

Surface characterisation of anodic films of Pb–Sn alloy electrodes: the effect of Sn on the photoelectrochemical properties

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Abstract

Oxide thin films of Pb–Sn alloy electrodes were synthesised by potentiodynamic anodisation in hot alkaline solution of sodium sulfate. Films were characterised by various analytical techniques: XRD, SEM, Raman spectroscopy and XPS. The XRD and Raman investigations reveal that the increase in concentration of Sn in the alloy suppresses the formation of the photoactive phase α -PbO but it increases the formation of the conducting phase, α -PbO₂. XPS results indicate the presence of both divalent and tetravalent Pb as well as tetravalent Sn on these films. It also gives evidence for the decrease in α -PbO content upon anodisation of the alloy Pb–Sn electrodes.

Keywords: Lead tin oxide; Anodic oxide of Pb–Sn alloy; Conductivity of Pb–Sn alloy oxide; Photoelectrochemistry of Pb–Sn alloy oxide and Sn doped lead oxide

1. Introduction

Tetragonal lead oxide (α -PbO) is one of the well studied semiconductors and is photoactive in the visible region of the solar spectrum. It is found that the most effective photoactive phase is α -PbO mixed with small amount of α -PbO₂ (designated as PbO_{*n*} with $1 < n < 2$ [1]) rather than pure α -PbO. However, such films are found to be highly resistive. In order to improve the conductivity and other electrochemical properties of PbO_{*n*}, doping the oxide films with Sb, As, Bi, Ca and Sn has been tried [2,3]. Of these metals, Sn is reported to increase the conductivity of PbO_{*n*} thin film prepared by anodic oxidation of Pb–Sn alloy containing various concentration of Sn [4,5]. A systematic study was therefore carried out to investigate the role of Sn on the photoelectrochemical properties of PbO_{*n*} thin film prepared by anodic oxidation of Pb–Sn alloy containing various concentration of Sn.

2. Experimental

2.1. Preparation and fabrication of Pb–Sn alloy electrodes

Binary Pb–Sn alloys with various Sn concentration (0.1–10 wt.%) were prepared following the standard procedure

[4] and the fabrication of the electrodes as discussed in detail elsewhere [6]. Anodic oxidation of alloy electrodes was carried out and the film was characterised for its structure.

2.2. Electrosynthesis of oxide films

All electrochemical studies were performed by using freshly prepared doubly distilled water and AR-grade chemicals without further purification. A bipotentiostat (model AFRDE 4, Pine, USA) coupled to an XY-t (Houston-2000) recorder was used to carry out voltammetric studies. A single compartment three electrode assembly was used for making thin films, in which the working alloy electrode was of 1 cm² area with Pt (4 cm²) as the counter-electrode and saturated calomel electrode (SCE) as the reference. Prior to oxidation, the working electrode surfaces were successively polished on 1000c grit paper, on roughing stone using water as lubricant and finally with methanol–acetic acid mixture. Electrodes were further cleaned by keeping them at hydrogen evolution potential for 2 min to ensure a pure metallic surface before anodisation. Potentiodynamic anodisation of Pb–Sn alloy was carried out at 80°C in the potential range from –1.25 V to +2.35 V with a sweep rate 200 mV s⁻¹. After 20 min of continuous anodisation [7], the electrode was taken out of the electrolysis bath and washed thoroughly in doubly distilled water followed by drying in air at 120°C for 2 h.

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2.3. Characterisation of oxide films

The oxide films were characterised by X-ray diffraction (XRD; JEOL:JDX-300). The Raman spectrum was recorded using a Jobin youn Ramanor Hg 2S spectrometer equipped with a scattered signal detector (Raman Digit 03 DC photometer). Scanning electron microscopy (SEM; Akashi ISI 40 W) was used for recording the surface morphology of the oxide films. Surface analysis of the oxide films was carried out with a Shimadzu ESCA-850 apparatus with Mg K α X-ray source ($h\nu = 1253$ eV). Sputtering of the film surface was performed with an argon ion gun under an accelerating voltage of 2 kV, a pressure of 10^{-6} mbar and a current density of 20 mA cm^{-2} . The binding energy values were calculated from reference C 1s core level at 284.5 eV. Films for X-ray photoelectron spectroscopic (XPS) studies were made of 0.36 cm^2 area and 2 mm thick alloy foil whose rear side was temporarily insulated by an organic insulating coating during anodisation. After anodisation the coating was removed by suitable organic solvent to obtain an ohmic contact.

