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Comparison between Derived Sol-Gel and conventional methods for the preparation of Dimensionally Stable Ta/IrO₂ Anodes for oxygen evolution

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Abstract

The elaboration of inert anodes suitable for oxygen evolution in acidic media was investigated. These electrodes are formed of a tantalum substrate covered by a catalyst layer of iridium oxide IrO_2 . In this work, the catalyst coating was obtained by thermal decomposition of coating solutions prepared by two methods: (1) the derived Sol-Gel method using iridium acetylacetonate ($[\text{CH}_3\text{COCH}=\text{C}(\text{O})\text{CH}_3]_3\text{Ir}$) dissolved in an isopropanol – acetic acid mixture and (2) the classic method which uses a solution of iridium tetrachloride dissolved in a ethanol – isopropanol mixture. These electrodes were characterised by electrochemical and physical techniques. The use of the derived Sol-Gel method for the preparation of Ta/ IrO_2 electrodes yields very active electrocatalytic layer, such an electrocatalytic coating may be expected to be used for short time electrolysis runs with high rates of production.

Key words

Tantalum, iridium dioxide, oxygen evolution, Sol-Gel, DSA®

1. Introduction

Dimensionally Stable Anodes (DSA®) are made of a transition metal oxide coating deposited by thermal way on a valve metal substrate. Iridium dioxide-based anodes (Oxygen-DSA®) are currently used for electrochemical processes with oxygen evolution. The classic industrial oxygen-DSA® uses titanium as substrate and a catalytic coating made of a mixture of tantalum oxide (Ta_2O_5) and iridium oxide (IrO_2). These oxides are prepared by thermal decomposition of tantalum chloride (TaCl_5) and hexachloro-iridic acid (H_2IrCl_6), both dissolved in alcoholic media [1].

Previous studies [1-4] have shown that tantalum is a better substrate than titanium because of its higher resistance against corrosion in acidic media. However, using tantalum as substrate can produce, from 400°C , during the thermal treatment, some insulating Ta_2O_5 at the Ta/catalyst interface. The Ta_2O_5 formation process can be controlled by using a solution containing only iridium tetrachloride as precursor and a specific temperature program for the

thermal treatment [3]. The catalyst coating of the Ta/IrO₂ anode is prepared by a succession of thin layers, each of them being obtained by successively painting at room temperature the precursor solution and then annealing the IrCl₄ salt in air. The thickness of 1 μm, corresponding to a loading of around 1.6 mg/cm², for the coating needs around 20 layers. Consequently, the structure of the catalytic coating would be heterogeneous. Moreover some residual iridium chloride, not decomposed during the pyrolysis, can remain in the coating, decreasing the catalytic performance of the coating.

For a few years, the Sol-Gel technique [5-9] has been proposed as an alternative to the traditional method of preparation of DSA® electrodes. This technique would be a possible way for improving the homogeneity of the electrocatalytic layer and to avoid its contamination by residual chlorine. The preparation of IrO₂ coatings by the conventional Sol-Gel method requires the use, as precursor, of iridium tetraethoxide dissolved in a mixture of anhydrous ethanol and ethylene glycol [7] or ammonia [8].

In the objective to improve the performances of the electrocatalytic coating and to limit the dry corrosion of the tantalum substrate, we tried to use the Sol-Gel technique to form the IrO₂ catalyst coating. However, iridium tetraethoxide was not commercially available and furthermore difficult to prepare by synthesis. For this reason, we used an alternative method called the derived Sol-Gel method, like that developed by Mattos-Costa et al. [10] for making the binary oxide Ru_xIr_{1-x}O₂.

2. Experimental part

2.1 Preparation of the electrodes.

The derived Sol-Gel precursor solution was prepared by diluting 100.9 mg of iridium acetylacetonate ([CH₃COCH=COCH₃]₃Ir) in a mixture composed of 6 ml of isopropanol and 4 ml of acetic acid. Due to the very low solubility of the iridium precursor and its low rate of dissolution in this solvent, the mixture was placed in an ultrasonic bath during approximately 30 minutes to complete the dissolution and the homogenisation of the solution.

At the same time, a conventional solution of precursor was prepared with the same iridium concentration as in the last solution: it was made up of 68.8 mg of IrCl₄ dissolved in a mixture composed of 5 ml of ethanol and 5 ml of isopropanol, according to the method

presented by P. Palau [3] and by Mattos-Costa in ref. [10] but using here H_2IrCl_6 as Ir^{IV} precursor.

