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Characterization and stability of doped SnO_2 anodes

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Doped tin dioxide electrodes have been prepared by a standard spray pyrolysis technique. The electrochemical behaviour of these electrodes has been investigated by cyclic voltammetry in sulphuric acid using the Fe^{2+}/Fe^{3+} redox couple system as test reaction. Oxygen evolution has been used to study the stability of doped SnO_2 electrodes. The SnO_2 electrodes doped with antimony and platinum exhibit the highest stability. XPS analysis shows that the oxidation state of Sn, Sb and Pt are +4, +3 and +2, respectively, the probable species being SnO_2, Sb_2O_3 and PtO.

Keywords: *SnO_2 anodes, doping, high overvoltage anodes, surface analysis, oxidation, water treatment*

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1. Introduction

There are several methods for treating industrial wastewater containing organic and inorganic pollutants: biological treatment, incineration, adsorption, chemical and electrochemical oxidation and/or reduction.

Although biological processes are the easiest and the most economic processes for wastewater treatment, their application is not always possible, especially for effluents with high concentrations of organic or toxic compounds. In such cases, the introduction of previous chemical or electrochemical oxidation stages has become an attractive alternative for the treatment of wastewater effluents. Electrochemical oxidation methods have proved to be more efficient than chemical ones for removal of some organic pollutants (i.e., phenolic compounds). Thus, chemical oxidation of phenol by ozone or hydrogen peroxide with Fe^{2+} as catalyst yields 30% reduction in TOC (total organic carbon) [1, 2]. In contrast, the use of electrochemical oxidation methods results in a 38% and 90% TOC removal when platinum and doped SnO_2 are employed, respectively [3–8]. Kötz *et al.* [5, 6] were the pioneers in the study of physical and electrochemical properties of doped SnO_2 anodes. These electrodes present a low resistivity, high chlorine and oxygen evolution overpotentials, a high exchange current density for the $Ce^{3+} \rightarrow Ce^{4+}$ reaction and an efficiency and a rate of phenol removal much higher than for Pt and PbO_2.

The higher TOC removal when electrochemical oxidation methods are used have been attributed by Comninellis and Pulgarin [7, 8] to the oxidation of phenol and intermediate products to CO_2.

Thus, an adequate electrode for the elimination of organic pollutants should present a high oxygen overpotential, a high electrical conductivity and also good stability. The doped SnO_2 electrode satisfies these requirements.

The aims of this work are twofold: the preparation of stable electrodes for oxidative purposes and the characterization of SnO_2 electrodes doped with antimony or antimony and platinum. The techniques used to characterize the electrodes were scanning electron microscopy (SEM), energy dispersion X-ray (EDX), X-ray photoelectron spectroscopy (XPS) and cyclic voltammetry.

2. Experimental details

2.1. *Electrode preparation*

Several metal substrates, temperatures and solvents were tested for the preparation of the doped SnO_2 electrodes [9, 10]. Due to the fact that the best results obtained by us have been using Ti and ethanolic solutions, the present study will focus on this material and solution.

Doped Ti/SnO_2 electrodes were prepared by a standard spray-pyrolysis method [5, 11, 12]. The spray solution used for the preparation of the SnO_2 electrode doped with antimony was 10 g $SnCl_4.5H_2O$ and 1 g $SbCl_3$ in 100 ml of ethanol–HCl mixture; the same solution with 1 g Pt (2.1% H_2PtCl_6) was used for obtaining the best platinum and antimony doped electrodes. The titanium substrate, a wire of 0.5 mm diameter (99.6% of purity, Goodfellow Metals), was previously etched in a 10% oxalic acid solution for 1 h, then rinsed with water and heated to 400 °C. The ethanolic solution was then sprayed onto the titanium with an air-atomizing spray at a fixed distance of

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40 cm. Then, the electrode was heated for 10 min at 400 °C. The above operation was repeated at least five times. The thickness of the doped SnO_2 films depends on the number of spray-pyrolysis sequences. Finally, further heat treatment for 1 h at 600 °C was carried out.

The same experimental procedure was used for the preparation of electrodes with sheet and expanded titanium substrates (IMI 125 type, INAGASA).

