

Chemical vapor deposition of SnO₂ coatings on Ti plates for the preparation of electrocatalytic anodes

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Abstract

SnO₂ coatings have been deposited by metal-organic chemical vapor deposition (MOCVD) on Ti plates using SnEt₄ and O₂ as reactive gas mixture. The thickness, morphology and microstructure of these coatings are controlled by the growth conditions. The deposition process has been used for the preparation of Ti/IrO_x/SnO₂ electrodes that were tested for the anodic oxidation of organic pollutants in industrial wastewater. These anodes exhibit a high overpotential for oxygen evolution and a good efficiency for the elimination of total organic carbon (TOC) from wastewater. Electrochemical impedance measurements were used to characterize the activity of the interface SnO₂/aqueous media as a function of time during the oxidation process. The influence of the grain size, thickness and surface pre-treatment of the Ti substrate on the electrocatalytic properties is discussed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: SnO₂; Oxide coatings; MOCVD; Electrode materials; Electrochemical oxidation

1. Introduction

There is an increasing interest in electrochemical oxidation of organic pollutants in industrial wastewater owing to progress in the performance of electrode materials and a better knowledge of the mechanisms involved [1,2]. Comparison of different anodes has shown that Ti/SnO₂ is one of the best candidates [1,3]. For instance, Ti/SnO₂ anode allows a quasi complete elimination of total organic carbon (TOC) [4]. The high efficiency of SnO₂ anodes for combustion of organics is due both to an accumulation of OH[•] radicals on the surface produced by H₂O discharge and a low concentration of O-vacancies in the bulk, which blocks oxygen transfer into the oxide lattice and maintains active OH[•] on the surface [1].

Recently, we reported an MOCVD process for the deposition of SnO₂ films on Ti substrates which allows good control of their microstructure [5]. In this work, SnO₂ anodes were prepared by this MOCVD process and they were tested in a model electrolyte to gain

further insight into the phenomena governing the electrocatalytic properties of SnO₂ films in relation to their main features.

2. Experimental

2.1. Electrode preparation

Ti plates were used as substrates (22×22×0.8 mm³). They were etched in hot HCl (35%) for 1 h, rinsed with distilled water and dried in air. This cleaning procedure increases the surface roughness (1.0–1.5 μm) and subsequently, improves the film adhesion and maximizes the specific area of the electrodes. The IrO_x films were deposited by dip coating into an ethanol solution of IrCl₄ (15 wt.%). The solvent was evaporated at 353 K for 10 min, the sample was then heated in air at 773 K for 5 min. These steps were repeated five times to increase the thickness and, at the end, the samples were annealed in air at 773 K for 1 h.

The SnO₂ coatings were grown on the IrO_x-pretreated Ti substrates in a horizontal hot-wall MOCVD reactor operating under low pressure. SnEt₄ and O₂ were used as molecular precursors. The MOCVD process was previously described by Amjoud et al. [6]. The substrates were placed in the isothermal zone (30 cm long)

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Table 1
MOCVD conditions used for the growth of SnO₂ coatings

Electrode	Position ^a (cm)	Duration (min)	IrO _x thickness ^b (mg cm ⁻²)	T (K)	Mole fraction x(SnEt ₄)
B3	~23	505	0.50	613	10 ⁻³
E1	19.5	505	0.74	613	10 ⁻³
G1	25.1	270	0.97	653	10 ⁻³
G2	29.7	270	1.15	653	10 ⁻³
H1	24.6	505	1.01	613	2×10 ⁻³
H2	28.0	505	0.98	613	2×10 ⁻³

The other parameters were kept constant: total pressure = 13.3 kPa; O₂ flow rate = 280 sccm; N₂ flow rate (carrier gas) = 20 sccm; reactor diameter 2.4 cm.

^a Position of the electrode in the CVD reactor defined as the distance from the entrance of the reactor.

^b Relative thickness values of the IrO_x films determined from weight gain measurements. This corresponds to thicknesses in the range 0.5–1 μm using IrO₂ density of 11.7 g cm⁻³.

one behind the other along the reactor axis. The MOCVD conditions are reported in Table 1. The deposition temperature, the initial SnEt₄ mole fraction (*x*) and the position of the samples in the reactor were varied while the other parameters were kept constant.

