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# Preparation of lead and tin oxide thin films by spin coating and their application on the electrodegradation of organic pollutants

**Abstract** In this work, lead and tin oxide films ($Pb_xO_y/SnO_2$) were prepared, using the spin coating technique. The influence of the temperature and duration of the thermal treatment on the final film composition were analysed. The metallic oxide films that were prepared, $Pb_xO_y/SnO_2$, were characterized by means of XRD, SEM/EDS and cyclic voltammetry. When different experimental preparation conditions were used different lead oxide phases were obtained. The electrochemical studies show that the films are stable and can be used as electrodes. Finally the films were tested as electrodes for the electrochemical degradation of a $CHCl_3$ aqueous solution.

**Keywords** Lead oxides · Spin coating films · Electrocatalytic oxidation

## Introduction

Electrochemistry is a clean, versatile and powerful tool for the destruction of organic contaminants in water [1, 2]. Depending on the nature of the organic contaminants, electrochemical oxidation or reduction can be applied. However, the efficiency of the process depends on several parameters such as electrode material, applied potential/current, pH and pollutant concentration. In what concerns the electrochemical oxidation, the anode material should be stable over a wide range of potentials and present high overpotential for oxygen evolution, which usually constitutes a side reaction of the degradation process. The electrocatalytic material must be chemically stable and electrically conductive.

There are many studies reporting the ability of lead oxide as anode material for the oxidation of organic

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compounds [1–5]. This metal has low cost and its major problem, the toxicity, can be avoided if no Pb loss occurs during the electrocatalytic process. Lead oxide is already used for other purposes, such as lead-acid or lithium secondary batteries [3, 5, 6].

Lead oxide films have been prepared by dip-coating sol-gel methods [1, 7], electrodeposition [2, 4, 5], thermodeposition [4] and spray pyrolysis [3, 6]. On the other hand, published work reported that the use of $SnO_2$ electrodes did not show any catalytic activity for electrochemical oxidation reactions unless doped [1, 2]. The presence of a tin oxide in lead oxide film has been seen as a way to alleviate some passivation problems due to the presence of the poorly conducting oxide, α-PbO [7]. Based on this fact, we expect the presence of $SnO_2$ not to change the electrocatalytic performances of lead oxides.

The purpose of this work was to use spin coating procedures to obtain $Pb_xO_y/SnO_2$ thin films and study their ability as electrocatalysts for pollutant degradation. In this paper, we report on the characterization of the films by XRD, SEM-EDS, and the results of preliminary electrochemical tests. The electrochemical studies were performed with electrodes selected from the prepared ones on the basis of their mechanical stability and composition. $CHCl_3$ was used as a standard contaminant.

## Materials and methods

All reagents were analytical grade (Aldrich or Panreac) and used as received. The solutions were prepared with triply deionized water with high resistance obtained from a Milipore-G system.