2.2. *Electrode characterization*

Different techniques were applied to characterize the properties of the doped SnO_2 electrodes. The electrochemical behaviour of doped SnO_2 electrodes was studied by cyclic voltammetry. The voltammograms were obtained with a standard set-up using a potentiostat (HQ Instruments, model 101), a generator (EG&-G PARC, model 175) and an X–Y recorder (Philips PM 8133). The electrolyte was a 0.5 M sulphuric acid solution prepared from Merck suprapur and Millipore water or a 0.5 M H_2SO_4 + 5×10^{-2} M $FeSO_4$ (Merck p.a.) solution. The solutions were deoxygenated by bubbling nitrogen (N-50) before each experiment and an inert atmosphere was maintained over the working solution during the experiment. The counter electrode was a platinum wire and the potentials were measured versus a reversible hydrogen electrode immersed in 0.5 M sulphuric acid and connected to the cell through a Luggin capillary. The cyclic voltammograms were usually recorded at room temperature at a sweep rate of 50 mV s^{-1}.

Surface analysis was performed by X-ray photoelectron spectroscopy (XPS) using a ESCALAB 210 spectrometer. The X-ray source was MgK_α of energy 1253.6 eV with a power of 240 W. The samples were placed on 'posiloc' standard sample holders. A binding energy (BE) of 284.9 eV, corresponding to the C 1s peak was used as an internal standard. The pressure in the analysis chamber was maintained below 2×10^{-9} mbar during the measurements.

Scanning electron microscopy (SEM) was employed to observe the surface morphology of the electrodes using a Jeol (JSM 840). SEM also provided information on the different elements present on the surface using the energy dispersive X-ray detector (Link QX 200 EDX).

The thickness of the coatings were determined by the step method using a profilometer (Surfometer SF 220).

2.3. *Stability test*

The oxygen evolution reaction was used to study the stability of doped SnO_2 electrodes in 0.5 M H_2SO_4 or 0.5 M K_2SO_4 (Merck p.a.) solutions. The potential versus time curves of the doped SnO_2 electrodes at constant current density (referred to a geometric area of the electrode of 0.08 cm^2) depends on the polarization time and on the previous history of the electrode. An increase of 1 V in the potential was adopted as an indication of the loss of electrocatalytic activity of doped SnO_2 electrodes [13]. This potential increase can be produced by the formation of a passivated surface layer, probably caused by the hydration of the SnO_2 layer and/or the passivation of the layer-substrate interface [5, 14].

3. Results and discussion

3.1. *SnO_2 electrodes doped with antimony*

Figure 1 (solid line) shows the voltammogram recorded in a 0.5 M H_2SO_4 solution for a SnO_2 electrode doped with antimony with a five spray-pyrolysis sequence. The voltammogram is featureless in this potential range and little information is obtained about the composition and behaviour of the electrode surface. At potentials below 0.3 V the onset of a cathodic process becomes evident. The current associated with this process increases with decreasing potential and eventually overlaps the hydrogen evolution current. No peaks or waves appear before oxygen evolution, which begins at approximately 2.2 V. Compared to the behaviour observed for a platinum electrode in the same electrolyte and for the same current density, oxygen evolution is shifted positively about 500 mV.

To check the charge transfer rate through the doped SnO_2 electrode-electrolyte interface, the voltammetric behaviour of the redox system Fe^{3+}/Fe^{2+} was studied. From the value of the peak potential and from the value of the difference between the potential of the anodic and cathodic peaks (ΔE_p), a direct estimate of the reversibility of the system, that is, the electron transfer rate, could be obtained. Figure 2 shows the stabilized voltammogram obtained with this electrode for a 0.5 M H_2SO_4 + 5×10^{-2} M $FeSO_4$ solution at 50 mV s^{-1}. Well defined reduction and oxidation peaks are observed at about 0.65 and 0.75 V, respectively. The potentials of the anodic (E_p^a) and cathodic (E_p^c) peaks shift with scan rate, increasing the value of $E_p^a - E_p^c = \Delta E_p$. The peak separation, from 96 to 120 mV (for 50 and 200 mV s^{-1}, respectively), is always greater than that expected for a reversible one-electron process ($\Delta E_p = 59$ mV). However, the doped SnO_2 electrode behaves better than a platinum electrode at all scan rates (ΔE_p values from 104 to 136 mV).