In order to compare their performances, electrodes of each type were prepared following the same protocol [3]:

- 5 minutes at $T = 80^\circ\text{C}$, 5 minutes at $T = 400^\circ\text{C}$ for the first four layers (to avoid an excessive oxidation of the tantalum substrate),
- 10 minutes at $T = 80^\circ\text{C}$, 10 minutes at $T = 430^\circ\text{C}$ for the following layers,
- 1h30 at $T = 450^\circ\text{C}$ for the final annealing treatment.

To minimize the number of service life tests, two electrodes with a $1\ \mu\text{m}$ thickness of oxide coating were prepared by each process. The first difference is the number of coating layers necessary to obtain this thickness: 60 for the traditional method and 180 for the derived Sol-Gel method. Thus, the derived Sol-Gel technique increased sensibly the time required to prepare the electrodes.

2.2 Characterisation of the electrodes

Electrodes were characterized by two types of methods: (i) ex-situ characterization by physical analysis techniques allowed surface and crystallographic properties to be examined; (ii) electrochemical characterization used for comparing first the anodic stability of each electrode and then their electroactive surface lets compare anodic stability of materials and their electrochemical activity.

2.2.1 Physical techniques of characterisation

- Thermogravimetric (TGA) measurements have been carried out with a Q600 SDT TA Instrument. The operating conditions were: (i) air atmosphere, (ii) platinum crucible, (iii) temperature range between 20°C and 1200°C and (iv) heating rate $20\ ^\circ\text{C}\ \text{min}^{-1}$.

- Differential Sweeping Calorimetry (DSC) was used to determine the enthalpy values involved in the course of IrO_2 formation using the classic and derived Sol-Gel methods. Samples of solutions were heating in the $20\text{-}1200^\circ\text{C}$ temperature range with a rate of $20^\circ\text{C}/\text{min}$.

- The morphology of catalytic coatings surface was observed by Scanning Electron Microscopy (SEM) using a LEO-435VP microscope equipped with an EDS probe INCA 200.

- The X-Ray diffraction (XRD) spectra were carried out on a recording diffractometer Siemens D500. The operating conditions were:

- K_{α} radiation of a copper anticathode ($L = 1.54056 \text{ \AA}$).
- filter of nickel and graphite monochromator.
- scanning rate of $0.05^{\circ}/\text{step}$ and $20\text{s}/\text{step}$ during the measurements of crystal size and $0.01^{\circ}/\text{s}$ during the analyses for determination of the different phases.
- angular range: $20^{\circ} < 2\theta < 90^{\circ}$.

The spectra obtained for IrO_2 coatings were deconvoluted by using specific software elaborated in our laboratory. The deconvolution process allows first the diffraction peaks to be separated, then the position to be determined and subsequently the iridium dioxide crystallites average size to be measured using the Warren-Averbach method [11].

2.2.2 Determination of the voltamperometric charge by cyclic voltammetry.

Electrodes prepared by each method were compared by using cyclic voltammetry at 50 mV/s [12]. Their surface was correlated to the voltammetric charge (q) which was calculated from the cyclic voltammogram by using an electronic integrator EGG 379. All the experiments were performed in a three-electrode cell containing H_2SO_4 1M at 25°C . An $\text{Hg}/\text{Hg}_2\text{SO}_4/\text{K}_2\text{SO}_4$ (sat) electrode, connected to the working electrode via a Luggin capillary, was used as reference and the counter electrode was formed with a spiral Pt-Rh wire.

2.2.3 Accelerated service life test.

The stability of anodes was estimated by using an accelerated service life test. This procedure was performed by applying to the anode a constant current density of 50 kA/m^2 (1A to the surface area of the electrode used). In the course of a DSA® test, the voltage remains stable or increases slowly. At the end of the electrode life, the voltage increased sharply. The service life was considered completed as soon as voltage increase exceeded by two volts its initial value.

The anode surface area (0.2 cm²) was delimited by a heat-shrinkable sleeve (Viton) bored after heating by means of a grip ($\varnothing = 5\text{mm}$). The counter electrode was a zirconium wire ($\varnothing 2\text{mm}$) placed in a tube of glass in order to avoid the hydrogen - oxygen mixture. At the beginning and at the end of the service life test, the potential variation of the counter electrode was controlled with respect to a Hg/Hg₂SO₄/K₂SO_{4(sat)} reference electrode. The concentration of the sulphuric acid (30 % in mass) and the temperature (80°C) provided a high conductivity to the solution. Furthermore, at the temperature used, there were not secondary reactions occurring, such as sulphur and persulphate formation on the anode and hydrogen sulphide evolution on the cathode [13].