### $Pb_xO_y/SnO_2$ films preparation

Pb and Sn oxide films were prepared by deposition from a $PbO_2/SnO_2$ suspension, using a spin coating technique. The $PbO_2/SnO_2$ (1:1) solid mixture was dispersed in ethylene glycol and then used in the preparation of films. The film supports were stainless steel disks, 0.5-mm thick, 15-mm in diameter, (Goodfellows). Prior to use, the substrate
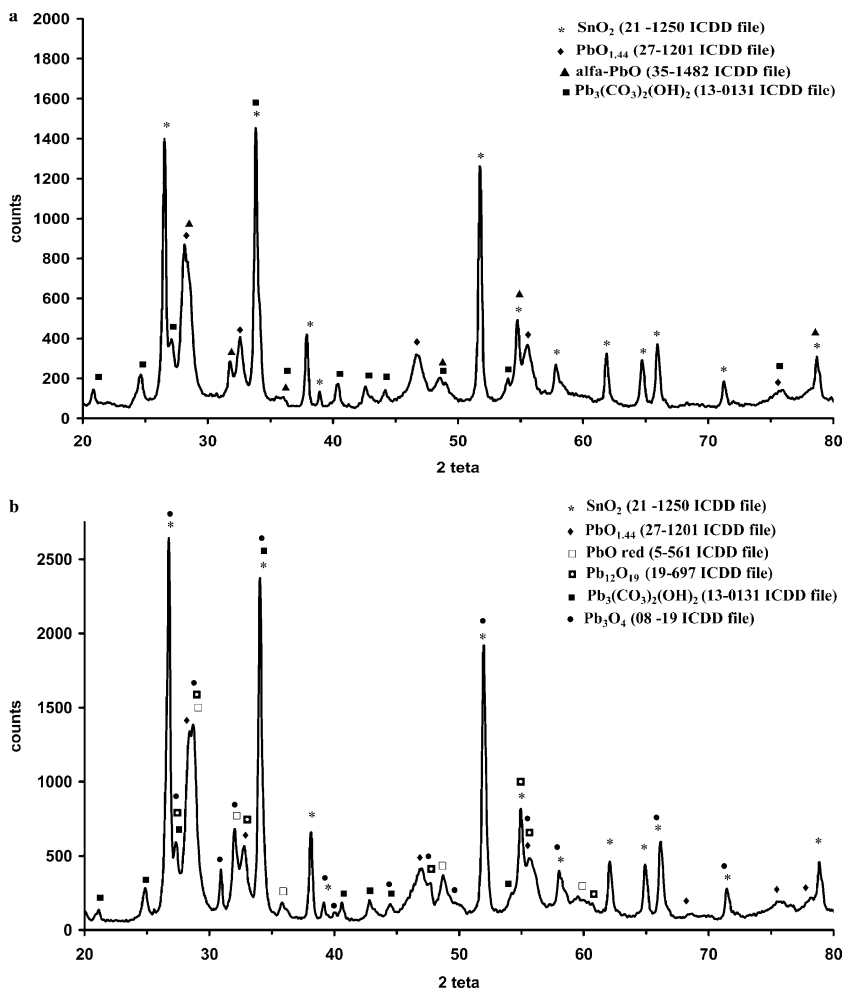
was treated with emery papers until it appeared free of scratches and other defects. Then, it was degreased with acetone in an ultrasonic bath and finally washed with water.

The spin coater used was a Model P6708 from SCS. An amount of 100 μl of dispersion was spun on a piece of substrate at a speed of 5,000 rpm for 50 s under a nitrogen stream. The solvent evaporation was performed at 100 °C for 20 min. The films were then heated at 350 °C or 450 °C during 2 h or 5 h. Depending on the experimental conditions the obtained films displayed colours ranging from brown to orange.

## Instrumentation

X-ray powder diffraction was performed using a Philips X-ray diffractometer (PW 1730) with automatic data acquisition (APD Philips v3.5B) using Cu kα radiation ($\lambda = 0.15406$ nm) and working at 30 kV/40 mA. The diffraction patterns were collected in the range $2\theta = 20$–$80°$ with a 0.02° step $2\theta$ and acquisition time of 2 s/step. SEM images and EDS measurements were carried out on a JEOL (JSM-35C)/NORAN(VOYAGER) system operating at 15 keV. The samples were previously coated with evaporated carbon.
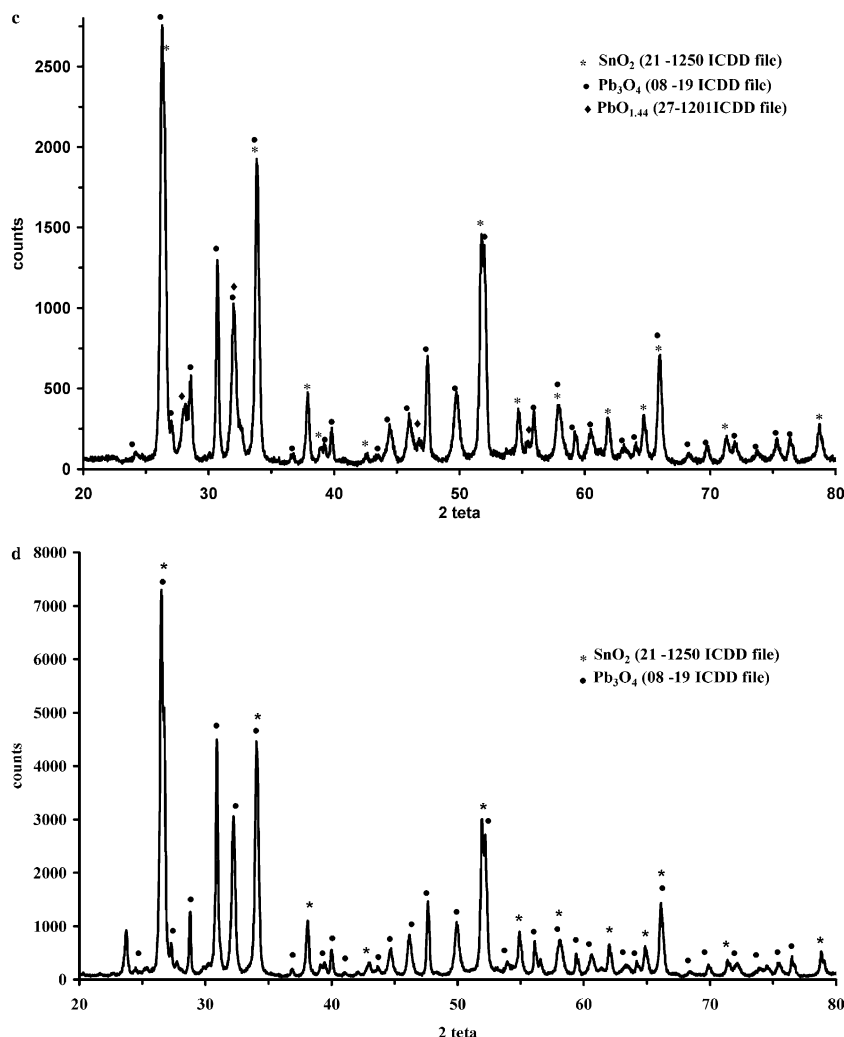
## Electrochemical measurements