2.2. Sample characterization

The surface morphology and microstructure of the coatings were investigated before and after electrochemical tests by SEM and XRD (Cu Kα). The surface roughness was measured using a profilometer (Talystep). The relative average value of the film thickness of as-prepared electrodes was determined from weight gain measurements. The real thicknesses were measured after electrochemical tests on cross-sections by SEM.

2.3. Electrochemical measurements

Electrochemical characterization was performed in a three-electrode cell: the working electrode (exposed area 2 cm²), an SSE reference electrode (saturated K₂SO₄/Hg₂SO₄) and a platinum auxiliary electrode. The electrochemical impedance (EI) measurements were performed using a Solartron 1250 Frequency Response Analyzer over a frequency range from 65 kHz to several Hertz with five points per decade using 10-mV peak-to-peak sinusoidal voltage and a Solartron 1287 electrochemical interface. The electrolyte solution (0.14 M Na₂SO₄) was maintained at room temperature and mechanically stirred during the electrochemical tests. The efficiency of the electrochemical oxidation was investigated by measuring the total organic carbon (TOC) in model electrolyte (oxalic acid) using a Shimadzu TOC 5050A instrument.

3. Results and discussion

3.1. Electrode characteristics

The IrO_x underlayers exhibited a dry-mud like morphology constituted of irregular paving-stones of a few micrometers, separated by cracks resulting from the shrinkage during the annealing step at 773 K. The average thickness was approximately 500 nm but large disparities were observed along the sample. The IrO_x layers were amorphous and oxygen-deficient compared to IrO₂ stoichiometry.

The SnO₂ coatings were deposited with a growth rate in the range of 6–14 nm min⁻¹ depending on the conditions. They were uniform, compact and exhibited good conformal coverage of the surface. As a result, the surface roughness of as-prepared electrodes reflected that of the Ti substrate. However, it tends to increase with the thickness of the SnO₂ coating. (Table 2). The SnO₂ films had a good crystallinity. The electrodes prepared at 653 K (G1, G2) exhibited a surface morphology constituted of faceted crystallites while those prepared at lower temperatures had smaller grains and a more nodular morphology. Observations on cross-sections revealed equiaxed growth with some porosity. The dependence of both the mean grain size and crystallite size on the growth conditions is in agreement with results observed on other substrates [5,6]. The SnO₂ films were slightly textured either in the (110) or (200) direction (Table 2). The influence of the parameters on the preferential orientation of the growth is more difficult to determine, probably because of the high roughness of the Ti substrates. It seems that the (110) preferential orientation is favored by high deposition temperatures and high values of *x*(SnEt₄). However, due to the depletion, local values of *x*(SnEt₄) decreases along the reactor and the texture can change from (110) to (200) as observed for electrodes H1 and H2 (Table 2). When the O₂/SnEt₄ ratio is sufficiently high, the (200) texture is promoted, likely because this crystal plane exhibits the highest density of oxygen atoms: the O/Sn atom ratio per surface unit is 0.132 Å⁻² for (200) and 0.047 Å⁻² for (110). However, at this stage, no direct correlation has been found between the microstructure and the performance of the anodes. Surface morphology and microstructure of SnO₂ coatings after electrochemical runs do not reveal specific corrosion features (Table 2).

3.2. Electrochemical properties

Fig. 1 shows the typical variation of the potential vs. time as observed by EI measurements. The same behavior was observed for the different samples: in the first region, the potential increases slightly with time, then rises to a maximum before reaching a constant value for longer immersion times. Typically, a failure of the

Table 2
Morphological and microstructural features of the SnO₂ coatings as-prepared and after electrochemical test