3. Results and discussion.

Comparison of the two methods for preparing DSA® electrodes needs preliminary analyses in order to provide information for understanding their behaviour under electrolysis conditions.

3.1 Ex-situ Characterisation.

3.1.1 Scanning electron microscope observations.

Figures 1a and 1b evidence the difference of the surface morphology of the anodes prepared by each process. The derived Sol-Gel method (Fig. 1b) leads to a layer with a microstructure of small catalyst particles, homogeneous over the entire surface whereas the coatings elaborated by the traditional method exhibit more heterogeneities such as pores, cracks and agglomerates on the surface (Fig. 1a). These observations are in agreement with those reported by Murakami et al. [8].

3.1.2 TGA measurements.

Figure 2 shows the thermogravimetric recordings plotted during the pyrolysis of the precursor prepared by the classic (1) and the derived Sol-Gel (2) methods. These curves evidence that the new precursor is the most reactive since the IrO₂ formation temperature is lower for the derived Sol-Gel method (270°C) than for the classic one (580°C). This result

can be explained by an autocatalytic process in the course of pyrolysis. According the DSC measurements, the enthalpy of the precursor conversion into oxide is higher in the case of the derived Sol-Gel method than for the conventional method (-15580 J/g and -74.7 J/g respectively); these results suggest that the higher heat release during the course of the derived Sol-Gel precursor, could explain the autocatalytic effect by the earlier IrO₂ formation.

3.1.3 X-Ray diffraction.

The electrodes prepared by the two methods were analyzed by X-Ray diffraction. The comparative analysis of the spectra is shown on figure 3. The following differences can be observed:

- (i) diffractograms revealed the presence of both iridium metal and iridium dioxide on the derived Sol-Gel electrode whereas only IrO₂ was observed on the traditional electrode.
- (ii) iridium dioxide prepared according to the traditional method was more crystallized than that stemming from the derived Sol-Gel method : the half widths of diffraction peaks of IrO₂ were narrower and higher.
- (iii) tantalum substrate was easier oxidized (presence of TaO_x for $2\theta = 37.3^\circ$ and 39.4°) during the pyrolysis of the precursor using the derived Sol-Gel method.

According to previous researches [5,7,10], the presence of oxide and metal phases in DSA® prepared by the derived Sol-Gel method is usual and difficult to avoid, since it is due to the disproportionation of Ir^(III) (iridium III acetylacetonate) into Ir^(IV) (IrO₂ oxide) and metal Ir. However, the precipitation of both metal and oxide is tightly favoured by a higher degree of hydrolysis in the precursor solution [7]. In the case of the traditional method, the Iridium disproportionation cannot occur since the precursor contains only tetravalent iridium, while Lodi et al. [14], observed that pyrolysis of solutions containing iridium trichloride dissolved in a water - isopropanol mixture came with the disproportionation of Ir^{III} into oxide and metal, and that low temperatures of pyrolysis favoured this reaction.

The oxidation of the tantalum substrate observed in the case of the derived Sol-Gel method can be explained by the formation of IrO₂ colloidal particles of small size (< 500 nm) which increases the interfacial area and catalyses the reactions of the substrate with the air (oxygen) in the course of pyrolysis. Furthermore, the heat release by the pyrolysis of the

precursor, as mentioned in § 3.1.1, should cause local increases of temperature and facilitate the oxidation of the tantalum substrate.

Table 1 compares the intensities of the crystal plans of IrO₂ prepared by the two methods with that of IrO₂ powder (not textured). Results show more similarities between the IrO₂ powder and IrO₂ formed by derived Sol-Gel method; herein we conclude that IrO₂ prepared by derived Sol-Gel method is not textured [15]. Furthermore, the growth of the layers prepared by the traditional method followed the plan (101). The analysis of the XRD patterns makes it possible to determine the size of the crystals of IrO₂ in the two crystal plans (110) and (101); values presented in Table 2 confirms that the derived Sol-Gel process leads to the formation of smaller catalyst particles. This comparison is valid for each crystal plan considered for the measurement. The values obtained are similar to those given by Tereso and Pereira [9] and Mattos-Costa, Lima-Netto, Machado and Avaca [10] (6-7 nm) for oxides of the binary mixture RuO₂-IrO₂ worked out by the derived Sol-Gel method.