2.4. Photoelectrochemical (PEC) and impedance studies

The PEC measurements were done by using a conventional cell consisting of the oxide film as the semiconductor electrode and a large area (4 cm^2) Pt as the counter electrode in $0.1 \text{ M Fe(CN)}_6^{4-/-3-}$ electrolyte at a pH of 9.2 (buffer). The light source was a 250 W/24 V tungsten halogen lamp. Impedance studies were carried out using the same PEC cell with saturated calomel reference electrode. A potentiostat/galvanostat (PAR-273) coupled with a frequency analyser (FRA-1255, Schlumberger) was used for these studies. The real and imaginary part of the cell impedances were plotted in a range of superimposed AC frequency (Nyquist plot) to calculate the oxide coating resistance.

3. Results and discussion

All cyclic voltammograms of the anodisation process of Pb–Sn alloy with varying concentration of Sn are similar in nature to pure lead except for Sn concentration greater than 1% (Fig. 1). A small additional anodic current, indicated by A_1 (more distinguishable with a Pb–10 wt.%Sn electrode) at lower anodic potential region may be attributed to the following reaction:



It is interesting to observe that the ratio of the anodic current peak associated with the formation of PbO_2 (A_3) and PbO (A_2) increases as the concentration of Sn increases in the alloy, as if the formation of PbO is inhibited and enhancement in PbO_2 formation occurs. However, the fact that PbO_2 is formed by oxidation of PbO layers [8] suggests that Sn must be enhancing the electrochemical reaction responsible for the conversion of PbO to PbO_2 . The shift in the overpo-

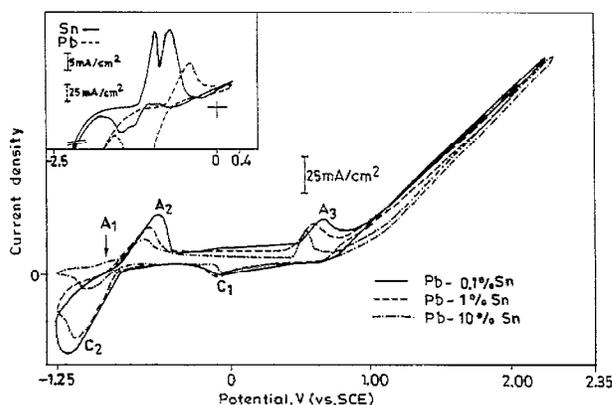


Fig. 1. Cyclic voltammogram of Pb–Sn alloy electrodes in $0.1 \text{ M NaOH} + 0.1 \text{ M Na}_2\text{SO}_4$. Inset: pure Sn and Pb electrode.

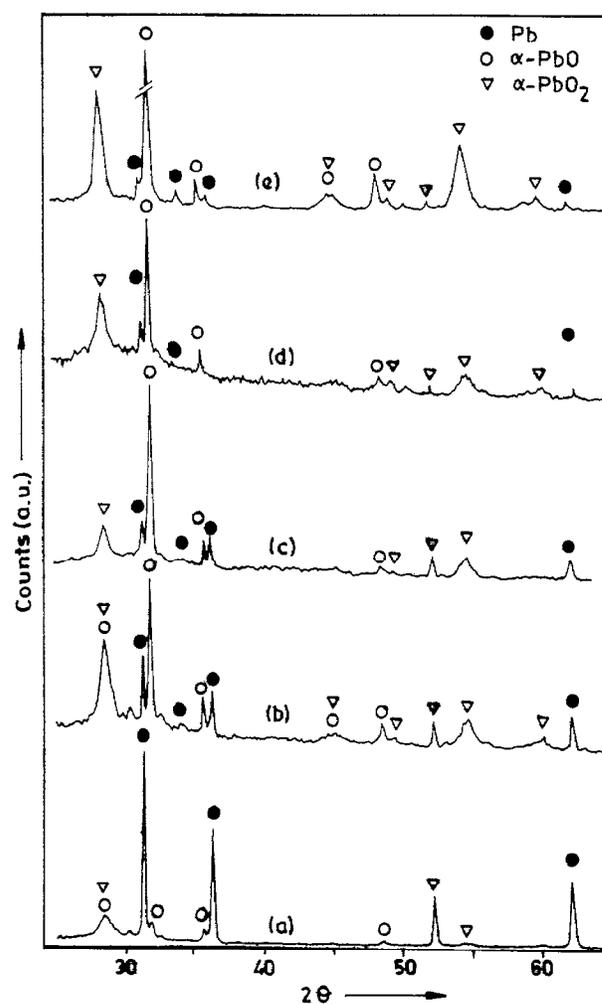


Fig. 2. XRD patterns of the oxide films of Pb–0.1wt.%Sn alloy obtained after various anodisation time; (a) 1.2 min; (b) 5 min; (c) 20 min; (d) 30 min; (e) pure Pb; 20 min.

