

Effect of Solvent on the Preparation and Characterization of DSA[®]-Type Anodes Containing RuO₂-TiO₂-SnO₂

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Ânodos contendo óxidos de rutênio, titânio e estanho suportados em Ti metálico foram preparados por decomposição térmica para investigar o efeito do solvente (HCl/H₂O e isopropanol) na composição real de eletrodos de óxidos. As soluções precursoras e suas misturas foram analisadas por Espectrofotometria UV-Vis. A morfologia e a composição dos recobrimentos foram analisadas por Microscopia Eletrônica de Varredura (MEV) e Energia Dispersiva de raios X (EDX). A área eletroquimicamente ativa e a estabilidade dos eletrodos foram estabelecidas por meio da caracterização voltamétrica (HClO₄ 1,0 mol L⁻¹) e testes de vida útil, respectivamente. Os resultados mostram que a composição e a morfologia dos recobrimentos variam drasticamente em função do solvente. Eletrodos preparados a partir de isopropanol apresentam excelente concordância entre as composições nominais e as experimentais, maior área eletroquimicamente ativa e excelente estabilidade quando comparados àqueles que utilizaram HCl. A preparação das misturas precursoras em isopropanol aumenta o tempo de vida dos eletrodos RuO₂-TiO₂-SnO₂.

Anodes containing ruthenium, titanium, and tin oxides supported on metallic Ti were prepared by thermal decomposition of precursor salts in order to investigate the effect that changing the solvent (from HCl/H₂O to isopropanol) would have on the real composition of the mixed oxide electrodes. The precursor solutions and their mixtures were analyzed by UV-Vis Spectrophotometry. Coatings morphology and composition were analyzed by Scanning Electronic Microscopy (SEM) and Energy Dispersive X-ray (EDX). Determination of the electrochemically active area and electrode stability was performed by voltammetric characterization (1.0 mol L⁻¹ HClO₄) and service life (SL) tests, respectively. Electrodes prepared from isopropanol showed excellent agreement between the nominal and experimental composition and they presented higher electrochemically active area and better stability when compared to those prepared in the presence of HCl. Preparation of the precursor mixture in isopropanol increases RuO₂-TiO₂-SnO₂ electrodes service life.

Keywords: ruthenium oxide, tin oxide, DSA[®], isopropanol, service life

Introduction

The use of the well-known DSA[®]-type anodes by the chlorine-alkali industry has motivated new research areas to seek materials as efficient as those used in chlorine production. The search for new electrocatalysts has been greatly responsible for the advances in electrocatalysis seen in the last century.¹ Studies on oxide mixtures have allowed the application of these materials in several areas, such as organic oxidation² and electrochemical degradation of industrial wastes.³⁻⁶

Such electrodes are usually prepared on a metallic titanium support by thermal decomposition of precursor salts previously dissolved in an appropriate solvent. The most frequently employed catalyst oxides are: IrO₂,^{2,3,7,8} RuO₂,^{2,7,9,10} Co₃O₄,¹¹ and PbO₂.^{4,12} Oxides such as TiO₂,^{6,9,13} ZrO₂,¹³ Ta₂O₅,^{13,14} and SnO₂^{4,9,10,15} are used as stabilizers and modulators. In general, a mixture is employed in order to avoid the use of expensive catalysts and to modulate the desired properties of the electrodes. SnO₂ is frequently used as a modulator because, besides producing a synergetic effect with the RuO₂ catalyst toward the oxygen evolution reaction (OER) and the oxidation of organic compounds, it

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increases the stability of ceramic coatings when compared to TiO_2 .^{9,16-20}

The standard method used for the preparation of mixed oxide coatings to be employed as anodes consists in the thermal decomposition of suitable precursor salts dissolved in $\text{HCl}/\text{H}_2\text{O}$ 1:1 (v/v).²¹ This methodology will be called SM/HCl from now on in this work.

Ternary oxide electrodes containing Ru-Ti-Sn have been previously investigated.^{9,15,17,22,23} However, tin losses of up to 50% have been observed in the end of the thermal decomposition process. The greatest difficulty in preparing electrodes containing Sn by this process is the proper control of the amount of SnO_2 in the coating, since SnCl_4 volatilization occurs at temperatures above 114 °C.^{8,24} Therefore, careful control of the preparation parameters is essential to maintain the desired SnO_2 content.

Ru-Ti-Sn oxides have been prepared by the Pechini-Adams method to avoid Sn losses.²⁵ This method is a good alternative since it helps one to overcome Sn volatilization. This is possible because the Sn atoms are fixed at a polyester chain formed during the resin preparation.¹⁸ Another alternative route is the sol-gel technique,²⁶⁻²⁸ which has also been claimed to produce good control of the Sn content. Besides being less expensive and more reproducible than the sol-gel method (SGM), the polymeric precursor method (PPM) also produces highly stable electrodes. Nevertheless, PPM is still expensive and takes more experimental steps when compared with the standard route.