3.2 Electrochemical characterisation

Cyclic voltammograms of the H₂SO₄ solution (1M at 20°C) were recorded in the voltage range implying only capacitive current; in other words, no electrochemical reaction implying protons can occur in this potential range. Consequently, the area of the voltammogram $I=f(E)$ represents the electrical charge of the electrode; this charge is directly proportional to the electrode area. So this method allows the working area of each electrode to be compared.

3.2.1 Cyclic voltammetry

Cyclic voltammogram recorded in the [-0.5, +0.75 V/ref] potential range are presented on Figures 4a and 4b for each method of preparation. It can be noticed that the method of preparation of the oxide layers did not influence the shape of the voltammograms. The voltammogram area is far more extended in the case of the derived sol gel method (4b), compared to the traditional one (4a). This fact proves that the derived Sol-Gel electrodes have higher active surface, presumably because this way of preparation generates more porosities in the catalyst layer. Let us note that the measurement of the area by cyclic voltammetry provides a reasoned basis to predict the catalytic properties of oxide electrodes [16-18]. So,

this result suggests that the electrode prepared with the derived Sol-Gel methodology has better electrocatalytic properties than the traditional one.

3.2.2 Correlation between voltamperometric charge and surface properties of the anodes

Table 3 presents the voltamperometric charges determined by integration of the anodic part of the voltammograms for each electrode sample. The data of the first line highlights the more extended active surface in the case of the derived Sol-Gel method compared with the traditional one. These values can be correlated with the surface porosities of the samples, measured using a specific treatment of the cyclic voltammogram based on the scanning potential rate. At low potential scan rate, the complete surface area which is active includes the external surface and the inner porosities of the electrode; whereas at high potential scan rate, only the external surface of the electrode is active because of the reaction limitation by diffusion of the species in the porosities. Figure 5 illustrates the difference of the electrode behaviour in each case. We have shown experimentally that the charge can be expressed as functions of the potential scan rate by the following relations proposed by Ardizzone *et al.* [19]:

$$q = q_s + \frac{a}{\sqrt{v}} \quad a = \text{constant} \quad (1)$$

$$1/q = 1/q_t + b \cdot \sqrt{v} \quad b = \text{constant} \quad (2)$$

q , q_s and q_t are the anodic charge measured experimentally, the anodic charges associated to the external active surface and the total active surface of the electrode respectively; v is the potential scan rate. By extrapolation of the linear relationships of $q = f(v^{-1/2})$ when $1/\sqrt{v} \rightarrow 0$, and $1/q = f(\sqrt{v})$ when $\sqrt{v} \rightarrow 0$, it is possible to determine q_s et q_t referring to Eqs. (1) and (2) respectively, and consequently to estimate the external surface porosity by calculating the ratio q_t/q_s which corresponds to the ratio of the total surface versus external surface: S_t/S_{ext} .

Table 3 shows that the active surface of the electrode, measured by the surface area of the voltammogram is favoured by a low porosity of the external anode surface; the active surface of an electrode prepared by the derived Sol-Gel technology is about 2.5 times more significant than that the prepared by the traditional method, and it is seen with the surface porosity data, which is lower.

Globally, results presented in Tables 2 and 3 suggest that the crystallographic structure of the electrocatalytic coating influences sensibly the electrochemical behaviour of the electrode.

3.2.3 Anodic stability of the electrodes

In order to appreciate the stability under anodic polarization of each sample, accelerated service life tests were performed. Figure 6 evidences that the service life of the electrode prepared by the derived Sol-Gel technology is very short compared to the electrode prepared by the traditional method. The ratio between the respective service life is about 4 (Table 4). The low stability of the electrode prepared by the derived Sol-Gel method can be explained by the following reasons:

- (i) Iridium is present on the electrode; this metal has a low stability under positive polarization [20],
- (ii) the oxide catalyst particles are of small size and are brittle when they are in contact with oxygen evolution [3],
- (iii) the high exothermic conversion reaction of the iridium III acetylacetonate onto the tantalum substrate, during the preparation of the electrodes, should promote a significant oxidation of the substrate: the tantalum oxide formed acts as an insulator barrier.

4. Conclusion

The derived Sol-Gel method should be an interesting alternative for the production of oxygen DSA® having homogeneous catalytic layers not contaminated by residual chlorine. The use of the derived Sol-Gel method for the preparation of Ta/IrO₂ electrodes yields very active electrocatalytic layers; however such electrocatalytic coatings may be expected to be used only for short electrolysis runs with high rates of production. This study puts into evidence that, under anodic polarization, these catalytic layers exhibit a lower stability than the catalyst prepared by the conventional method. These different behaviours result probably from the iridium metal formation by disproportionation of the iridium (III) salt in the solution of precursor used in the derived Sol-Gel technique; under positive polarization, the Iridium metal is not stable.