All electrochemical measurements were carried out in a three-compartment glass cell with glass-frit separators. A Pt wire was used as secondary electrode, and an Hg/HgSO$_4$ (SSE) system as reference electrode. All potentials are reported with respect to this reference electrode unless otherwise stated. The electrochemical studies were carried out in 0.01 M $K_2SO_4$ and 0.01 M $K_2SO_4$ + 0.005 M $CHCl_3$ aqueous solution. The electrochemical measurements were carried out using a Voltalab 32 Radiometer apparatus connected to an IMT 102 interface, controlled by a personal computer through the VoltaMaster 2 software. The electrode geometric area is 3 cm$^2$.

## Results and discussion

The semiconducting films of Pb and Sn oxides were prepared by deposition of a PbO$_2$/SnO$_2$suspension, using a spin coating technique followed by a thermal treatment. When PbO$_2$ thin films were prepared using the same technique, materials with very poor adherence to the substrate were obtained. To solve this problem we have tried to prepare films with SnO$_2$ in order to increase the mechanical stability of the final material. The metallic

**Fig. 1** X-ray powder diffraction patterns of Pb$_x$O$_y$/SnO$_2$ films prepared at **a** 350 °C for 2 h; **b** 50 °C for 5 h; **c** 450 °C for 2 h and **d** 450 °C for 5 h. Symbols represent the ICDD files

**Fig. 1** (Contd.)



oxide films prepared, $Pb_xO_y/SnO_2$, were characterized using XRD, SEM/EDS and cyclic voltammetry. The influence of the temperature and duration of the thermal treatment on the final solid phase composition was studied. When different experimental conditions were used distinct lead oxide phases were obtained. After the

**Table 1** XRD phase identification of the $Pb_xO_y/SnO_2$ films prepared

| Temperature | Time[a] | |
|---|---|---|
| | 2 h | 5 h |
| 350 °C | SnO$_2$ (file 21-1250) | SnO$_2$ (file 21-1250) |
| | PbO$_{1.44}$ (file 27-1201) | PbO$_{1.44}$ (file 27-1201) |
| | α-PbO (file 35-1482) | PbOred (file 5-561) |
| | Pb$_3$(CO$_3$)$_2$(OH)$_2$ | Pb$_{12}$O$_{19}$(file 19-697) |
| | (file 13-0131) | |
| | | Pb$_3$(CO$_3$)$_2$(OH)$_2$ |
| | | (file 13-0131) Pb$_3$O$_4$ |
| | | (file 08-19) |
| 450 °C | SnO$_2$ (file 21-1250) | SnO$_2$ (file 21-1250) |
| | PbO$_{1.44}$ (file 27-1201) | Pb$_3$O$_4$(file 08-19) |
| | Pb$_3$O$_4$(file 08-19) | |

[a]Phases indexed to the ICDD files [8]

characterization, the films were used as electrodes for the electrochemical degradation of CHCl$_3$ aqueous solutions.

Structural and morphological characterization

The XRD patterns show the existence of well-crystallized samples. All the diffraction lines were indexed according to JCPDS-ICDD data [8], and the results are presented in Table 1 and Fig. 1. For convenience and due to the co-existence of different phases some lines are not marked; however, all of them were indexed during the identification process. The patterns attest that the obtained phases have a clear dependence on the temperature and duration of the heating treatment. This result is in agreement with the work done by Kumar and Sharon [9].