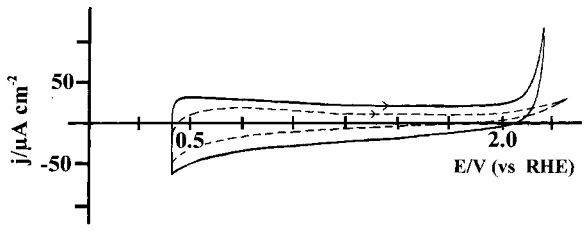

Fig. 1. Voltammograms for a SnO_2 electrode doped with antimony with five spray-pyrolysis sequence in 0.5 M H_2SO_4. v = 50 mV s^{-1}. (——) before and (- - -) after 5 h of electrolysis at 10 mA cm^{-2} in 0.5 M H_2SO_4.

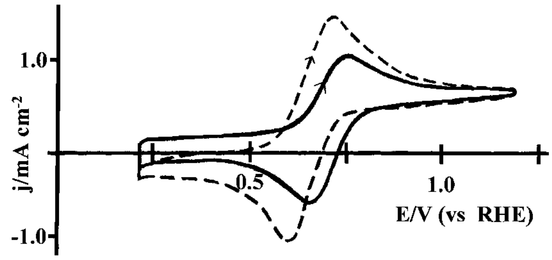

Fig. 2. Voltammetric behaviour of a SnO_2 electrode doped with antimony (——) and with antimony and platinum (0.2%) (- - -) with a five spray-pyrolysis sequence in 5×10^{-2} M. $FeSO_4$ + 0.5 M H_2SO_4 solution. v = 50 mV s^{-1}.

The SEM photomicrographs of the surface of the SnO_2 electrode doped with antimony are shown in Fig. 3. These figures show a slightly rough surface, with the particles of SnO_2 small and uniformly distributed.

The presence and distribution of Sn and Sb on the electrode were studied by EDX. The results indicate a homogeneous distribution of the components (Sn, Sb) on the electrode. Sn and Sb are detected in a proportion of 23.5% and 6%, respectively, while titanium is detected at 66.6%. This detection indicates that the thickness of the SnO_2 film is, according to Rosinskaya *et al.* [15], lower than 2 μm.

Profilometric measurements were carried out on a titanium sheet partially covered with SnO_2 doped with antimony (five spray-pyrolysis sequences). A coating thickness lower than 1 μm is obtained. This result is in agreement with that obtained from EDX measurements. Thus, it can be concluded that SnO_2 films formed by a five spray pyrolysis sequence are very thin. The holes created during the pre-treatment of titanium (holes from 3 to 6 μm have been previously observed using this pre-treatment [9]) are mainly covered during spray pyrolisis.

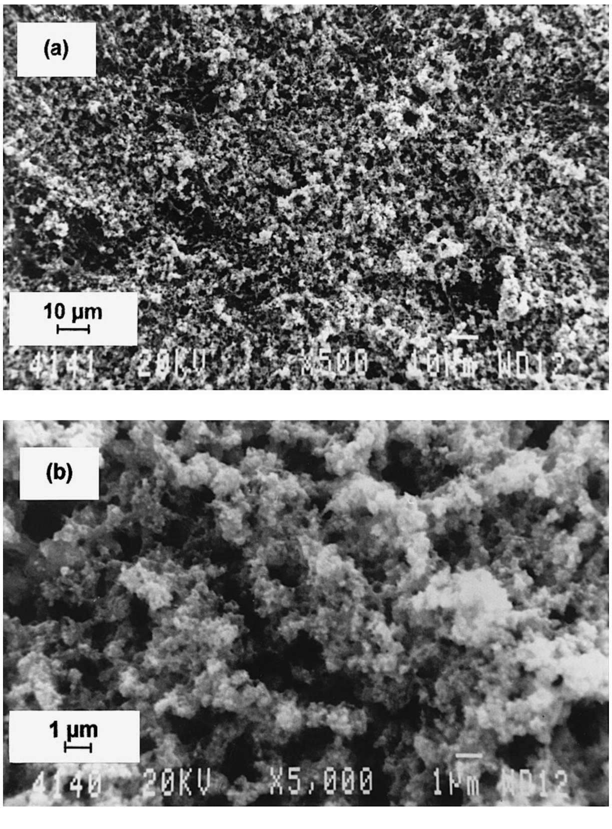

Fig. 3. Scanning electron micrograph of a SnO_2 electrode doped with antimony with a five spray-pyrolysis sequence.