Increasing the annealing temperature to oxidize the Ir metal into IrO₂ risks to favour the oxidation of the Ta substrate into Ta₂O₅ and meanwhile insulating the substrate.

A better method to prepare the electrocatalytic layer with the derived Sol-Gel method could be the use of a Ir^{IV} compound as precursor to avoid the further disproportionation reaction. Thus, it could be possible, by dissolving the Ir^{III} precursor in an ethanol-water mixture, to oxidize it into a Ir^{IV} compound by addition of a powerful oxidant such as hydrogen peroxide [6] and consequently to prevent the disproportionation of the precursor.

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Table 1. Distribution of the intensity of the principal crystal plans of the IrO₂ phase for the two methods of preparation. Reference: powders of iridium oxide [15].

<i>Lattice</i>	Intensity		
	Traditional method	Derived Sol-Gel method	IrO ₂ powder ref [15]
(110)	62	100	100
(101)	100	84	90
(211)	36	51	55
(220)	27	35	12

Table 2. Crystals sizes of IrO₂ of the (110) and (101) plans for the 2 methods of preparation.

<i>Method used</i>	IrO₂ crystal size (nm)	
	(110)	(101)
Traditional	11.1	19
Derived Sol-Gel	5.4	7.9

Table 3. Standardized anodic charge measured for the two methods.

	Derived Sol-Gel method	Traditional method
Standardized anodic charge (10³ C m² g⁻¹)	1.261	0.281
Surface porosity	2.47	4.60

Table 4. Influence of the preparation method versus the standardized service life of Ta/IrO₂ electrodes.

	Derived Sol-Gel method	Traditional method
Standardized service life (h m² g⁻¹)	3.2	12.5

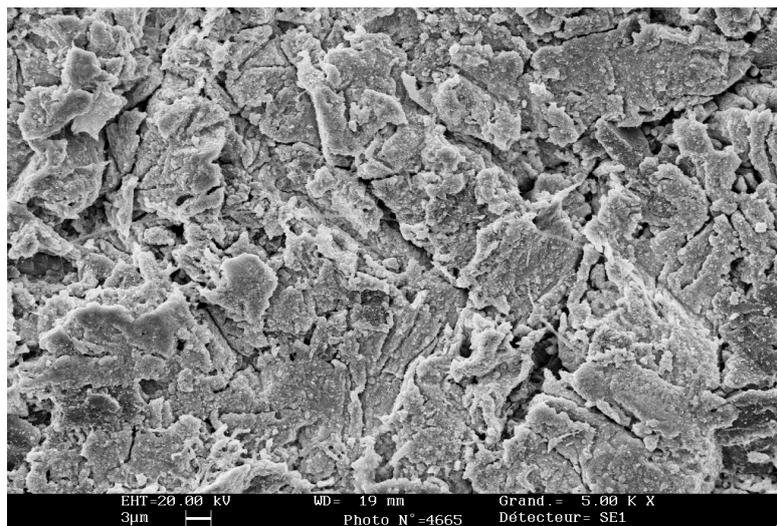


Fig. 1a

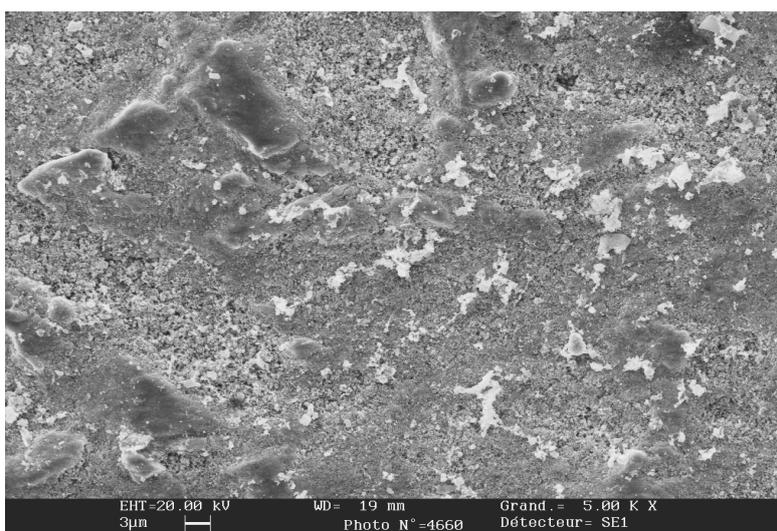


Fig. 1b

Figs. 1a and 1b. Microscopic observations of the electrocatalytic coatings carried out by (1a) the traditional method and (1b) the Derived Sol-Gel method (X 5000).