Electrode	R_a (μm)	Thickness		Mean grain size (μm)	Surface morphology	D(110) ^b (nm)	T(110) ^c	T(200) ^c
		(mg cm^{-2}) ^a	(μm)					
B3 as-prepared	–	1.54	–	≤ 0.5	Nodular	12	1.72	0.98
E1 as-prepared	0.85	3.00	–	0.5–1	Nodular	21	1.18	1.66
E1 after test	–	–	2.8	0.5–1	Nodular	15	1.19	1.65
G1 as-prepared	1.58	3.50	–	1–2	Faceted	27	2.29	0.61
G1 after test	–	–	3.9	1–2	Faceted	26	2.19	0.69
G2 as-prepared	1.49	1.70	–	0.3–1	Nodular	43	1.84	1.07
G2 after test	–	–	2.5	0.3–1	Nodular	43	1.96	0.93
H1 as-prepared	1.77	4.38	–	1–2	Faceted	17	2.14	0.63
H1 after test	–	–	4.6	1–2	Faceted	17	1.94	0.78
H2 as-prepared	1.70	4.81	–	~ 1	Nodular	14	0.84	2.03
H2 after test	–	–	4.5	~ 1	Nodular	16	0.85	2.01

^a Relative value determined from weight gain measurements.

^b Mean crystallite size determined by XRD using the Scherrer formula.

^c Texture coefficient determined by XRD using the formula $T_{hkl} = (I_{hkl}/I_{0hkl}) / [N^{-1} \sum (I_{hkl}/I_{0hkl})]$.

electrode results in an irreversible sharp decrease of the potential to the characteristic value of the base material (not observed in Fig. 1). When such a failure occurs the lifetime of the electrode is determined by this test. The behavior shown in Fig. 1 has been previously observed and reveals an activation process of the electrode surface. This process is reversible if no failure of the electrode occurs.

To understand this electrochemical behavior, EI measurements were carried out for different times corresponding to different potential values. It must be underlined that usually, impedance diagrams are measured under stationary conditions. In our case, it is difficult to reach a stationary state and for this reason, the impedance diagrams are plotted in a limited frequency range (65 kHz to several Hz). Thus, data acquisition is rapid (5 min) and we assume that during the measurement, the system was under stationary conditions.

The impedance diagrams plotted in Fig. 2 are characterized by a well-defined capacitive loop. In the high-frequency range, the intersection with the real axis gives

the electrolytic resistance ($20 \Omega \text{ cm}^2$) and in the low-frequency range, the polarization resistance R . From the diagrams plotted for different immersion times, the values of the parameters associated to the capacitive loop were considered in order to follow the modifications of the interface SnO₂/Na₂SO₄ solution with time. The capacitance values were determined by the expression: $C = 1 / (2\pi f_{\text{max}} R)$, where f_{max} corresponds to the maximum of the imaginary part of the impedance.

Fig. 3 illustrates the variation of R and C with time for sample E1. It can be seen that the resistance increased significantly with time whereas the capacitance decreased slightly. Such a behavior can be attributed to slight changes in the SnO₂ layer because the capacitance ($C < 1 \mu\text{F cm}^{-2}$) is much lower than the usual value found for double layer capacitance ($\sim 50 \mu\text{F cm}^{-2}$).

Semi-conducting SnO₂ layers exhibit a relatively high n-type conductivity due to O vacancies, which induce donor levels in the band gap. As a result, the resistivity is very sensitive to the microstructure as well as the

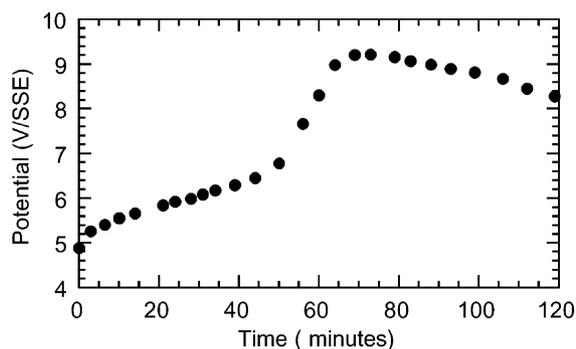


Fig. 1. Evolution of the electrode potential with time in the electrolytic solution for sample E1 (applied current density $I = 5.8 \text{ mA cm}^{-2}$).