From the electrochemical results, that is, a high oxygen overpotential and good electrochemical behaviour as deduced from the electron transfer rate for the Fe^{3+}/Fe^{2+} couple, the electrode obtained with a five spray-pyrolysis sequence is a good candidate for the oxidation–elimination of organic compounds. To verify the chemical and electrochemical stability of this electrode with time, it was employed as anode for oxygen evolution using a 0.5 M H_2SO_4 solution at a constant current density of 10 mA cm^{-2} (Fig. 4, squares). It can be seen that after 4 h electrolysis the difference $E(t) - E(t = 0)$ increased 1 V and reached 4.5 V after 5 h. Figure 1, dashed line, shows the voltammogram of this electrode in H_2SO_4 after 5 h of electrolysis. The voltammetric profile of this electrode has changed showing a decrease in current for all potentials. Also, the oxygen evolution has shifted to more positive potentials. Figure 5, solid line, shows the voltammetric behaviour of the Fe^{3+}/Fe^{2+} redox system on this electrode. The voltammogram has dramatically changed, showing a large decrease in the value of the anodic and cathodic current peaks and a shift of these peaks to more positive and negative potentials, respectively. The separation between peak potentials is now 600 mV instead of 96 mV (Fig. 2). This result clearly shows that the electrode has lost its electrocatalytic activity after working in sulphuric acid for 5 h.

A plausible explanation for this behaviour is the formation of a passivating layer at the substrate–film interface [5], which imparts low conductivity to the electrode [9]. This passivating layer may be formed because the electrolyte solution is in contact with the titanium substrate due to the small thickness of the film (lower than approximately 1 μm) or its high porosity.

The stability of the electrode can be improved by increasing the thickness of the SnO_2 film by increasing the number of spray-pyrolysis sequences. The

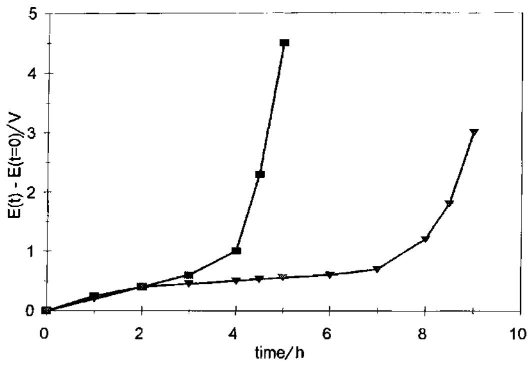

Fig. 4. $E(t) - E(t = 0)$ against electrolysis time in 0.5 M H_2SO_4 for SnO_2 electrodes doped with antimony with: (■) five spray-pyrolysis sequences, (●) nine spray-pyrolysis sequences. j = 10 mA cm^{-2}.

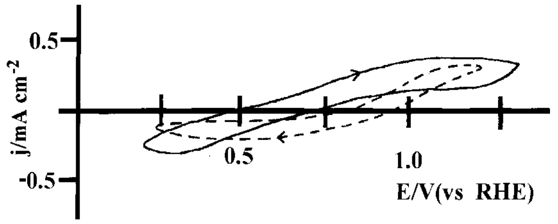

Fig. 5. Voltammetric behaviour of SnO_2 electrodes doped with a five spray-pyrolysis sequence in 5×10^{-2} M $FeSO_4$ + 0.5 M H_2SO_4. Key: (——) SnO_2 doped with antimony after 5 h of electrolysis at 10 mA cm^{-2}; (- - -) SnO_2 doped with antimony and platinum after 60 h of electrolysis at 40 mA cm^{-2}. v = 50 mV s^{-1}.

initial electrochemical behaviour of a SnO_2 electrode doped with antimony obtained after nine spray-pyrolysis sequences is similar to that obtained after five sequences (Figs 1 and 2, solid line). However, the stability of the electrode measured as the time for obtaining $E(t) - E(t = 0) > 1$ V, increases from 5 to 9 h of electrolysis at 10 mA cm^{-2} in 0.5 M H_2SO_4 (Fig. 4, triangles).