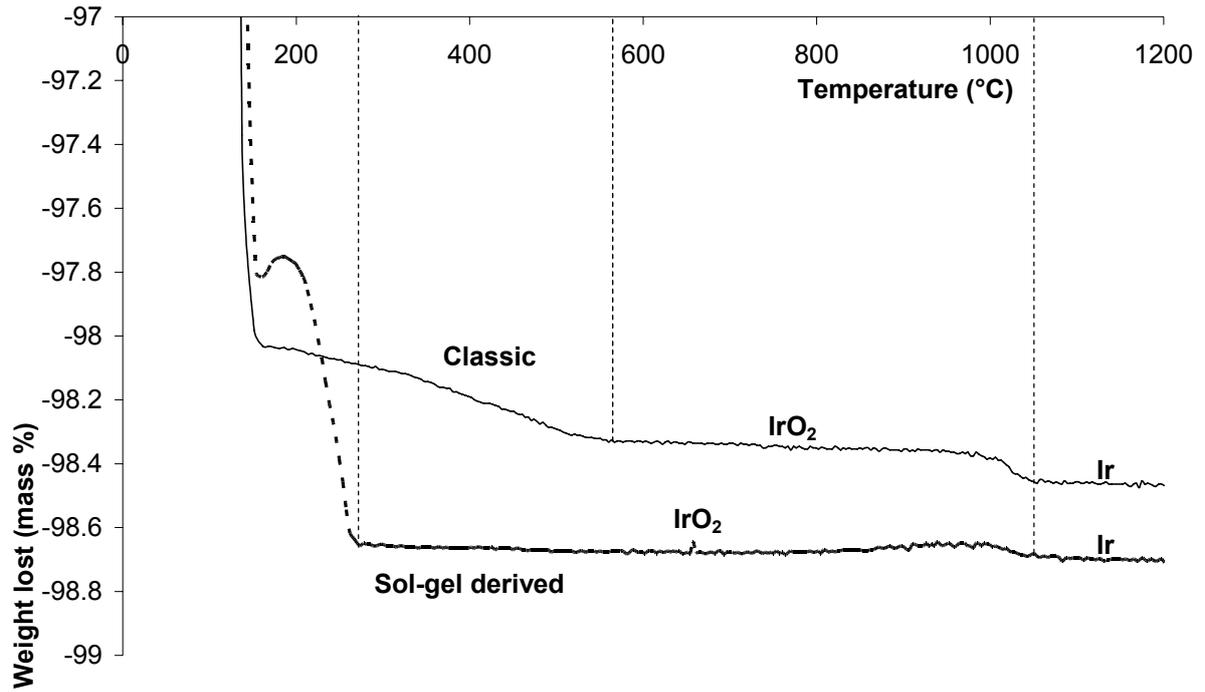


Fig. 2. Compared thermogravimetric analysis of classic and Derived Sol-Gel method.