tentials for oxidation processes (A_1 and A_2 , Fig. 1) towards the cathodic region also suggests that Sn is catalysing the formation of PbO and PbO_2 . Pavlov et al. [5] have also suggested that Sn favours the formation of PbO_2 . If this conclusion is correct then there is a need to confirm that anodised

Pb–Sn alloy films contains less PbO and more PbO₂ as we increase the Sn concentration in the Pb–Sn alloy.

The nature of growth of the oxide film was characterised by XRD (Fig. 2) for a single composition (0.1 wt.% Sn) for various times of anodisation. It can be seen from Fig. 2 that a considerable amount of α -PbO formation takes place after only about 5 min of anodisation. Diffraction peaks belonging to metallic Pb are detected at the initial stage of anodisation and the maximum α -PbO content is observed only after 15–20 min. The nature of the growth of oxide films due to anodisation of Pb–Sn alloy electrodes of various Sn content was studied by XRD (Fig. 3). The XRD line at $d=3.11$ (labelled 1 in Fig. 3) matches with α -PbO and α -PbO₂. In pure lead oxide the intensity of this line is sensible but as the alloy electrode containing Sn undergoes oxidation the intensity of this line initially decreases. When the Sn concentration exceeds 1 wt.% in the alloy the intensity of line 1 (Fig. 3) increases. It may be argued that Sn facilitates the oxidation of PbO to PbO₂. So the abrupt increase in intensity of this line in the case of Pb–Sn alloy oxide may be due to the increase in PbO₂ content of the film. A further support come from the observation that the XRD line at $d=2.80$ Å belongs only to α -PbO. As the Sn concentration increases in the alloy, the intensity of this line decreases which necessarily indicates

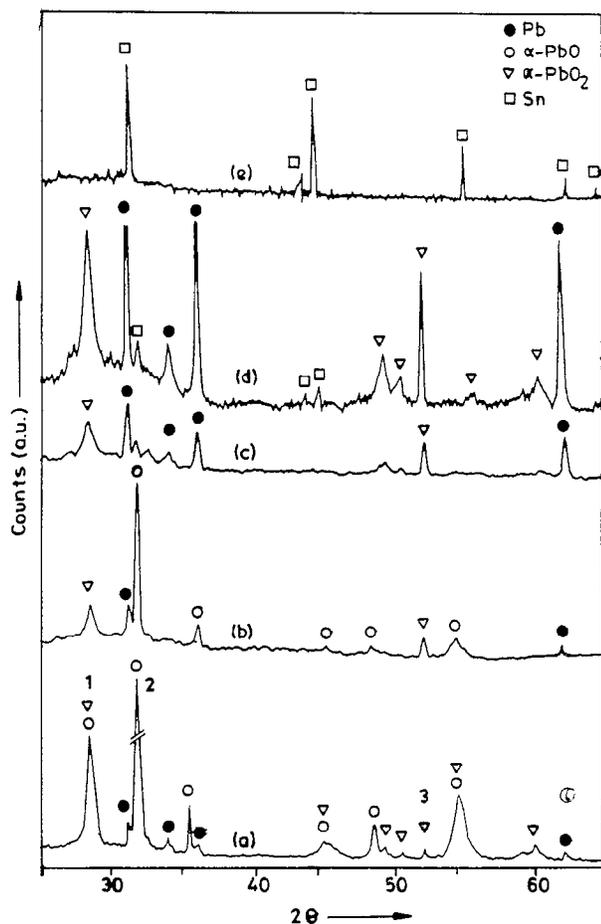


Fig. 3. XRD patterns obtained after 20 min of anodisation of (a) pure Pb; (b) Pb–0.1wt.%Sn; (c) Pb–1wt.%Sn; (d) Pb–10wt.%Sn; (e) Pure Sn.

