty of the electrodes towards the OER. Fig. 5 shows the Tafel
plots obtained from the polarization curves ($j$–$E$ curves) for
the Ti/SnO$_2$–Sb(13–$x$)–Ru(x)–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 den-
sities 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 elec-
trocatalytic 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 param-
eters 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 reveal materials-specific reaction mechanisms and/or,
directly, the conditions of adsorption of reaction intermediates.
The Tafel slope ($a$) for a multi-electron process, such as the oxygen
evolution reaction, is $BF/2.3RT$ [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 $n = 0$. In general, the best electrocatalysts are those with
lower Tafel slopes and lower $b$ values (higher $j_0$).

The Tafel slope, determined in the linear region close to the reversi-
ablest 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
Ti/SnO$_2$–Sb(13%)–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 pro-
posed 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 [3,31,46]: (i) gas bubble
formation and pore closure effects; (ii) the saturation of higher oxi-
cation state active oxycations, e.g., Ru(VII), which results in pore
blocking and (iii) a change in the reaction mechanism involving cor-
sorption 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$_2$SO$_4$ solution for Ti/SnO$_2$–Sb(13–$x$)–Ru(x)–Pt(3%) electrodes.](image)

![Fig. 6. Tafel slope and Tafel line $y$-intercept ($b$) for Ti/SnO$_2$–Sb(13–$x$)–Ru(x)–Pt(3%) electrodes as a function of the nominal Ru content.](image)
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 effects from mere surface area (geometric) 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

\( \text{Ti/SnO}_2\text{–Sb}(13 – x)\text{–Ru}(x)\text{–Pt}(3\%) \) 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 low-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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