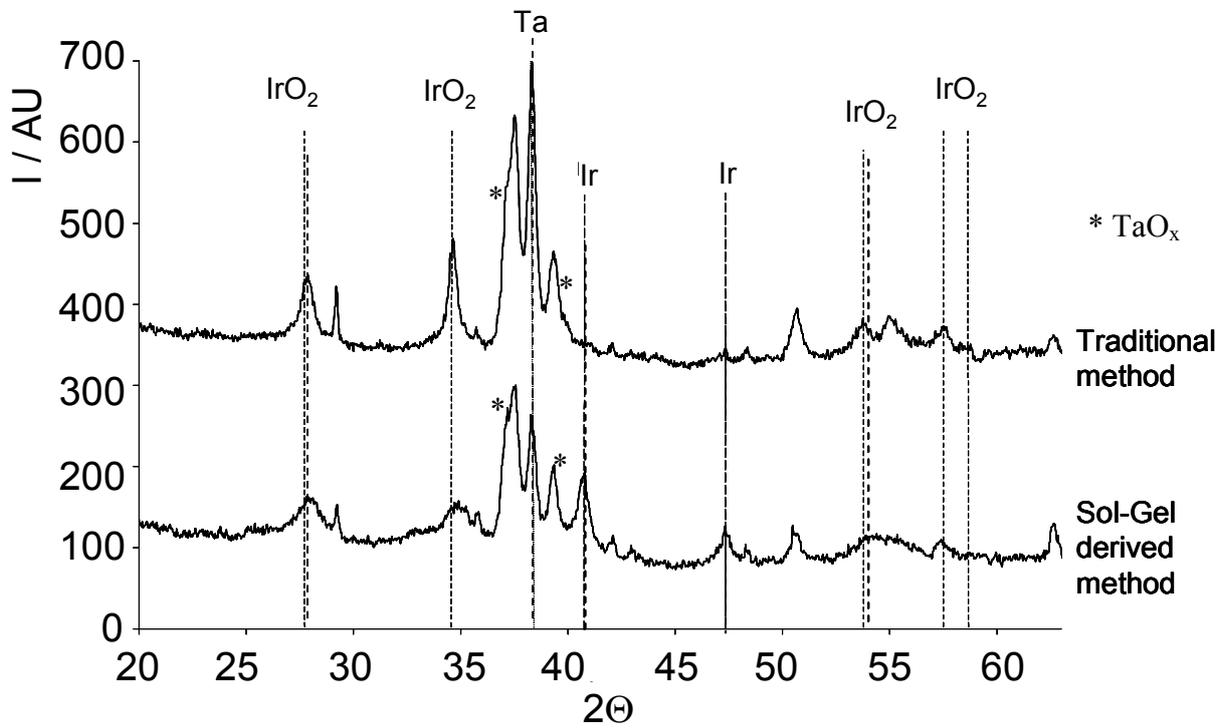


Fig. 3. XRD spectra of the Ta/IrO₂ electrodes prepared according to the traditional method and the Derived Sol-Gel method.

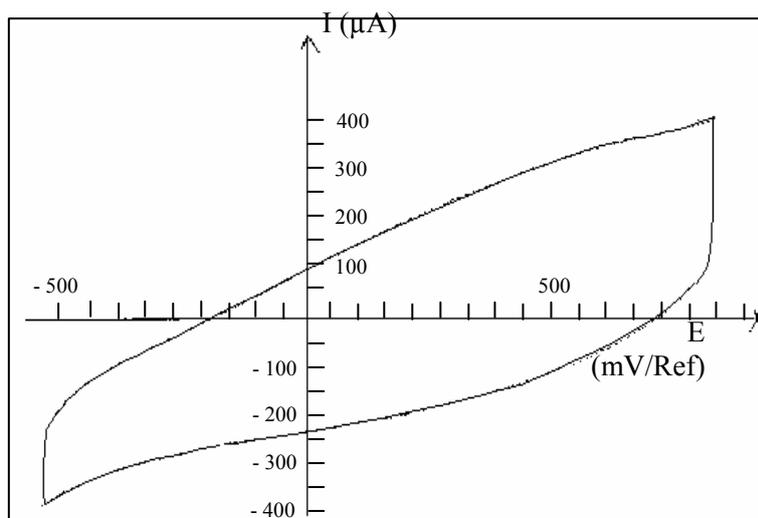


Fig. 4a

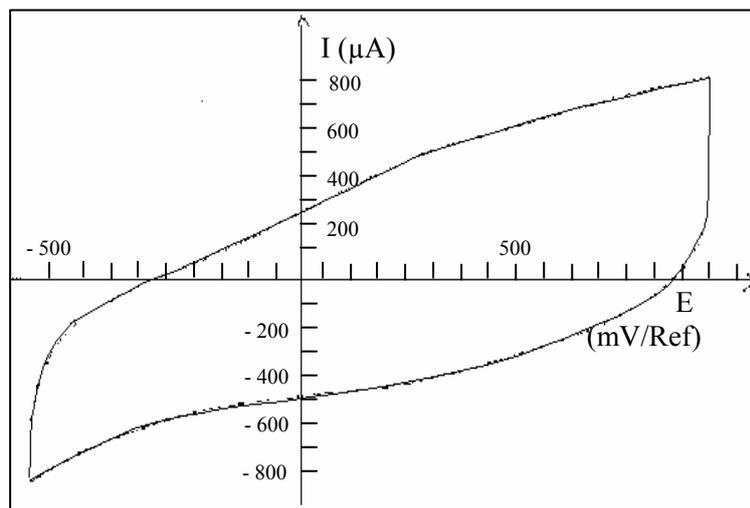


Fig. 4b

Figs. 4a and 4b: Cyclic voltammograms of the electrodes prepared according to two protocols: (4a) traditional and (4b) Derived Sol-Gel. $[\text{H}_2\text{SO}_4] = 1 \text{ M}$ at 25°C . $v = 50\text{mV/s}$. Potential scale: 50 mV/cm .