that the α -PbO content of the film decreases. Moreover the line at $d=1.80$ Å (labelled 3 in Fig. 3) belongs to α -PbO₂. With increase in Sn concentration in the alloy, the intensity of this line (i.e. 3 in Fig. 3) increases abruptly, indicating that Sn helps the conversion of PbO to PbO₂. Therefore it can be concluded that an increase of Sn in the alloy adversely affects the growth of α -PbO content in the oxide layer and is complemented by the appearance of peaks due to the α -PbO₂. The absence of SnO or SnO₂ in the XRD pattern of the oxide film may be due to limitation of the detection sensitivity of the XRD machine. Also it was observed from an independent experiment that anodisation of pure Sn metal under identical conditions gave only a thin film of oxide which was transparent to X-rays and showed only the metallic Sn lines in the XRD pattern (Fig. 3(e)). This may also be considered as a reason for not getting the lines due to oxide phases of Sn in the resulting Pb–Sn alloy oxide film. This is also supported by the CV studies.

The Raman spectrum (Fig. 4) of the pure PbO film clearly shows a strong line at 150 cm⁻¹ and a complementary line at 350 cm⁻¹ which indicates the presence of α -PbO [9]. As we dope Sn in Pb matrix, the intensity of the strong line diminishes significantly (Fig. 4(b) and (a)) which implies that the α -PbO content of the oxide film decreases. As we know that PbO₂ is black in colour and has a self-absorbing property [10], the decrease of the intensity in Raman spectra may be regarded as reflecting the increase in PbO₂ content of the film. These results are in agreement with the XRD results.

Fig. 5 shows the typical XP spectra of Pb 4f and Sn 3d core levels. For a comparison, the spectra of pure and partially

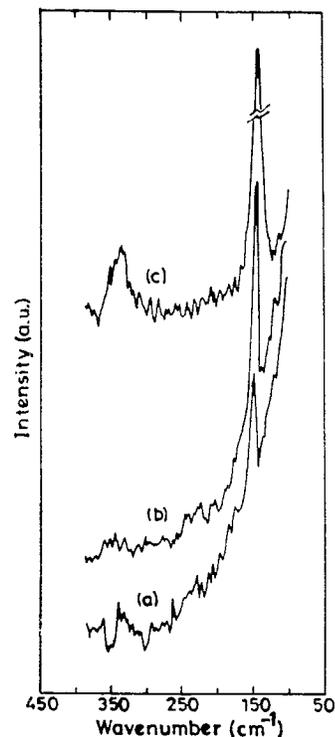


Fig. 4. Raman spectra of various anodic films: (a) Pb–10wt.%Sn substrate; (b) Pb–0.1wt.%Sn; (c) Pure Pb.