3.2. *SnO_2 electrodes doped with antimony and platinum*

It has been shown that the electrocatalytic activity and the resistance to corrosion of these types of electrode can be increased if mixed oxides are used [16]. One of these oxides is the active component while the other improves resistance to anodic dissolution. The preparation procedure is crucial in determining the final properties.

For this reason, another possible method for enhancing the stability of the electrode, in addition to the thickening of the SnO_2 film, is to obtain coatings of mixed oxides of tin and platinum on titanium substrate. Figure 6, solid line, shows the voltammogram in a 0.5 M H_2SO_4 solution for a SnO_2 electrode doped with antimony and platinum prepared with a five spray-pyrolysis sequence with a 10% $SnCl_4.5H_2O$ + 1% $SbCl_3$ + 0.42% H_2PtCl_6 in ethanol–HCl mixture. The oxygen evolution is shifted to less positive potentials than those obtained with a SnO_2 electrode doped only with antimony (Fig. 1, solid line). During the negative sweep a small peak near 0.6 V is also obtained, which could be associated with the presence of platinum because this peak does not appear in a SnO_2 electrode without platinum (Fig. 1, solid line).

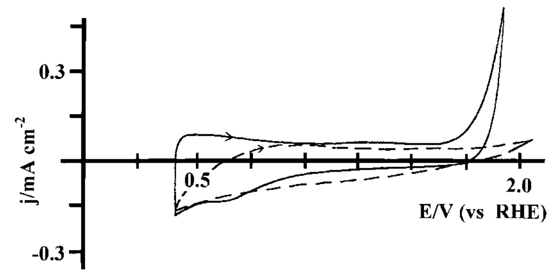

Fig. 6. Voltammetric behaviour of a SnO_2 electrode doped with antimony and platinum with a five spray-pyrolysis sequence in 0.5 M H_2SO_4. Key: (——) before and (- - -) after 60 h of electrolysis at 40 mA cm^{-2}. v = 50 mV s^{-1}.

Figure 2 (dashed line) shows the voltammogram for this electrode in a 0.5 M H_2SO_4 + 0.05 M $FeSO_4$ solution. Good behaviour with respect to the Fe^{3+}/Fe^{2+} redox couple is observed. The ΔE_p values are very similar to those obtained with a platinum electrode. Figure 7 (circles) shows the stability of the SnO_2–Sb–Pt (0.2%) electrode (five spray pyrolysis) in electrolysis at a constant current density of 40 mA cm^{-2} in a 0.5 M H_2SO_4 solution. The electrode potential increases by 1 V from the initial value after 60 h of electrolysis. Figures 5 and 6 (dashed lines) show the voltammograms for this electrode after 60 h of electrolysis in 0.5 M H_2SO_4 + 0.05 M $FeSO_4$ and 0.5 M H_2SO_4 solutions, respectively. The voltammograms clearly show a decrease in electrocatalytic activity for the Fe^{3+}/Fe^{2+} reaction with electrolysis time.

If the number of pyrolysis processes is increased to 15 and the proportion of platinum in the spray solution also increases from 0.2 to 1% the voltammetric behaviour is similar to that obtained with the latter electrodes but the stability increases. Figure 7 (triangles) shows that the life time of this electrode is now of 425 h for an electrolysis at 40 mA cm^{-2} in 0.5 M H_2SO_4. The lifetime of the electrode for electrolysis experiments conducted in neutral solution (0.5 M K_2SO_4) at a constant current density of 40 mA cm^{-2}, is approximately 760 h (Fig. 7, squares).

Figure 8 shows the morphological details of the surface of the electrode obtained from a 10% $SnCl_4.H_2O$ + 1% $SbCl_3$ + 2.1% H_2PtCl_6 ethanolic–HCl mixture and fifteen spray-pyrolysis processes on a wire titanium substrate. The surface presents an uniform distribution of particles and is more granulated and spongy than that obtained for a SnO_2 electrode doped with antimony and a five spray-pyrolysis sequence (Fig. 3).