The objective of this work was to prepare and characterize electrodes containing RuO_2 , TiO_2 , and SnO_2 supported on titanium in order to understand the influence of the solvent on the morphological and electrochemical properties of the mixed oxide coatings. Different nominal compositions were prepared by the standard thermal decomposition method (SM) employing either $\text{HCl}/\text{H}_2\text{O}$ or a non-aqueous solvent (isopropanol).

Experimental

Pretreatment of the metallic supports

The metallic Ti supports (1 cm²) from Realum Ind. Com. Ltda were blasted with steel spheres (0.5 μm) in order to increase their roughness and obtain better fixation of the oxide coating. The support was then washed with water and stocked in isopropanol (Merck) for at least two days. Afterwards, the Ti support was firstly submitted to boiling water which had been purified by the Milli-Q system for 30 min. The support was then degreased in isopropanol (30 min) and

submitted to a chemical attack performed with boiling 20% (v/v) HCl (Merck) for 5 min, followed by etching in boiling 10% (m/v) oxalic acid (Synth) for 20 min. The support was finally washed with plenty of water and dried at low temperature (80 – 90 °C), to allow solvent evaporation. The precursor mixtures were then immediately applied onto both faces of the freshly pretreated Ti supports.

Preparation of Ti/RuO₂-TiO₂-SnO₂ electrodes

The electrodes were prepared by the standard methodology (SM) using two different solvents ($\text{HCl}/\text{H}_2\text{O}$ 1:1 v/v (SM/HCl) or isopropanol (SM/ISO)) to dissolve $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ (Aldrich), TiCl_4 (Aldrich), and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (Merck). Two sets of electrodes with the following nominal composition were prepared: (i) the binary electrodes $\text{Ti}/\text{Ru}_{0.30}\text{Ti}_{0.70}\text{O}_2$ (B1), $\text{Ti}/\text{Ru}_{0.30}\text{Sn}_{0.70}\text{O}_2$ (B2), and $\text{Ti}/\text{Ru}_{0.55}\text{Sn}_{0.45}\text{O}_2$ (B3); and (ii) the ternary electrodes $\text{Ti}/\text{Ru}_{0.25}\text{Sn}_{0.35}\text{Ti}_{0.40}\text{O}_2$ (T1), $\text{Ti}/\text{Ru}_{0.25}\text{Sn}_{0.60}\text{Ti}_{0.15}\text{O}_2$ (T2), and $\text{Ti}/\text{Ru}_{0.30}\text{Sn}_{0.20}\text{Ti}_{0.50}\text{O}_2$ (T3). The ruthenium and titanium precursor solutions and the tin solution were standardized by gravimetry and atomic absorption spectroscopy, respectively. The precursor mixtures were applied onto the metallic support by brushing. Afterwards, the solvent was evaporated at low temperature (80 – 90 °C), and the Ti-supports were introduced into an oven at a controlled temperature (400 and 500 °C) for 5 min, under O_2 -flux (5 dm³ min⁻¹). This procedure was repeated until the desired nominal oxide loading (1.05-1.35 mg cm⁻²) was reached. This value is calculated taking a nominal thickness (ϕ) as 2 μm. The layers were finally annealed for 1 h at the same temperature, under O_2 -flux. Details of the preparation and electrodes final mounting are described elsewhere.²⁹

Cell, equipment, and solutions

The surface morphology and composition of the mixed oxide coatings were analyzed by Scanning Electronic Microscopy (SEM) and Energy Dispersive X-ray (EDX) using a Leica-Zeiss LEO 440 SEM microscope coupled to an Oxford 7060 analyzer, and a Zeiss 940 microscope coupled to a ZAF 4FLF link analytical system.

The precursor solutions and mixtures used in the preparation of the electrodes were diluted (6.5×10^{-5} mol L⁻¹) and analyzed by UV-Vis Spectrophotometry in order to investigate the effect of the solvent employed in the preparation process on the ruthenium oxidation state. These

analyses were performed in the visible region ($\Delta\lambda = 300$ to 700 nm) by using a Beckman DU 70 spectrophotometer.

All solutions used in this work were prepared with water purified by the Millipore-Milli-Q system ($18 \text{ M}\Omega \text{ cm}^{-1}$), and they were deoxygenated by N_2 bubbling.

The electrochemical studies were performed on an EG&G PARC 273A potentiostat / galvanostat controlled by the M270 software, using HClO_4 (1.0 mol L^{-1}) (Carlo Erba) as supporting electrolyte, at room temperature. All experiments were repeated at least twice. Two platinum wires (15 cm) were used as counter electrodes and a reversible hydrogen electrode (RHE) was used as the reference.

The open circuit potential (E_{oc}) for freshly prepared electrodes was recorded after 30 minutes in the supporting electrolyte, under vigorous N_2 -flux.