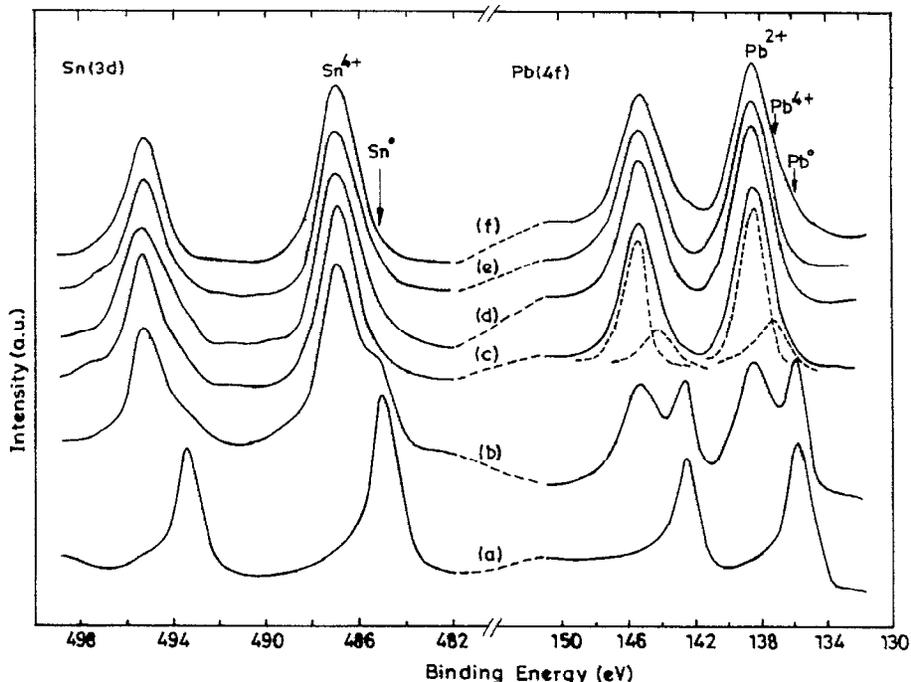


Fig. 5. XPS spectra of various electrodes: (a) Pb–0.1wt.%Sn; (b) partially anodised (5 min) Pb–0.1 wt.%Sn; and anodised (for 20 min) (c) pure Pb; (d) Pb–0.1wt.%Sn; (e) Pb–1wt.%Sn; (f) Pb–10wt.%Sn.

oxidized Pb–Sn alloys are included. In the Pb 4f region, the broad peak at 138.6 eV with an asymmetry at 137.7 eV can be deconvoluted into two components, the major peak being assigned to divalent Pb and the minor being to tetravalent Pb [11,12]. It is to be noted that the asymmetry increases with increase of Sn content indicating Sn-assisted growth of α -PbO₂. On the other hand, in the Sn 3d region, the peak at 487.1 eV indicate the tetravalent nature of Sn [13].

The O 1s spectra of the as-received and sputtered samples are shown in Fig. 6. It can be deduced from the figure that most of the Pb is present as carbonate–hydroxide (≈ 531 eV)

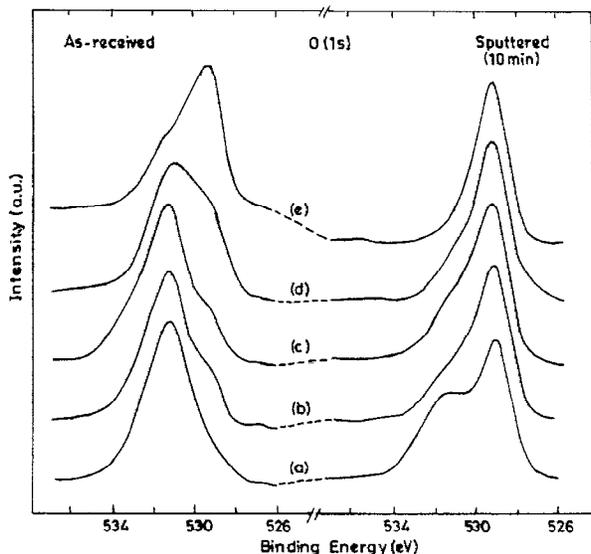


Fig. 6. XPS spectra of the anodised (20 min) electrodes: (a) Pure Pb; (b) Pb–0.1wt.%Sn; (c) Pb–1wt.%Sn; (d) Pb–3wt.%Sn; (e) Pb–10wt.%Sn.

on the external surface whereas the lower binding energy peaks belong to the bulk oxide (≈ 529 eV) [13]. The latter is noticed to a lesser extent in the case of undoped film, although the broad peak can be deconvoluted to two components. The fact that the O 1s binding energies for all of the lead oxides are nearly equal (≈ 529 eV) [13] means that the divalent and tetravalent species cannot be distinguished directly. On the other hand, they can be differentiated based on their reaction behaviour towards H₂O and CO₂. The higher binding energy features in the figure are due to the adsorption of H₂O and CO₂ on PbO whereas PbO₂ does not interact with these contaminants [13]. The pronounced increase of such high binding energy peaks suggests that anodisation of pure Pb, unlike the Sn-doped films, results in higher PbO content than PbO₂ on the surface. It is, however, interesting to note that with an increase of Sn content, the oxide peaks grow while the carbonate–hydroxide content decreases considerably, indicating the Sn-assisted growth of PbO₂ and hence the low or zero photoconductivity. It is also interesting to note that upon sputtering the oxides dominate except in the case of undoped film. The latter observation may be due to the porous nature of the electrode where the PbO contribution may be from the internal surfaces.

Shown in Fig. 7 are SEM photographs of anodised Pb and Pb–1 wt.%Sn electrodes. It can be seen that the Sn-doped film exhibits better intergrain connectivity compared with the porous nature of undoped film. These observations are further supported by XPS results (Figs. 5 and 6).