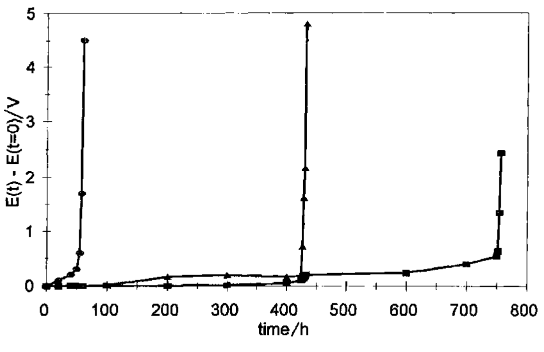

Fig. 7. $E(t) - E(t = 0)$ against time of electrolysis for SnO_2 electrodes doped with antimony and platinum with: (●) five spray-pyrolysis sequences from a 10% $SnCl_4$ + 1% $SbCl_3$ + 0.42% H_2PtCl_6 in ethanol + HCl solution in 0.5 M H_2SO_4, (▲) fifteen spray-pyrolysis sequences from a 10% $SnCl_4$ + 1% $SbCl_3$ + 2.1% H_2PtCl_6 in ethanol + HCl solution in 0.5 M H_2SO_4 and (■) fifteen spray-pyrolysis sequences from a 10% $SnCl_4$ + 1% $SbCl_3$ + 2.1% H_2PtCl_6 in ethanol + HCl solution in 0.5 M K_2SO_4. j = 40 mA cm^{-2}.

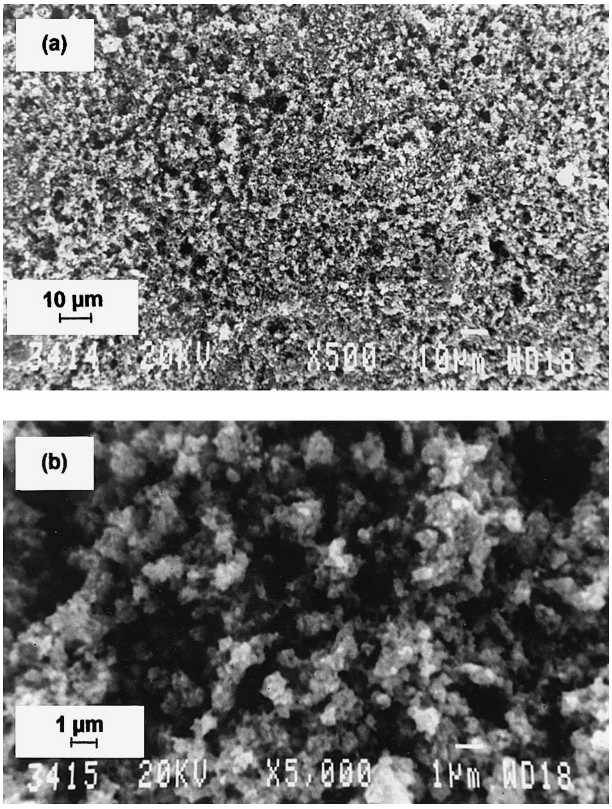

Fig. 8. SEM of a new SnO$_2$ electrode doped with antimony and platinum with a fifteen spray-pyrolysis sequence.