Stabilized electrodes were obtained after 50 scans between the cathodic and anodic limits ($+0.2$ and $+1.4 \text{ V vs. RHE}$, $v = 50 \text{ mV s}^{-1}$ in $1.0 \text{ mol L}^{-1} \text{ HClO}_4$) and chronopotentiometry curves (50 mA cm^{-2} for 1 hour). This procedure led to the coating's steady state condition. The anodic voltammetric charge (q_a) was determined by integration of the anodic region (i/E) between $+0.2$ and $+1.4 \text{ V vs. RHE}$ in the voltammetric curve using the M270 software.

The service life (SL) study was performed under galvanostatic conditions at high current density (400 mA cm^{-2}), under room temperature. The electrolysis period in which the electrode potential reached 6 V vs. RHE was termed as the electrode service life. Above this value, the electrode was considered inactive for OER.

Results and Discussion

Coatings morphology and composition

Representative SEM images of the mixed oxide coatings investigated in this work as a function of the solvent used in the precursor salts dissolution are presented in Figure 1. It can be seen that the morphology is essentially the same as a function of solvent. In general, both electrodes display a very cracked morphology, typical of coatings prepared by thermal decomposition.⁹ Electrodes prepared by SM/ISO exhibit besides the cracks portions agglomerated points (Figure 1B), similar to those observed by Terezo and Pereira.³⁰

Electrodes with different compositions prepared by SM/HCl are not significantly different. However, binary electrodes containing RuO_2 and TiO_2 (B1) prepared by SM/ISO present smooth morphology with agglomerated points

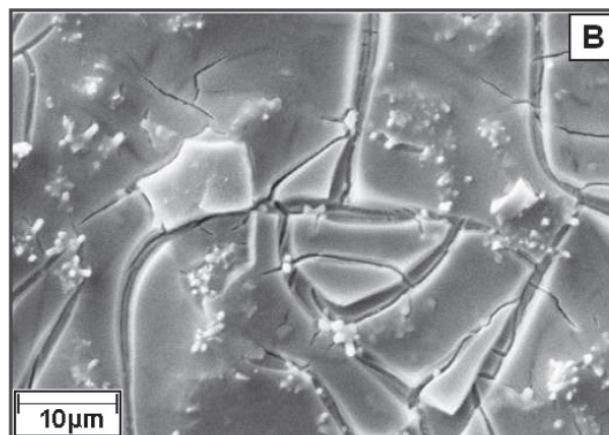
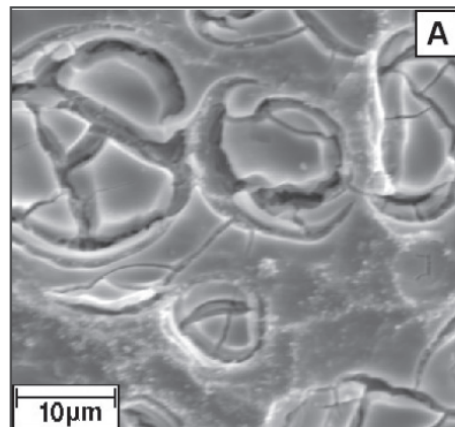


Figure 1. Representative SEM images (4000 x) for the T3 electrode ($\text{Ti/Ru}_{0.30}\text{Sn}_{0.40}\text{Ti}_{0.30}\text{O}_2$) as a function of the solvent: (A) SM/HCl, and (B) SM/ISO ($T_{\text{calc.}} = 400 \text{ }^\circ\text{C}$).

uniformly distributed (Figure 2A). On the other hand, binary coatings containing SnO_2 (B2 and B3) show predominantly cracked morphology and the small grains structure vanishes (Figure 2B), indicating that coatings containing high Sn content form less heterogeneous distributed structures than Ti-rich compositions. Concerning the ternary compositions, they present mixed morphology containing several cracks and agglomerated points.

EDX punctual analyses (2000 x) were performed on the agglomerated points (area marked in Figure 2A) for all the electrodes prepared by SM/ISO. These aggregates contain Ru-rich regions, that is, for the electrode with nominal composition $\text{Ti/Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$ the experimental composition $\text{Ti/Ru}_{0.92}\text{Ti}_{0.08}\text{O}_2$ was obtained. Segregation of the metal oxides at high temperature is frequently observed for this class of materials.^{31,32} The EDX analysis shows that substituting Ti for Sn significantly decreases Ru-segregation. For instance, for a nominal composition $\text{Ti/Ru}_{0.3}\text{Sn}_{0.7}\text{O}_2$, we obtained $\text{Ti/Ru}_{0.32}\text{Sn}_{0.68}\text{O}_2$. Systematization of the influence of the preparation route on the film