For all the films, Sn is always present as SnO$_2$ (*cassiterite*) (21-1250 ICDD file). The presence of [Pb$_3$(CO$_3$)$_2$ (OH)$_2$] (13-0131 ICDD file) in the 350 °C films can be seen as a result of the solvent (ethylene glycol) and lead oxides interaction, during the preparation of the film. Nevertheless when a higher temperature is used (450 °C) this intermediate compound is not stable and consequently does not appear in the final film composition.
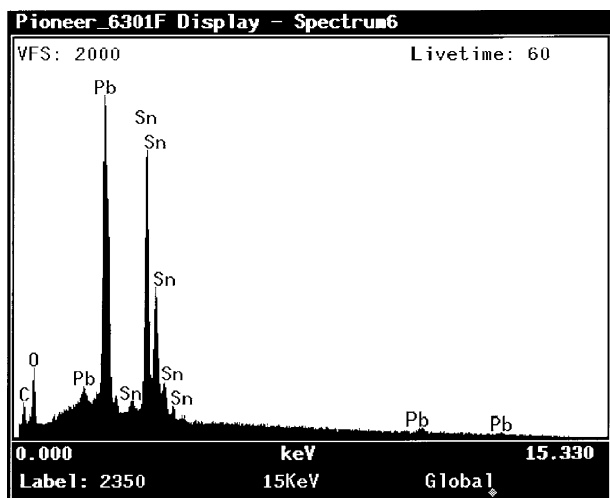
**Fig. 2** EDS spectrum of the $Pb_xO_y/SnO_2$ film prepared at 450 °C for 5 h

The PbO is present in the films prepared at 350 °C as two different phases: α-PbO (35-1482 ICDD file) and PbO red (05-561 ICDD file) for 2 h and 5 h of heating treatment, respectively. Similar results have been reported for
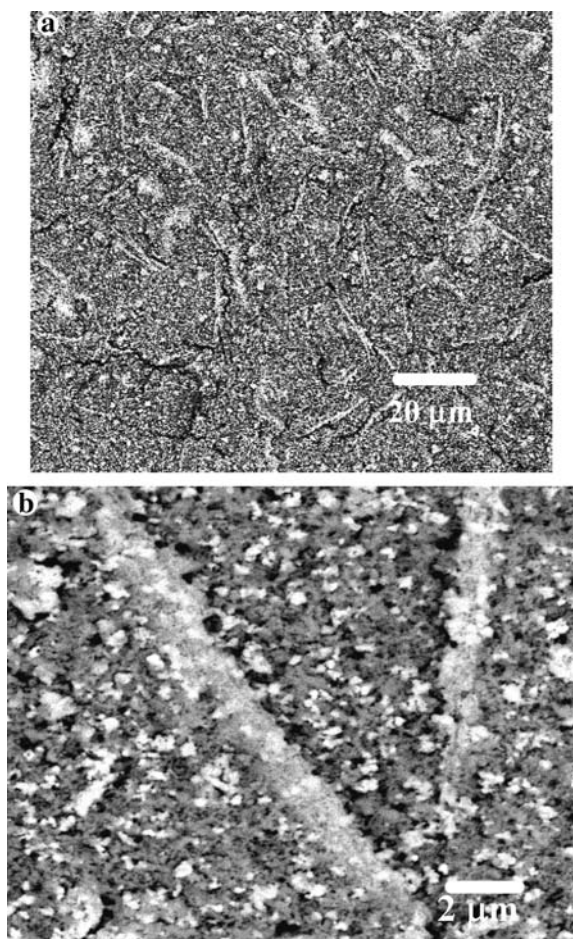


**Fig. 3** Scanning electron microscopy images of the $Pb_xO_y/SnO_2$ film prepared at 450 °C for 5 h. **a** Overview, **b** Detail

PbO thin films, presenting polymorphism, when heated at low temperature (250 °C) and during different periods of time [3]. On the other hand, when a $PbO_2$ film is heated for 24 h at 350 °C, Kumar and Sharon [9] found that $PbO_{1.57}$ was the only phase present. So, in our experimental conditions it is expected that the obtained PbO phases could be intermediates, changeable by increasing the heating time. Nevertheless, the presence of $SnO_2$ as the matrix material and/or the presence of $[Pb_3(CO_3)_2(OH)_2]$ can induce a different final composition.

