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Oxidation states of lead in anodic oxide films formed in sulphuric acid solutions containing antimony (III) species

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The oxidation states of lead in anodic oxide films formed in sulphuric acid solutions containing antimony(III) species were investigated by means of X-ray photoelectron spectroscopy. The presence of divalent lead ions in the anodic oxide films was confirmed. The content of α-PbO_2 in these anodic oxide films was found to be higher than that in films prepared in an antimony-free solution. The formation of the complex oxide, containing divalent lead ions and α-PbO_2, was studied.

1. Introduction

Anodic oxide films on Pb, formed in sulphuric acid solution at high anodic overvoltage, consist mainly of lead dioxide. However, it was concluded in earlier papers [1, 2] that anodic oxide films formed either on Pb–Sb alloy in sulphuric acid solution or on Pb in sulphuric acid containing Sb(III) species under the same conditions consist of lead dioxide and a complex oxide in which lead(II) and antimony(V) ions are present.

In order to obtain experimental evidence for the existence of lead(II) ions in the anodic oxide films, X-ray photoelectron spectrometric (XPS) measurements were taken for samples formed in H_2SO_4 with or without antimony(III) species at high anodic overpotentials.

2. Experimental

2.1. *Preparation of samples*

Circular lead plates (99.999% pure, 16 mm diameter, 2 mm thick) were used as the test electrodes. The preparation of the test electrode has been described previously [2]. The electrode was polarized to the desired anodic potential (either 1.50 or 1.60 V) where PbO_2 is formed. Samples prepared by potentiostatic oxidation were washed with distilled water for several seconds, dried in a low-vacuum chamber and then subjected to XPS measurements.

5 M H_2SO_4 was prepared from reagent-grade sulphuric acid and doubly distilled water, and pre-purified by electrolysis. Electrolytes containing antimony(III) species were prepared by dissolving Sb_2O_3 powder in 5 M H_2SO_4. Lead oxide and antimony oxide powders used for XPS measurements as reference materials were commercial samples.

An $Hg/Hg_2SO_4/5$ M H_2SO_4 reference electrode was used. All the experiments were carried out at 25° C.

2.2. *XPS measurements*

XPS measurements were taken by using a Shimazu-Du Pont ESCA 650B at pressures of 10^{-7} torr using MgK_α X-rays. Samples were set in sample holders with silver paste before mounting in the sample chamber. Argon-ion etching of the surface was carried out under 1×10^{-5} torr of argon with a beam energy of 5 kV. Pb 4f binding energies were determined with an Au $4f_{7/2}$ (84.0 eV) reference.

3. Results and discussion

Previous SIMS studies on the incorporation of antimony from the electrolyte solutions into the anodic oxide films [2] have been made for anodic oxide films formed by passing either 1 or 3 C at 1.50 and 1.60 V, respectively, in 5 M H_2SO_4 with and without 2×10^{-3} M Sb(III). When these samples were used for XPS measurements, how-

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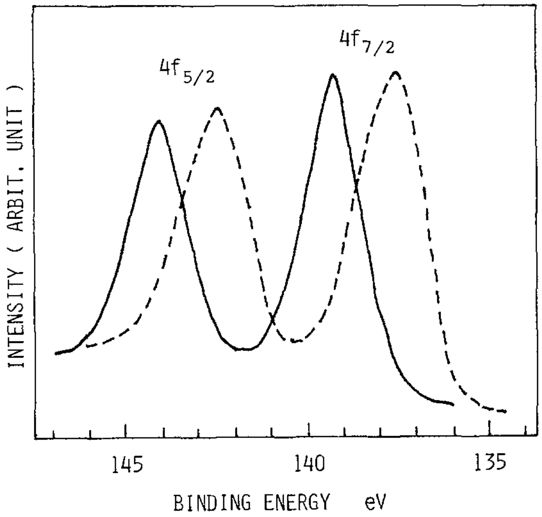

Fig. 1. Typical X-ray photoelectron spectra of Pb $4f_{5/2,7/2}$ on lead dioxide films prepared at 1.50 V. Broken line: formed in 5 M H_2SO_4; full line: formed in 5 M H_2SO_4 containing 2×10^{-3} M Sb(III).

ever, no marked difference in the binding energy of lead was observed with or without antimony, probably reflecting a low sensitivity of XPS. Therefore, thicker films were employed for XPS measurements. X-ray photoelectron spectra of anodic oxide surfaces formed by passing 15 C at 1.50 V are given in Fig. 1. The binding energies of both Pb $4f_{5/2}$ and $4f_{7/2}$ are clearly different for oxide films prepared in solutions with and without Sb(III) species. The values for the binding energies of Pb $4f_{5/2,7/2}$ on peak maxima obtained on four samples are listed in Table 1; also given in this table are results for Ar^+-ion-sputtered surfaces. Oxide films of ~10 nm were judged to be removed by the sputtering. As described in the experimental section, the binding energy of Au $4f_{7/2}$ was taken as 84.0 eV. In the measurements of data given in Table 1, the binding energy of C $1s_{1/2}$ was 284.8 ± 0.2 eV.