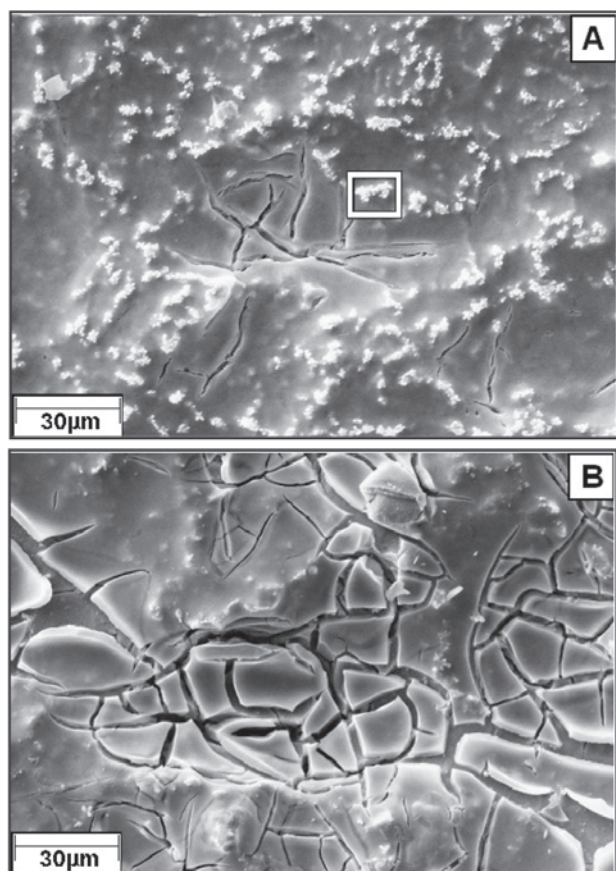


Figure 2. SEM images (2000 \times) for binary electrodes of nominal compositions: (A) B1, and (B) B2 prepared by SM/ISO ($T_{\text{calc}} = 400$ $^{\circ}\text{C}$).

composition is not easy because many effects may produce differences on the electrode materials. For example, a set of ternary films with nominal composition $\text{Ti/Ru}_{0.3}\text{Sn}_{(0.7-x)}\text{Ti}_x\text{O}_2$ prepared by the polymeric precursors route¹⁸ presented tin segregation instead of the Ru segregation observed for the coatings prepared by SM/ISO.

Overall EDX (500 \times) analyses were carried out to determine the experimental composition of the electrodes and are showed in Table 1.

Table 1. Comparison between the nominal and experimental compositions of the Ru/Ti/Sn coatings ($\phi = 2$ μm , $T_{\text{calc}} = 400$ $^{\circ}\text{C}$)

Electrode	Nominal and (experimental*) atomic percentage					
	SM/HCl			SM/ISO		
	Ru	Ti	Sn	Ru	Ti	Sn
T1	25 (36)	40 (40)	35 (24)	25 (29)	40 (40)	35 (31)
T2	25 (67)	15 (15)	60 (18)	25 (23)	15 (15)	60 (62)
T3	30 (49)	50 (50)	20 (01)	30 (27)	50 (55)	20 (18)
B1	30 (33)	70 (67)	(—)	30 (25)	70 (75)	(—)
B2	30 (90)	(—)	70 (10)	30 (32)	(—)	70 (68)
B3	55 (91)	(—)	45 (09)	55 (55)	(—)	45 (45)

*Data obtained by EDX overall analyses (500 \times).

A comparison between the nominal and experimental compositions as a function of the preparation method shows that the electrodes prepared by SM/HCl present significant reduction (80%) in the tin content. Such tin loss has been previously reported, and it is frequently associated with the evaporation of the precursor tin solution when it is in the oxidation state 4+.²⁴ SnCl_4 formation in the precursor solution was investigated by UV-Vis Spectrophotometry and it will be discussed further in this work.

The final composition of the DSA[®]-type anodes containing $\text{RuO}_2\text{-TiO}_2\text{-SnO}_2$ can be easily controlled by changing the solvent used in the preparation procedure as shown in Table 1. Data concerning the same nominal composition of metallic oxides prepared by SM/ISO shows an excellent agreement between the nominal and experimental data.

Increasing the temperature by 100 $^{\circ}\text{C}$ in the pyrolysis process (from 400 to 500 $^{\circ}\text{C}$) does not lead to any significant change in the electrodes morphological aspect or in the rate of tin loss.

We have shown that the solvents in which the precursors are dissolved have a strong influence on the coating's morphology and on their metal loading. The understanding of the influence of these parameters is a good way to control the desired properties of the different materials. For instance, the electrocatalytic activity of these materials strongly depends on geometrical and chemical (composition) factors once the activity toward oxygen evolution increases with electrochemical porosity.³³

Spectrophotometric analyses

Spectrophotometric studies were performed to clarify the phenomenon of tin loss observed for the coatings prepared by SM/HCl.