For the films prepared at 450 °C, it is observed that, increasing the thermal treatment time for 5 h, the $PbO_{1.44}$ (27-1201 ICDD file) changes to $Pb_3O_4$. Only the films prepared at 450 °C for 5 h show the $Pb_3O_4$(08-19 ICDD file) as the unique phase. In all the other films this element is present with different oxidation states. Our results are in accordance with those published in the literature [9] that state the existence of $Pb_3O_4$ as the unique phase obtained, when a $PbO_2$ film is heated for 24 h. Based on these results, we can say that the film prepared for 5 h present the more stable Pb oxide phase at the temperature 450 °C.

The EDS measurements performed on the prepared films have confirmed, as expected, the presence of Pb, Sn, O and C in the composition of the film (Fig. 2). This last peak can be attributed to the layer of evaporated carbon recovering the samples. After the electrochemical measurements, it is sometimes possible to visualize peaks due to the presence of K and S. They appear as impurities from the bath solution as a result of an inefficient electrode wash after the electrochemical experiments.

The morphology of the films were studied by SEM. Figure 3 shows two micrographies of the film prepared at 450 °C for 5 h. Similar morphologies were obtained for all other deposited films. The surface is apparently compact and uniform. The existence of some agglomerates of small rounded particles (Fig. 3b) can be associated with the presence of a lead- and oxygen-rich phase (lead oxides). The tin oxide presents a spherical geometry and is completely segregated from the $Pb_xO_y$ but uniformly spread through the film. These results are in agreement with published work indicating that the PbO has a columnar grain structure [10].

Electrochemical studies

Cyclic voltammetry studies were performed using the electrodes prepared at 450 °C, for 2 h and 5 h. The choice of these materials was made on the basis of their good mechanical stability and adherence to the substrate. Figure 4 shows the voltammograms obtained in 0.01 M $K_2SO_4$ aqueous solution at a sweep rate of 20 mV/s. The scan starts at the open circuit potential (Eoc = −0.530 V) and goes in the direction of the positive limit. For the electrode prepared for 5 h (Fig. 4b) an anodic wave (A1) centered at E = 1.320 V and a cathodic one (C1) at E = 0.175 V are formed. For the electrodes prepared during 2 h (Fig. 4a) an additional pair of peaks appear, (A2) at E = −0.820 V and (C2) at E = −0.370 V. The sharp increase in current after 1.7 V is due to oxygen evolution.

**Fig. 4** Cyclic voltammograms for a $Pb_xO_y/SnO_2$ electrode in 0.01 M $K_2SO_4$. Sweep rate 20 mV/s. $E_i = -0.530$ V. Electrode geometric area = 3 cm$^2$. Electrodes prepared at 450 °C for 2 h (*curve a*) and 5 h (*curve b*)
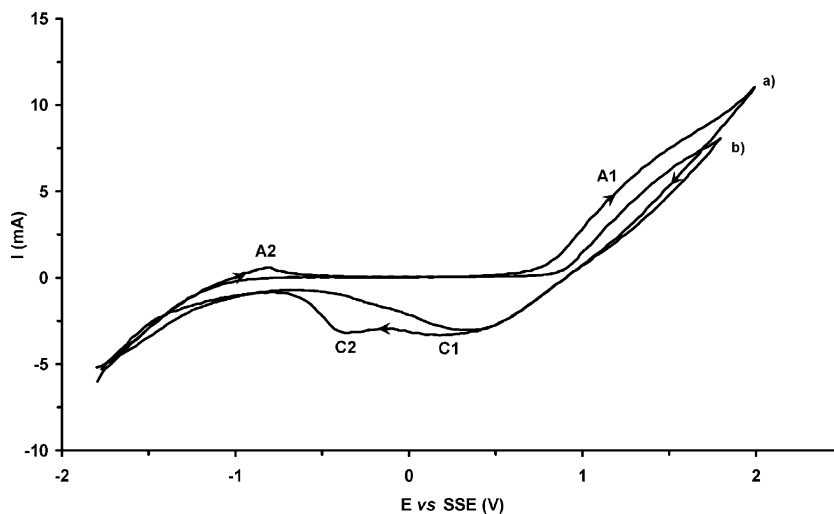
**Fig. 5** Cyclic voltammograms, obtained at different positive limits of potential, in 0.01 M $K_2SO_4$ for a $Pb_xO_y/SnO_2$ electrode, prepared at 450 °C for 2 h. Sweep rate 20 mV/s. $E_i = -0.530$ V. Electrode geometric area = 3 cm$^2$. Sequential scans order: *a, b and c curves*
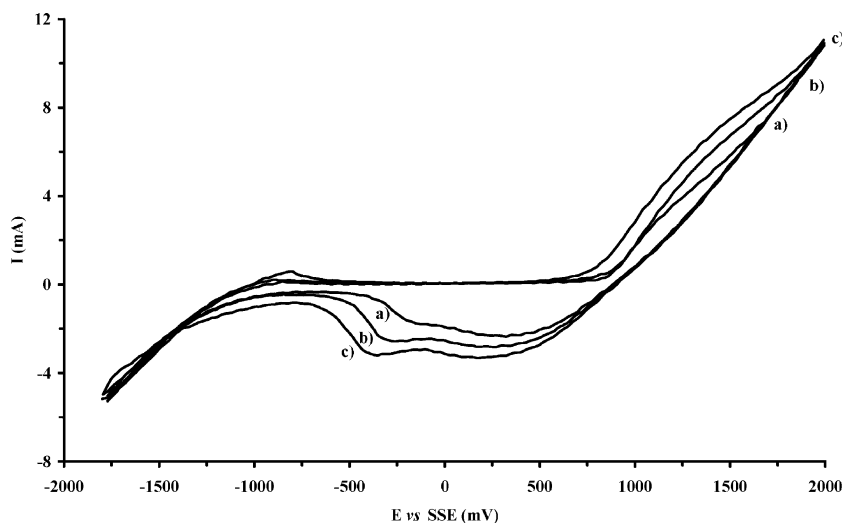
The difference on the voltammograms can be attributed to the different composition of the samples. Indeed, for the electrodes prepared for 5 h only the $Pb_3O_4$ phase is present while for the electrodes prepared for 2 h, the $PbO_{1.44}$ phase is also present. So the pair A1/C1 should be related to the redox processes occurring in the $Pb_3O_4$ phase, and A2/C2 with those occurring in the $PbO_{1.44}$ phase. The anodic wave A1 should be assigned to the $PbO_2$ formation and C1 to its reduction. This is in accordance with the results obtained for Pb–Ca–Sn anodes [10]. Figure 5 shows the influence of the positive potential limit. As it can be seen, no additional peaks are observed when the positive limit increases, and an increase in the cathodic peaks is clearly seen as it is expected.