Table 2. Binding energies (eV) of Pb $4f_{5/2,7/2}$ electrons for the pressed samples of PbO and PbO_2 powders

Sample		$4f_{5/2}$	$4f_{7/2}$
PbO†	Before sputtering	144.6	139.7
	After sputtering	144.5	139.7
PbO_2‡	Before sputtering	141.6	136.8
	After sputtering	142.3	137.3

† Rhombic-PbO.
‡ β-PbO_2.

The results in Table 1 indicate that the binding energy shifts to higher values when the oxide films are prepared in the presence of Sb(III) species. The shift to higher binding energies suggests the presence of a compound of low oxidation state [3, 4]. However, the values of binding energy for Pb $4f_{5/2,7/2}$ in this case were large compared to the reported values [3, 4].

Table 2 shows the Pb $4f_{5/2,7/2}$ binding energies obtained on the pressed disc surfaces of rhombic-PbO and β-PbO_2 powders decorated with Au. The value of C $1s_{1/2}$ binding energy in this case was 284.7 ± 0.4 eV. After the Ar^+-ion sputtering, Pb $4f_{5/2}$ and $4f_{7/2}$ binding energies of β-PbO_2 were shifted to higher values by 0.7 and 0.5 eV, respectively, but not so for rhombic-PbO. In the case of β-PbO_2, a partial reduction of Pb(IV) to Pb(II) must have been caused by the Ar^+-ion bombardment [5].

It is evident that all the values of Pb $4f_{5/2,7/2}$ binding energies listed in Table 1 are in the range

Table 1. Binding energies (eV) of Pb $4f_{5/2,7/2}$ electrons for samples formed by passing 15 C before and after sputtering for 10 min by Ar^+-ion beam

Sample		*Before*		*After*	
		$4f_{5/2}$	$4f_{7/2}$	$4f_{5/2}$	$4f_{7/2}$
1.50 V	5 M H_2SO_4	142.5	137.6	142.4	137.5
	5 M H_2SO_4 containing 2×10^{-3} M Sb(III)	144.1	139.3	143.6	138.9
1.60 V	5 M H_2SO_4	142.6	137.8	142.6	137.7
	5 M H_2SO_4 containing 2×10^{-3} M Sb(III)	144.1	139.4	143.8	139.1