Figure 3 shows the UV-Vis spectra obtained for the ruthenium precursor solution as a function of the solvent used in the electrode preparation. In acid solvent, two well-defined bands at 379 and 477 nm are obtained. In isopropanol, these bands shift (389 and 441 nm) and have lower absorptivities than those obtained in the case of the electrode prepared in acid solvent. These differences can be attributed to changes in d-d transitions and to the charge transfer [Ru-Cl] complex as a function of the solvent used.³⁴

Both precursor solutions exhibit an orange-brown color which is typical of Ru (IV) salts.³⁵ Since the ruthenium precursor solutions were prepared by dissolving a certain amount of $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, which should be colorless if ruthenium was maintained at the 3+ oxidation state,³⁵ we

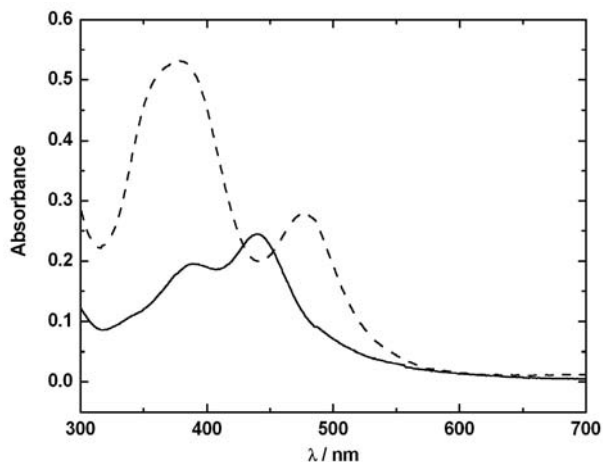


Figure 3. Spectrum of the ruthenium precursor solution dissolved in (—) SM/HCl and (---) SM/ISO; $[\text{RuCl}_3 \cdot n\text{H}_2\text{O}] = 6.5 \times 10^{-5} \text{ mol L}^{-1}$.

can infer that the precursor salt dissolution promoted the formation of ruthenium IV in both solvent. The Ru^{3+} cation bounded to a water molecule of its coordination sphere, $\text{Ru(III)}\text{---OH}_2$, allow electron transfer between the metallic center and the water molecule.³⁶ This hypothesis was confirmed when we dissolved a non-hydrated ruthenium III salt, K_3RuCl_6 , synthesized according to a procedure described elsewhere.³⁷ Dissolution of K_3RuCl_6 in both solvents investigated in this work produces colorless solutions, typical of Ru(III). However, the oxidation, on purpose, of the non-hydrated ruthenium (III) solution with a few drops of H_2O_2 produces an intense orange-brown solution, indicating the presence of a Ru(IV) complex. The spectrum obtained after the oxidation of the K_3RuCl_6 solution is similar to those presented in Figure 3.

Figure 4 shows the spectra obtained for the precursor solution containing ruthenium (solid line) and for the mixture ruthenium/tin (dash line), in both solvents investigated in this work.

When the solvent used in the preparation is aqueous HCl, it is possible to observe that the orange-brown ruthenium solution becomes colorless after tin addition, presenting only one less intense band (341 nm) typical of ruthenium III complexes.³⁵ Therefore, the changes observed in acid medium are associated with the following redox reaction:



On the other hand, ruthenium and tin precursor mixture in isopropanol does not show any significant change in the spectrum (Figure 4B). Thus, an inhibition of the redox reaction between ruthenium and tin is observed in this solvent. So, isopropanol could possible

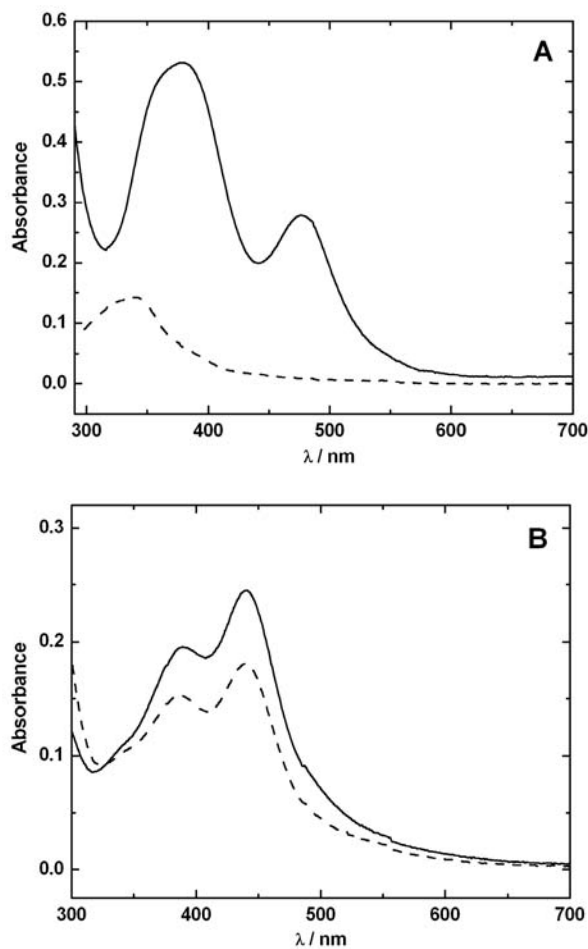


Figure 4. Spectra of the ruthenium precursor solution (—) before and (---) after the addition of the tin precursor solution obtained as a function of the solvent: (A) SM/HCl and (B) SM/ISO.

act as a solvating species, inhibiting electron transfer between the metallic centers.