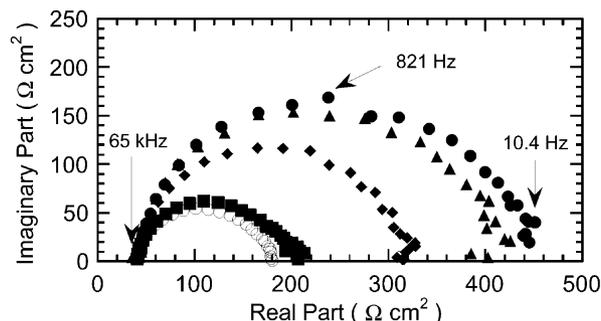


Fig. 2. EI diagrams obtained in galvanostatic mode for the sample E1 for different times in Na₂SO₄ solution ($I = 5.8 \text{ mA cm}^{-2}$): (○) 3 min; (■) 30 min; (◆) 70 min; (▲) 88 min; (●) 100 min.

bulk and surface composition. During the activation period, the stoichiometry of the SnO_{2-x} layer is probably improved due to the oxidizing medium (anode) and consequently, its resistance would increase as observed (Fig. 3). Furthermore, it is known that OH^\bullet radicals strongly interact with the SnO_2 surface in such electrochemical process [1]. These reactive species may also contribute to the increase of the resistance of the oxide layer. At this stage, it is assumed that the electrode activation corresponds to the period required to reach a steady state for these processes, which are both reversible.

3.3. Electrode performances: degradation tests

It is well known that SnO_2 exhibits electro-catalytic properties for the oxidation of organic pollutants present in wastewater [3,4]. For instance, an increase of the degradation rate of phenol by a factor greater than 5 has been reported using an SnO_2 anode ($50 \text{ mg TOC A h}^{-1}$) compared to Ti anode ($8.7 \text{ mg TOC A h}^{-1}$) in acidic medium [4]. Fig. 4 shows the typical variation of the TOC vs. electrolysis time obtained with SnO_2 electrode prepared by MOCVD. It appears that all the organic compounds have been destroyed in less than 24 h. The high value of the reaction rate of the oxalic acid degradation ($173 \text{ mg TOC A h}^{-1}$) reveals the promising performances of the CVD SnO_2 electrodes. This reaction rate is significantly higher than that deduced from a previous work ($60 \text{ mg TOC A h}^{-1}$) [7]. This difference may be due to the fact that both the process used for SnO_2 deposition (CVD and pyrolysis) and the tested pollutant (oxalic acid and phenol) were different. In order to compare the electrode efficiency for the same pollutant, we have determined the reaction rate of oxalic acid oxidation using a commercial DSA electrode (Ti/ RuO_2) and we found a value lower by a factor of approximately 3 ($60 \text{ mg TOC A h}^{-1}$), which confirms the higher performances of the CVD SnO_2 electrodes.

In addition to good electrocatalytic activity, an important requirement for anodes is a long lifetime. From this point of view, relatively large divergences have been

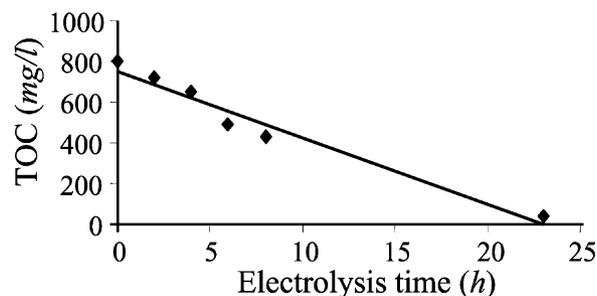


Fig. 4. Variation of the total organic carbon (TOC) vs. the electrolysis time showing the good efficiency of a Ti/ $\text{IrO}_x/\text{SnO}_2$ electrode (B3) for the degradation of oxalic acid ($V=200 \text{ ml}$; $I=48 \text{ mA}$; anode area 10 cm^2 ; $T=298 \text{ K}$; electrolyte $0.14 \text{ M H}_2\text{SO}_4$; $[\text{Oxalic acid}]=42 \text{ mmol l}^{-1}$). The degradation rate in mg TOC A h^{-1} unit can be determined using the initial and final TOC concentration in a given period according to $[(\text{TOC}_i - \text{TOC}_f) V] / [I (t_i - t_f)]$.

observed for the lifetime of CVD SnO_2 anodes prepared by this multi-process ranging from few hours to more than 11 months.