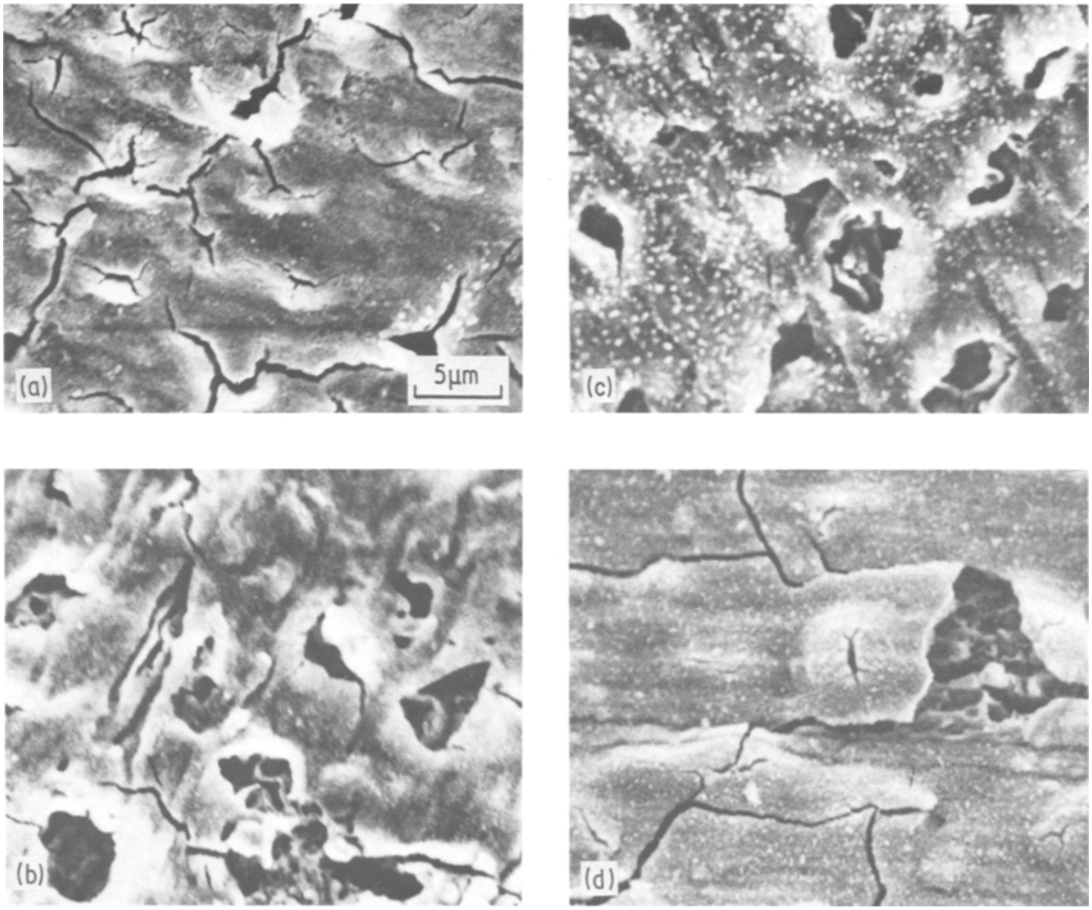

Fig. 2. SEMs of the surfaces of the oxide films formed by passing 15 C at 1.50 V in (a) 5 M H_2SO_4 and (b) 5 M H_2SO_4 containing 2×10^{-3} M Sb(III) and at 1.60 V in (c) 5 M H_2SO_4 and (d) 5 M H_2SO_4 containing 2×10^{-3} M Sb(III).

between the values of binding energies for PbO and PbO_2 powders listed in Table 2. Those for sample surfaces prepared in the antimony-free solution are close to the values obtained on PbO_2 powder, while those for samples prepared in solutions containing Sb(III) species are close to the values obtained on PbO powder.

Fig. 2 shows SEM photographs of the surfaces used for XPS measurements. Although no remarkable difference in morphology was observed, $PbSO_4$ crystallites, which were believed to form during washing with distilled water, are recognized on the anodic films formed at 1.60 V in an antimony-free solution. Even by the Ar^+-ion sputtering, the situation was not changed. However, the existence of the crystallites does not affect the results of XPS binding energy measurements (Table 1).

Fig. 3 shows the X-ray diffraction patterns of the films used to obtain Fig. 2. The radiation used was CuK_α radiation. The signals of both α- and β-PbO_2 were clearly observed, as well as the intense signal of Pb(111). If the ratios of signal intensities for 25.5° [β-PbO_2(110)] and 28.6° [α-PbO_2(111)] to those for 32.0° [β-PbO_2(101)] are obtained, it is found that the former is almost the same between the four kinds of samples, but the latter is different. The films prepared in the presence of Sb(III) species give ratios higher by 60% for the films formed at 1.50 V and by 70% at 1.60 V.

According to Burbank [6], the presence of antimony in the grid metal gives rise to an increased content of α-PbO_2 in the active material formed. It is concluded from the present X-ray diffraction study that antimony species in solution

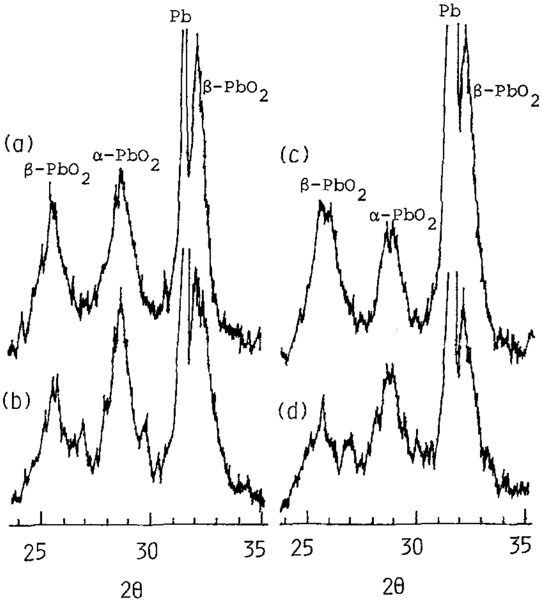

Fig. 3. X-ray diffraction patterns of the oxide films formed by passing 15 C at 1.50 V in (a) 5 M H_2SO_4 and (b) 5 M H_2SO_4 containing 2 × 10^{-3} M Sb(III) and at 1.60 V in (c) 5 M H_2SO_4 and (d) 5 M H_2SO_4 containing 2 × 10^{-3} M Sb(III).

also promote the deposition of α-PbO_2 in the anodic oxide films, as postulated by Abdul Azim and Ismail [7].

It is evident from the results given above that anodic oxide films formed under high anodic overvoltages in 5 M H_2SO_4 solution containing Sb(III) species contain Pb(II), which is related to formation of complexed oxides consisting of Pb^{2+}, Sb^{5+} and O^{2-}, and a relatively high amount of α-PbO_2. Such phenomena may arise as a result of a similarity in crystal structures between α-PbO_2 and the compound $PbSb_2O_6$ (a probable candidate for the complexed oxide [8]). If so and if the dimensions of atomic arrays of $PbSb_2O_6$ are almost the same as those of α-PbO_2, then the increased X-ray diffraction signals of α-PbO_2, observed for oxide films prepared in the presence of Sb(III) species, will be brought about by superposition of those of $PbSb_2O_6$.

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