Therefore, results obtained by spectrophotometry are useful in order to provide adequate explanation for the EDX data. The tin loss phenomenon is directly related with Sn^{4+} formation which occurs before the thermal treatment. Once Sn^{4+} is formed, it can be easily lost during the pyrolysis stages because it is volatile at temperatures above 114°C .²⁴ A similar result was observed by Lassali et al. for mixtures containing iridium and tin.⁸ This suggests that changing the solvent is a good way of controlling the film compositions, once isopropanol inhibits the redox reaction between the ruthenium and tin metallic centers.

Electrochemical characterization

Table 2 shows the E_{oc} and q_a values obtained for freshly prepared electrodes as a function of the solvent used in the precursor solution. Analysis of the E_{oc} -values shows

that the surface electrochemistry is controlled by the Ru (III) / Ru (IV) redox transition ($2 \text{RuO}_2 + 2 \text{H}^+ + 2 \text{e}^- \rightleftharpoons \text{Ru}_2\text{O}_3 + \text{H}_2\text{O}$ ($E^\circ = 0.95 \text{ V vs. RHE}$)).³⁸ The E_{oc} -values do not depend on the precursor solvent, the ruthenium content, or the introduction of different amounts of modulator oxides (TiO_2 and/or SnO_2). The obtainment of constant E_{oc} -values as a function of composition has also been reported for a set of $\text{Ti/Ru}_{0.3}\text{Sn}_{(0.7-x)}\text{Ti}_x\text{O}_2$ electrodes prepared in isopropanol.¹⁷ On the other hand, electrodes with the same composition prepared by decomposition of polymeric precursors exhibit a shift towards less positive values as the tin amount is increased in the sample.¹⁸ This has been explained as being due to the contribution of the SnO_2 sites ($\text{SnO}_2 + 2 \text{H}^+ + 2 \text{e}^- \rightleftharpoons \text{SnO} + \text{H}_2\text{O}$ ($E^\circ = 0.108 \text{ V vs. RHE}$)), which shift the equilibrium of the ruthenium oxidation state.

Taking into account that E_{oc} reflects changes in the Ru (III) / Ru (IV) equilibrium surface, by using the Nernst equation one can find that $a_{\text{Ru(IV)}} = 0.014 \times a_{\text{Ru(III)}}$. So we conclude that the changes introduced in the experimental parameters (solvent/composition) are meaningless considering the high temperature (400 – 500 °C) used to produce the ceramic oxide. This is good evidence that a complete decomposition of the precursor was obtained in the case of all samples prepared in this work. Partial oxidation of the active sites upon changes in solvent or composition has been recently reported for Ir-based oxides.³⁹

Table 2. Open circuit potential (E_{oc}) and anodic charge (q_a) obtained as a function of the electrode composition and preparation methodology ($A = 2 \text{ cm}^2$, $\phi = 2 \text{ }\mu\text{m}$)

Electrode $T/\text{ }^\circ\text{C}$	SM/HCl		SM/ISO	
	$E_{\text{oc}}/\text{V RHE}$	q_a/mC	$E_{\text{oc}}/\text{V RHE}$	q_a/mC
T1 ₄₀₀	0.80	27.4	0.80	51.7
T1 ₅₀₀	0.78	9.8	0.86	18.5
T2 ₄₀₀	0.85	46.3	0.87	98.8
T2 ₅₀₀	0.85	20.6	0.87	25.1
T3 ₄₀₀	0.82	32.6	0.83	59.6
B1 ₄₀₀	0.84	32.8	0.84	40.6
B2 ₄₀₀	0.83	42.6	0.79	99.2
B3 ₄₀₀	0.93	22.6	0.92	53.4
B3 ₅₀₀	0.83	11.6	0.88	43.2

q_a obtained between + 0.2 and + 1.4 V vs. RHE.

Figure 5 shows the voltammetric profile obtained as a function of the solvent used in the preparation of the precursor solution. The general analysis of the voltammetric behaviour shows there is a large peak typical of the Ru (III) / Ru (IV) redox transition^{21,23} located in the region between + 0.4 and + 1.0 V vs. RHE for both samples.