4. Concluding remarks

The electrodes prepared in this work exhibit good electrochemical activity for the oxidation of organic pollutants. In order to increase the service life and to improve the reproducibility, damaged electrodes were characterized and it is assumed that one of the main shortcomings that cause the electrode failure is the irregularity of the IrO_x underlayer. Fig. 5 shows the good uniformity of CVD SnO_2 coatings that exhibit a good conformal-coverage of the surface roughness. However, the dip coating process used for IrO_x deposition does not allow a uniform coverage of the surface roughness. As a result, the IrO_x underlayer is preferentially deposited in the pits and concave zones of the substrate surface while prominences and tips are not coated. In the zones uncoated by IrO_x , the progressive chemical and anodic oxidation of the Ti substrate occurs to form TiO_2 . This insulator oxide irreversibly deactivates the electrode.

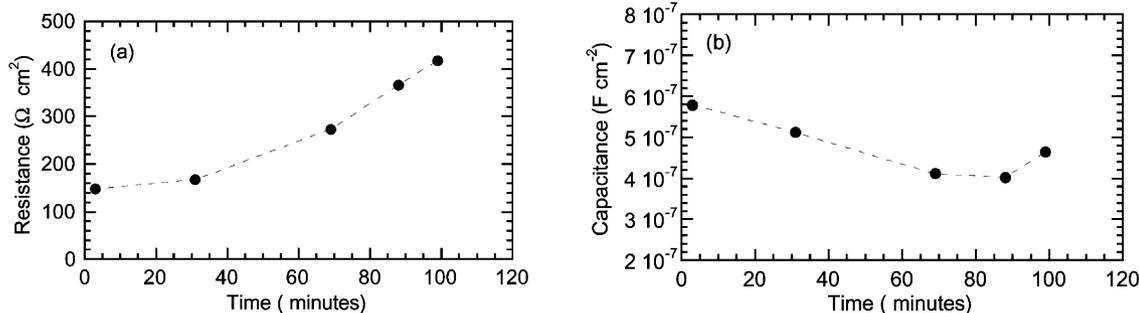


Fig. 3. Effect of activation time on resistance (a) and capacitance (b) taken from impedance diagrams for sample E1.

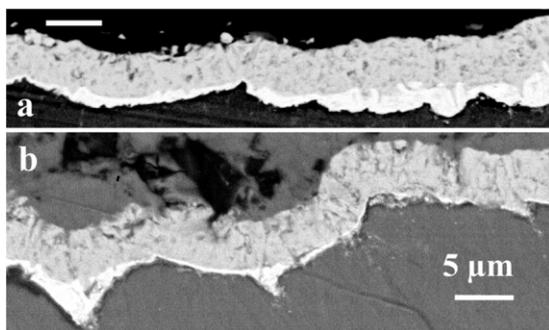


Fig. 5. Back scattered images (chemical contrast) of cross-sections of two electrodes showing the duplex structure constituted of an irregular IrO_x thin film on Ti substrate and an uniform SnO_2 MOCVD coating: (a) electrode G1; (b) electrode H2.

The thickness of SnO_2 films does not have great influence on the behavior of the electrode but the optimal value is in the range of 2–5 μm because microcracks have been observed for as-prepared thicker films, probably due to thermal stresses. Furthermore, deposition temperatures of SnO_2 films higher than 653 K are not suitable because the growth tends to be columnar, which increases the risk of open porosity

toward the interface and, subsequently, oxidation of the Ti substrate. We are continuing our efforts in optimizing these CVD SnO_2 electrodes.

Acknowledgements

The authors gratefully acknowledge Dr C. Cances for her assistance in the preparation of the electrodes and J.M. Morillas Gaston and F. Dupuy for their contribution to the characterizations.

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