The following processes should occur on the anodic sweep for the electrodes prepared for 2 h:

$$\begin{cases} Pb_3O_4 \\ PbO_{1.44} \end{cases} \rightarrow Pb_2O_3 \rightarrow PbO_2 \qquad (1)$$
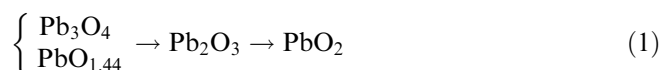
**Table 2** Redox potentials of possible reactions for the $Pb_xO_y$ system

| Redox reaction | Equilibrium potential/V vs. Hg/HgSO$_4$ (SSE) |
|---|---|
| $2Pb_3O_4 + H_2O \rightarrow 3Pb_2O_3 + 2H^+ + 2e^-$ | 0.040 |
| $Pb_3O_4 + 2H_2O \rightarrow 3PbO_2 + 4H^+ + 4e^-$ | −0.061 |
| $Pb_2O_3 + H_2O \rightarrow 2PbO_2 + 2H^+ + 2e^-$ | −0.095 |

and for the electrodes prepared for 5 h:

$$Pb_3O_4 Pb_2O_3 PbO_2 \qquad (2)$$

This proposal is in accordance with XRD data. From the voltammetric data, it has been possible to make the correspondence between the anodic and cathodic peaks and estimate the formal potential associated with each pair, 0.748 V and −0.595 V, respectively for the A1/C1