Electrodes prepared by the SM/ISO route present higher anodic charge (q_a) than those prepared by SM/HCl (see Table 2). The anodic charge can be taken as a

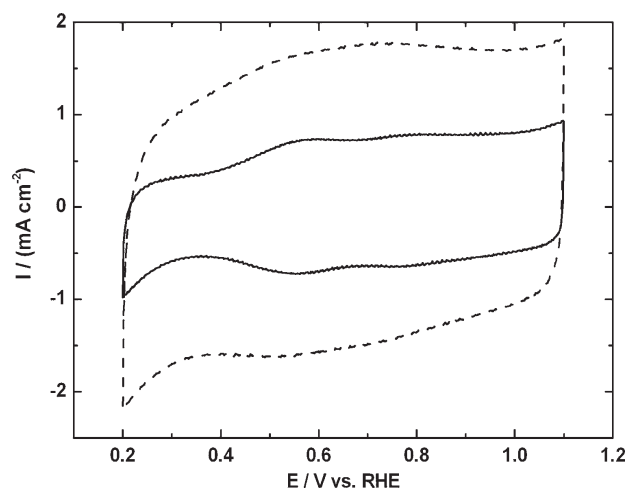


Figure 5. Cyclic voltammograms of the B3 electrode ($\text{Ti/Ru}_{0.55}\text{Sn}_{0.45}\text{O}_2$) as a function of the solvent: (—) SM/HCl and (---) SM/ISO. Supporting electrolyte: $1.0 \text{ mol L}^{-1} \text{HClO}_4$ ($v = 50 \text{ mV s}^{-1}$, $T_{\text{calc.}} = 400 \text{ }^\circ\text{C}$, $A = 2 \text{ cm}^2$).

measurement of the electrochemically active area,¹ which is affected by the specific electroactivity of the sites, and also depends on the coatings composition. Considering the total amount of loaded oxide and the catalyst atomic percentage obtained from the EDX analyses, the amount of catalyst loaded on the binary electrodes prepared by SM/HCl are quite different from the nominal composition due to the great Sn loss. As shown in Table 3 the binary compositions present a higher percentage of ruthenium for electrodes prepared by SM/HCl (B2 and B3) than SM/ISO ones. Nevertheless, no increase in q_a -values is observed, as would be expected when the catalyst amount is increased.⁹ For instance, for B2 composition the q_a -value obtained for SM/ISO (99 mC) is twice higher than the one obtained for SM/HCl (43 mC). This difference can be explained due partial sinterization of the deposited layers against the number of coating-calcination steps necessary to obtain the desired mass (20 times for SM/HCl and 8 times for SM/ISO).

The electrodes prepared by the SM/ISO route presented a good correlation between the nominal and experimental catalyst content. Considering that these values are in the same order of magnitude (0.2 - 0.4 mg cm^{-2}), increasing SnO_2 content promotes an increase in q_a -values. These changes are also observed macroscopically by SEM images, which showed an increase in the amount of cracks and fissures which, in principle, can increase the number of exposed active sites. Nevertheless, the formation of ultrafine oxide particles, as reported by sol-gel method,⁴⁰ cannot be ruled out in this case to explain the increase in charge.

Independent of the methodology employed in the electrode preparation, it can be seen that increasing the

calcination temperature from 400 to 500 °C leads to a reduction in the q_a values (Table 2). In other words, these electrodes' electrochemically active area is reduced because of active layer sintering.^{21,41}

Oxide coatings stability

The service life values obtained as a function of the preparation methodology and nominal composition are shown in Table 3.

Table 3. Service life (SL) obtained as a function of the solvent used in the precursor dissolution and the electrode nominal composition (supporting electrolyte: 1.0 mol L⁻¹ HClO₄, $i = 400 \text{ mA cm}^{-2}$, $T_{\text{calc}} = 400 \text{ °C}$, $5 \text{ dm}^3 \text{ min}^{-1} \text{ O}_2$ - flux, $A = 2 \text{ cm}^2$, $\phi = 2 \text{ }\mu\text{m}$)

Electrode	SM/HCl		SM/ISO	
	SL / h ^a	Ru ^b mg cm ⁻²	SL / h ^a	Ru ^b mg cm ⁻²
T1	14	0.26	50	0.21
T2	20	0.49	38	0.16
T3	09	0.38	30	0.21
B1	07	0.25	46	0.20
B2	12	0.67	149	0.22
B3	260	0.69	207	0.39

^aAverage of two sets of electrodes. ^bValues calculated from EDX data and the total oxide loaded.

The deactivation process of DSA®-type electrodes can take place through three routes, which may occur simultaneously or not. The first route can be attributed to the growth of a non-conductive TiO_x interlayer that becomes less doped with the catalytic oxide.⁴² In the second one, the catalytic material may be removed by the intense gas production.⁴³ The third route occurs when ruthenium undergoes oxidation and forms soluble Ru (VIII) species.²³

The SL studies were monitored by cyclic voltammetry so that we could follow the changes in the voltammetric charge throughout the electrolysis (Figure 6). In the end of the SL-test, all films investigated in this work exhibit a resistive aspect in the CV analysis. This can be explained by considering the growth of a TiO_x interlayer. However, a slight decrease in the voltammetric charge is also observed, indicating that a small degree of the catalytic material is lost. This decrease is much more pronounced for the electrodes prepared by the SM/HCl route, which displayed an intense orange-brown color typical of Ru (IV) after the SL test. This suggests that the deactivation of these electrodes should also happen due to a considerable amount of anodic dissolution of the coating.⁴³ Through the EDX analyses accomplished before and after the SL-test, it is possible to confirm that a significant reduction in the amount of catalytic material occurs in the case of

the electrodes prepared by SM/HCl, as well as the disappearance of the Ru-rich agglomerated points in coatings prepared by SM/ISO. Despite the observed anodic dissolution, the remaining amount of catalyst (0.09 mg cm⁻² of Ru) is higher than the minimum value necessary for the electrode to maintain its activity for OER.⁴⁴ This suggests that the main deactivation process for such electrodes is not the dissolution and/or oxidation of the catalytic material but the increase in the insulating TiO_x layer with electrode operation.