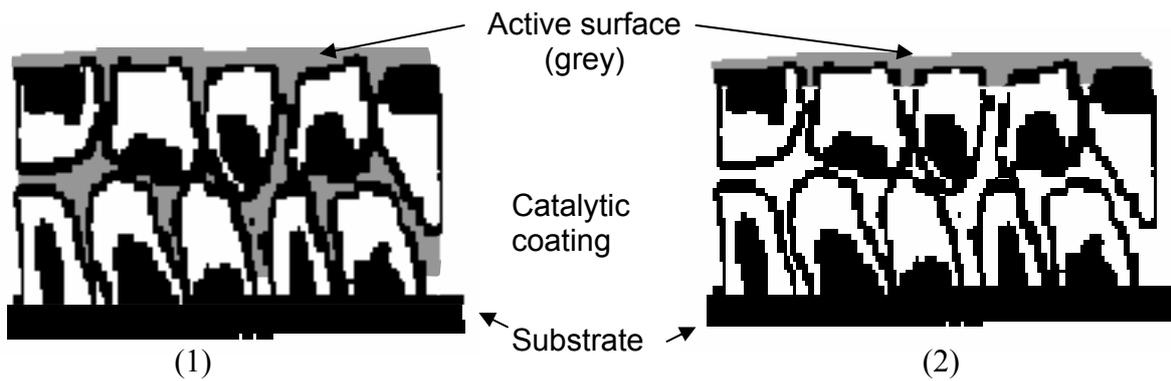


Fig. 5. Schematic interpretation of the active surface area of the electrode for a (1) low and (2) high potential scan rate.

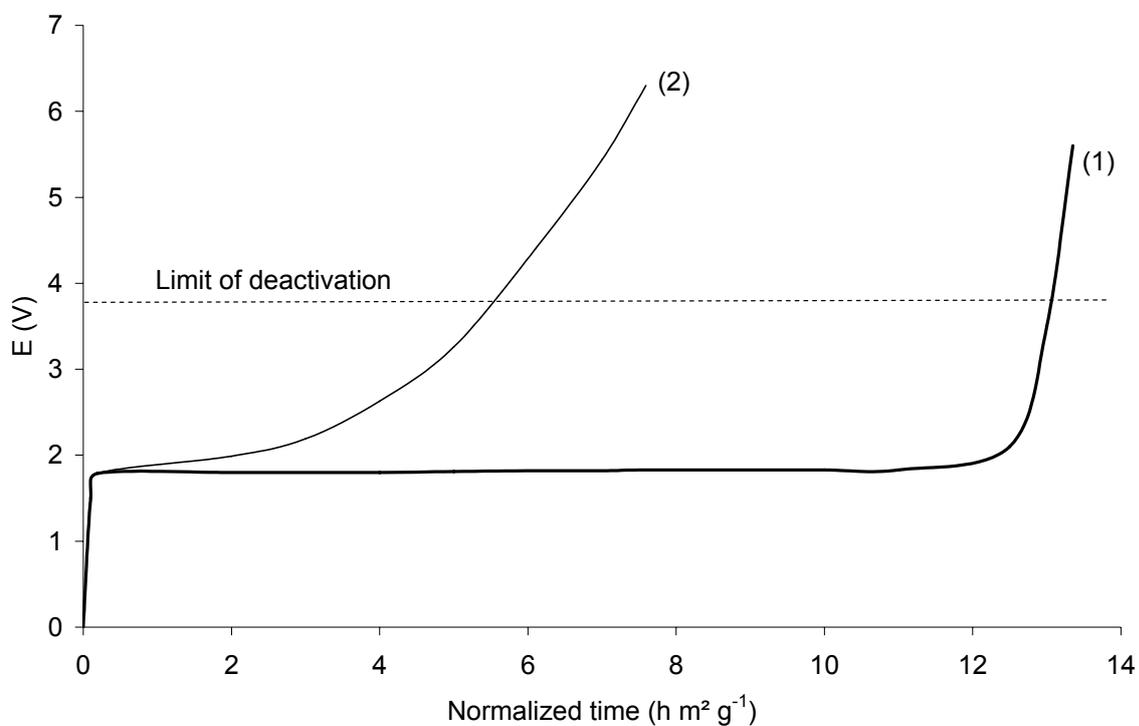


Fig. 6. Comparison of the typical potential variation versus time during the accelerated life test of the electrodes prepared by (1) traditional and (2) derived Sol-Gel method.