**Fig. 6** Cyclic voltammograms for a $Pb_xO_y/SnO_2$ electrode prepared at 450 °C for 5 h, obtained in 0.01 M $K_2SO_4$ (curve a) and 0.01 M $K_2SO_4$ + 0.005 M $CHCl_3$ (curve b). Sweep rate 20 mV/s. Electrode geometric area = 3 cm$^2$
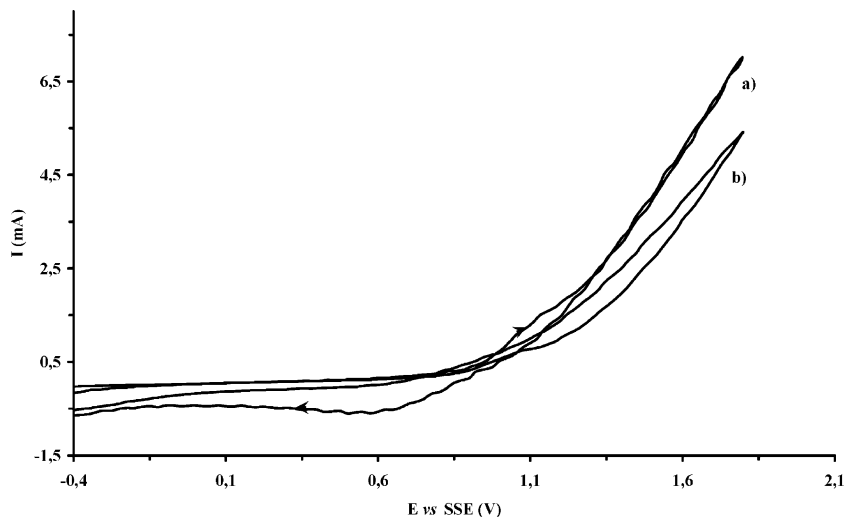
**Fig. 7** Chronopotentiogram for the $Pb_xO_y/SnO_2$ electrode prepared at 450 °C for 5 h, obtained in 0.01 M $K_2SO_4$ (curve a) and 0.01 M $K_2SO_4$ + 0.005 M $CHCl_3$ (curve b). Electrode geometric area = 3 cm$^2$. $I$ = 5 mA. Inset shows the chronopotentiogram obtained in 0.01 M $K_2SO_4$ + 0.005 M $CHCl_3$, for 4 h
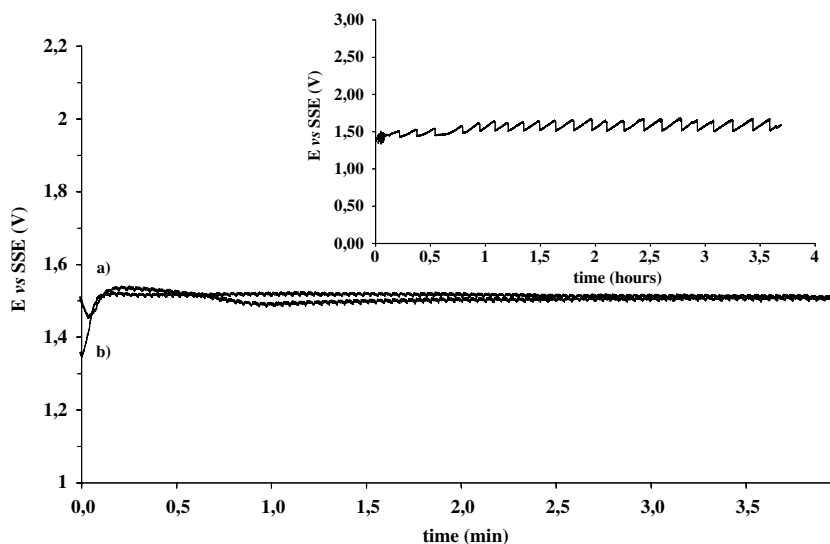
and A2/C2. On the basis of thermodynamic data [11], and assuming that only solid substances are involved, the redox potentials for the possible reactions occurring in the present experimental conditions were calculated and are summarized in Table 2. The estimated values for the formal potentials are higher than the calculated ones. The differences can be attributed to the presence of the $SnO_2$ matrix in addition to ohmic resistances due to grain boundaries.

In order to test the electrocatalytic ability of the films towards the degradation of $CHCl_3$ in aqueous solution, the electrodes prepared for 5 h were selected for the preliminary experiments. Figure 6 presents the voltammograms obtained in 0.01 M $K_2SO_4$ + 0.005 M $CHCl_3$ aqueous solution. For comparison, the voltammograms obtained in the absence of the $CHCl_3$ were also included (Fig. 6a). The voltammetric profiles are similar in the presence and in the absence of the $CHCl_3$. No cathodic peaks are observed and the anodic processes are retarded when the $CHCl_3$ is present. These results indicate
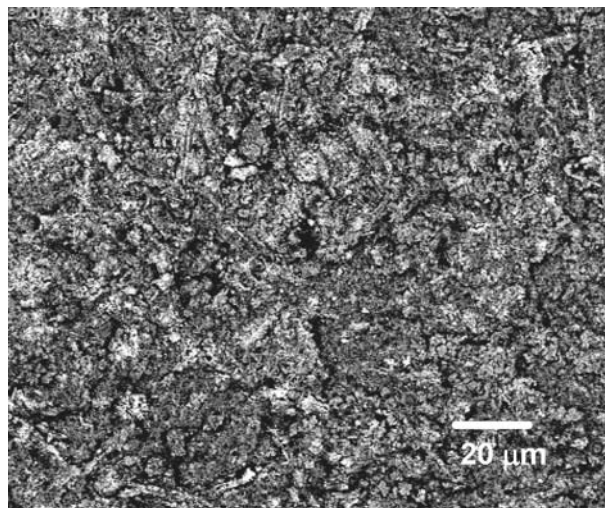
**Fig. 8** Scanning electron microscopy image of the $Pb_xO_y/SnO_2$ used electrode, prepared at 450 °C for 5 h