The resistivity of an oxide film obtained by the anodisation of Pb–Sn alloy containing different concentrations of Sn was studied from the Nyquist plot. The real and the imaginary

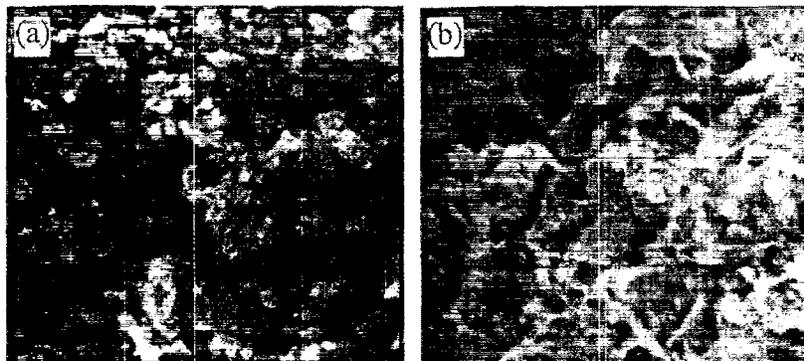


Fig. 7. SEM of anodised: (a) Pure Pb; (b) Pb-0.1wt.%Sn (original magnification: 1 cm = 1 μ m; reduced in reproduction by 85%).

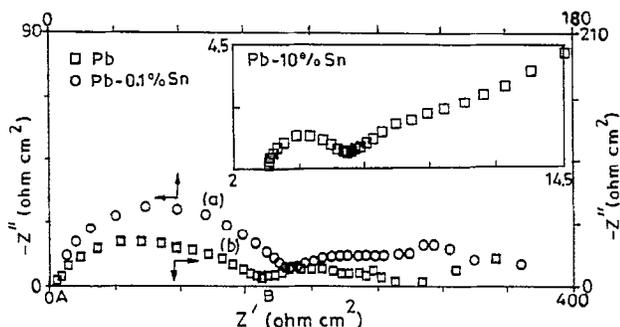


Fig. 8. Nyquist plots of anodic films of various Pb-Sn alloys.

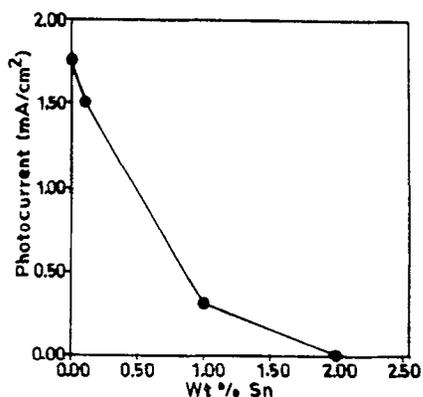


Fig. 9. Short circuit photocurrent of anodised Pb-Sn electrodes.

parts of the PEC cell impedance were plotted against a range of superimposed AC frequencies. The diameter of the semi-circle (labelled (a) and (b) in Fig. 8) indicates the resistance of the oxide coating. It can be seen from Fig. 8 that the oxide coating resistance decreases with increase in Sn concentration in the alloy. This must be due to an increase in PbO₂ phase in the oxide layer.

The photoactivity of these oxide films was studied and the short circuit current of the PEC cell is plotted against the Sn concentration in the alloy (Fig. 9). As the Sn concentration increases, the short circuit photocurrent output decreases rapidly and becomes negligibly small at an Sn concentration of 2 wt.%. Lowering of α -PbO content in the oxide film is attributed to such a marginal variation because this behaviour is obtained in spite of the fact that the resistance of the oxide

film is also decreasing with the increase in concentration of Sn (Fig. 8).

4. Conclusions

The following are the main findings derived in this study of the anodisation of Pb-Sn alloy electrodes in alkaline solution. Incorporation of Sn improves the electrical conductivity of the films. The best photoanode is obtained with a Pb-0.1wt.%Sn electrode, although its quantum efficiency was lower than that of the undoped Pb electrode. This is because the photoconductivity of the film decreases markedly as a consequence of the lack of the presence of photoactive α -PbO phase on the surface. Electrochemical studies reveal that Sn-doping reduces the formation of α -PbO and that it converts the α -PbO thus produced into α -PbO₂ during the electrolysis. Further physico-chemical studies support the sequential decrease of α -PbO content of the anodic films with increasing Sn content and that the oxidation of Sn on the outer surface may act as a barrier for the growth of α -PbO phase.

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