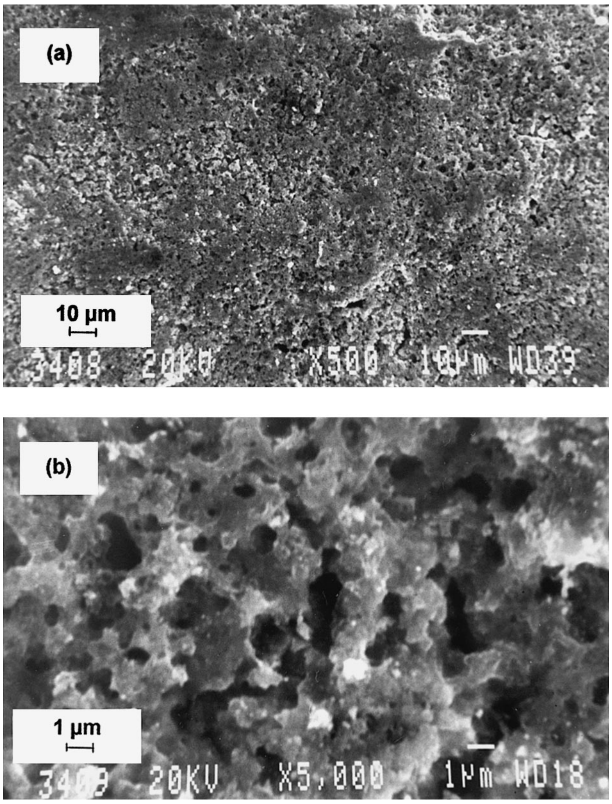

Fig. 9. Scanning electron micrograph of a SnO$_2$ electrode doped with antimony and platinum with a fifteen spray-pyrolysis sequence after 760 h of electrolysis in a 0.5 M K$_2$SO$_4$ solution at 40 mA cm^{-2}.

Titanium is not detected in the EDX analysis for this electrode and only tin, antimony and platinum are present in a proportion of 30.1, 51.5 and 18.4%, respectively. These data also indicate that the thickness of the doped SnO$_2$ film is higher than 2 μm. In fact, profilometric measurement yielded a film thickness of approximately 4 μm.

Figure 9 shows two photomicrographs of this electrode after 760 h of electrolysis in 0.5 M K$_2$SO$_4$ at 40 mA cm^{-2}. The surface morphology of the electrode has changed and is smoother. The results of the EDX data show a change in electrode composition, titanium now being detected. Tin, antimony, platinum and titanium are present in a proportion of 25.5, 34.3, 23.1 and 14.1%, respectively.

For industrial electrodes to be used in filter-press cells, additional experiments were carried out with electrodes prepared on titanium sheet and expanded titanium. The electrolysis of a 0.5 M H$_2$SO$_4$ solution at 100 mA cm^{-2} was carried out using a Ti(expanded)/SnO$_2$ electrode doped with 1% antimony and 1% platinum. The lifetime of this electrode increased to 1800 h, a value substantially higher than that obtained previously (425 h) even using a current density 2.5 times higher.

3.3. *XPS characterization*

XPS analysis was carried out to gain more information about the nature of the surface of the electrode before and after prolonged oxygen evolution. Figure 10 shows the XPS spectra for an electrode of

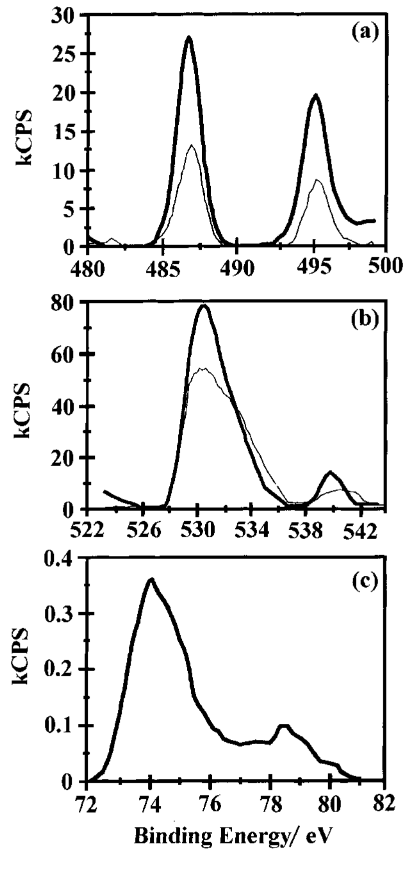

Fig. 10. XPS spectra of a doped SnO$_2$ electrode, obtained with a fifteen spray-pyrolysis sequence from 10% SnCl$_4$.5H$_2$O + 1% SbCl$_3$ + 2.1% H$_2$PtCl$_6$ in ethanol + HCl mixture, before the electrolysis process (thick line) and after 760 h of electrolysis in 0.5 M K$_2$SO$_4$ at 40 mA cm^{-2} (thin line). (a) Sn(3d$_{5/2}$); (b) Sb(3d$_{5/2}$)