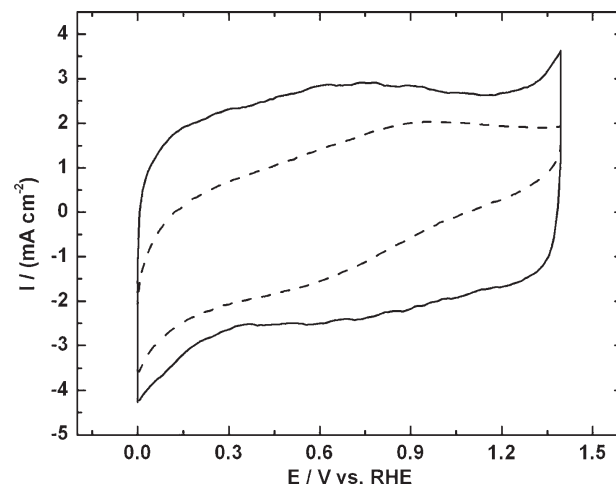


Figure 6. Representative cyclic voltammograms of Ti/Ru_{0.3}Ti_{0.7}O₂ electrode prepared by SM/ISO (—) before and (---) after the SL study. Supporting electrolyte 1.0 mol L⁻¹ HClO₄ ($v = 50 \text{ mV s}^{-1}$, $T_{\text{calc}} = 400 \text{ °C}$, $A = 2 \text{ cm}^2$).

It can be observed from the SL-test results that the stability of the electrodes depends on the total amount of loaded catalyst (Table 3). This parameter is directly related with the preparation methodology employed once the solvent strongly influences the final coatings composition. Considering electrodes containing a similar amount of the catalyst, it can be seen that the electrodes prepared by SM/ISO are more stable than those prepared by SM/HCl. Moreover, in the case of coatings prepared by SM/ISO, it can still be noticed that the replacement of TiO₂ with SnO₂ in the compositions produces an increase in the electrode stability. This behavior can be justified by the formation of solid solution between RuO₂ and SnO₂.¹⁰ Recent XRD investigation conducted in our laboratory⁴⁵ for RuO₂-SnO₂ prepared by SM/ISO showed that there is formation of a solid solution between RuO₂ and SnO₂ in any proportion. This happens because both SnO₂ and RuO₂ have the same structure (tetragonal) and very similar ionic radii ($r_{\text{Ru}^{4+}} = 0.076 \text{ nm}$ and $r_{\text{Sn}^{4+}} = 0.083 \text{ nm}$).²⁸ However, these oxides exhibit phase separation when prepared by SM/ethanol (immiscibility gap situated between 30 – 70 atom% of Sn nominal amount).¹⁰

It is not an easy task to compare SL data from different laboratories, especially when key parameters such as catalyst loading, support pre-treatment, coating thickness, supporting electrolyte, and pyrolysis process play an important role in the service life of the electrode materials.

It is worth to emphasize that the preparation of Ti/Ru_{0.3}Ti_{0.7}O₂ electrodes by SM/ISO renders the same stability (46 hours) as those obtained for electrodes prepared by PPM.¹⁸ However, the approach described herein for the nominal composition Ti/Ru_{0.3}Sn_{0.7}O₂ shows a significant increase in the service life (149 hours) for SM/ISO electrodes, if compared with other methods reported in the literature e.g., SM: 9 hours²³ and 12 hours⁴⁶ or PPM: 80 hours.¹⁸ This considerable increase in the SL has the advantage of combining an easy and cheaper process, with the perspective of an environmentally friendly treatment, when compared with the other methods reported in the literature.

Conclusions

In conclusion, the use of isopropanol as solvent for the precursor solutions eliminates the phenomenon of tin loss observed in the case electrodes prepared by SM/HCl, and it also furnishes coatings with higher electrochemically active area and stability. Moreover, the standard methodology that employs isopropanol represents a simple, inexpensive, and fast way of preparing mixed oxide electrodes. The easy solvent evaporation and the reduced number of brushing stages when compared with SM/HCl are advantages that make this procedure a very promising for the preparation of DSA[®]-type electrodes and an alternative route to more difficult and expensive techniques, such as the sol-gel method and precursor polymeric methods.

This work also shows the importance of relating the obtained results with the experimental composition of the electrodes, instead of relating them with the nominal composition.

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