**Fig. 9** X-ray powder diffraction pattern of $Pb_xO_y/SnO_2$ used electrode, prepared at 450 °C for 5 h. Symbols represent the ICDD files
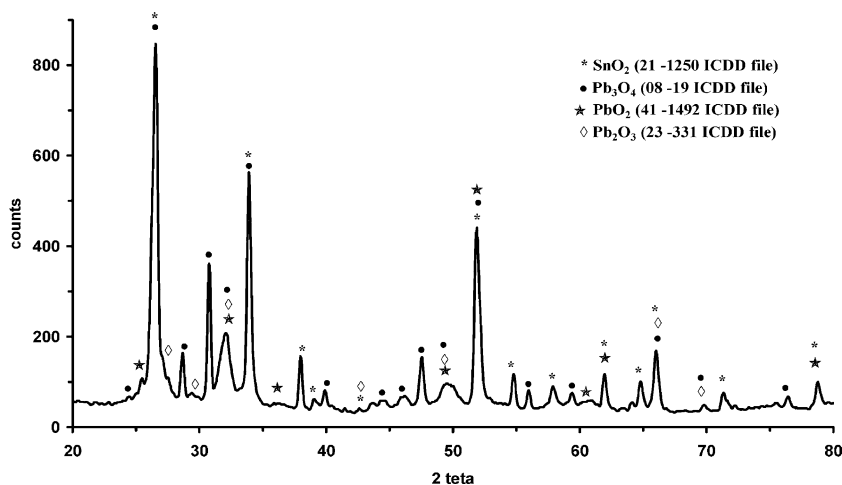


that probably the chloroform is adsorbed on the oxide surface inhibiting the oxidation processes on the electrode surface.

The oxidative degradation of the aqueous solutions of chloroform was performed at constant current, I = 5 mA for 4 h. Figure 7 shows the $E$ versus $t$ curves obtained in 0.01 M $K_2SO_4$ and 0.01 M $K_2SO_4$ + 0.005 M $CHCl_3$ aqueous solutions. Initially an increase of potential is observed for both solutions. This should be due to the formation of $PbO_2$. This is confirmed by the change of the electrode colour from orange to black and also by the XRD data. Afterwards the potential reaches a stable value, similar in both cases. This potential $\approx 1.5$ V corresponds to the oxygen evolution. No meaningful variations on the $CHCl_3$ concentrations were observed (SPME-GCMS was used), which is in accordance with the galvanostatic results as the inset of Fig.7 shows.

Electrodes stability

In order to evaluate the electrode's stability SEM/EDS, atomic absorption spectroscopy (AAS) and XRD studies were performed after the electrochemical measurements. The morphological characteristics of the deposited films before (Fig. 3a) and after (Fig. 8) the electrochemical measurements were similar. The solutions after the electrochemical studies were analysed by AAS. The presence of Pb or Sn in solution was not detected.

The electrodes were also characterized by XRD before and after use. A decrease on the crystallinity was observed for the used electrode. A set of representative XRD patterns for the system $PbO_2/SnO_2$ prepared at 450 °C for 5 h, after use, is presented in Fig.9. The XRD pattern for the used electrode shows the presence of $SnO_2$, $Pb_3O_4$ and $PbO_2$. The existence of a small quantity of $Pb_2O_3$ is not out of question, and it is easily explained by its intermediate character in the electrochemical process considered (Eqs. 1, 2). In addition, it was confirmed that the redox processes are reversible and so the material can be recovered after used by a simple polarization.

## Conclusion

From this work we can conclude that homogenous $Pb_xO_y/SnO_2$ films can be successfully prepared by spin coating technique. The obtained lead oxide phases depend on the preparation conditions namely time and temperature. The electrochemical studies performed led us to conclude that the films are stable and can be used as electrodes. Nevertheless further work will be necessary in order to select the optimum conditions for the chloroalkane degradation.

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