Table 1. Binding energies of XPS spectra of Sb $3d_{5/2}$, Sn $3d_{5/2}$ and Pt $4f_{7/2}$, corresponding to the SnO_2 electrode of Fig. 10, doped with antimony and platinum with fifteen spray-pyrolysis processes before electrolysis process

	Sb $3d_{5/2}$	*Sn* $3d_{5/2}$	*Pt* $4f_{7/2}$
BE/eV	530.4	486.7	74.1

Table 2. Binding energies of the XPS spectra of Sb $3d_{5/2}$, Sn $3d_{5/2}$ and Pt $4f_{7/2}$, corresponding to [17]

	O 1s	*Sn* $3d_{5/2}$	*Sb* $3d_{5/2}$	*Pt* $4f_{7/2}$
SnO_2	530.6	486.6		
SnO		486.9		
H_2O	533.1			
Sb			528.2	
Sb_2O_3			530.0	
Sb_2S_5			529.3	
Sb_2Cl_5			530.9	
Pt				71.2
PtO				74.2
PtO_2				75.0

SnO_2 doped with antimony and 1% platinum, obtained with a fifteen spray-pyrolysis sequence, before and after oxygen evolution for 760 h at 40 mA cm^{-2} in 0.5 M K_2SO_4. Before electrolysis the characteristic bands of Sn, O, Sb and Pt are visible in the spectra (untreated electrode, thick line). The features corresponding to Sb($3d_{5/2}$) and O(1s) overlap in Fig. 10(b). It is noteworthy that titanium was not detected on the surface either before or after electrolysis. Table 1 shows the binding energies corresponding to the features of Sb($3d_{5/2}$), Sn($3d_{5/2}$) and Pt($4f_{7/2}$) for the untreated electrode. The comparison of the binding energy of Sn($3d_{5/2}$) and Sb($3d_{5/2}$) with data from [17] (Table 2) indicates that the oxidation state of tin and antimony are +4 and +3, respectively, probably as SnO_2 and Sb_2O_3 . In [11] and [12] the authors indicate that the oxidation state of tin and antimony are +4 and +5, respectively, as SnO_2 and Sb_2O_5. In the case of platinum, the binding energy corresponds to a +2 oxidation state, probably PtO. Figure 10, shows the same features for the electrode after oxygen evolution (treated electrode, thin line). The oxidation state of Sn and Sb has not changed due to by oxygen evolution. In the case of Sb($3d_{5/2}$) and O(1s), (Fig. 10(b)) a broadening of the overlapped peak to higher binding energies is observed. This indicates that hydroxides and water are present in the outermost layer, this probably being responsible for the loss of electrocatalytic activity. This is in agreement with results of Kötz *et al.* [5] who suggest hydration of SnO_2 as the cause of deactivation. After electrolysis, platinum has been detected only at trace level.

4. Conclusions

Doped SnO_2 electrodes were prepared by the standard spray pyrolysis method. SnO_2 electrodes doped with antimony with and without platinum were characterized by cyclic voltammetry. The Fe^{3+}/Fe^{2+} redox couple was used to test the electrocatalytic activity of the various electrodes.

Oxygen evolution process in 0.5 M H_2SO_4 and 0.5 M K_2SO_4 solutions was used for testing the stability of the different doped SnO_2 electrodes. It was shown that an increase in the number of spray-pyrolysis sequences does not improve the electrocatalytic properties of the electrodes. However, the thickness of the film increases, and hence the stability of the electrode.

The presence of platinum in the SnO_2–Sb electrode also increases its stability. Thus an electrode prepared using a 10% $SnCl_4.5H_2O$ + 1% $SbCl_3$ + 2.1% H_2PtCl_6 ethanolic–HCl mixture and a fifteen spray-pyrolysis sequence on an expanded titanium substrate has a lifetime of 1800 h in 0.5 M H_2SO_4 at 100 mA cm^{-2}.

The XPS results show that the oxidation state of the Sn, Sb and Pt in a SnO_2 electrode doped with these two latter metals, are +4, +3 and +2 probably as SnO_2, Sb_2O_3 and PtO, respectively.

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