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Reconsideration of some fundamental aspects of anodic Pb(II) films on lead and its alloys in sulfuric acid solution

Hou-Tian Liu *, Qun-Zhou Wang, Wei-Fang Zhou

Chemistry Department, Fudan University, Shanghai, 200433, China

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Abstract

Recent results obtained from studies of the anodic Pb(II) film formed on lead and its alloys in sulfuric acid solution has enabled reconsideration of some of the fundamental aspects of the film. These include the conditions for growth of various phase compositions as well as ion transportation processes within the film. The interstitial liquid among the particles of the film may serve as the major passage for ion transportation in the film growth and conversion processes. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Anodic Pb(II) film; $PbSO_4$ semipermeable membrane; Ion transportation; Interstitial liquid; Antimony; Bismuth

1. Introduction

Many studies of the anodic film formed on lead and lead alloys in sulfuric acid solution have been carried out [1–7]. These are based on the wide application of lead–acid batteries and the associated interest in the electrochemical behaviour of lead. Researchers have not, however, reached a consensus on the phase composition and growth mechanism of the anodic film. The main reason is that it is difficult to determine the phase composition of the anodic film. Here, we review the relevant recent work of our group.

2. Phase composition of anodic film formed on lead in sulfuric acid solution in PbO potential region

For a lead electrode in H_2SO_4 solution within the potential region, -0.40 to $+0.95$ V vs. Hg/Hg_2SO_4, the electrode system $Pb/PbO/PbSO_4$ is formed [2–8]. A potential of 0.9 V is chosen to form the anodic film on lead since it is quite close to the potential of the anodic film at the positive grid after the battery has been discharged. The phase composition for the anodic film formed in 4.5 M H_2SO_4 solution at 0.9 V has long been debated together with the explanation of the cathodic peak at about -0.9 V in the linear sweep voltammogram (LSV) for the anodic film. Two problems are as follows: (i) Is the PbO layer composed of α-PbO or β-PbO? (ii) Between the PbO and $PbSO_4$ layers in the anodic film, is there quite a small amount of $PbO \cdot PbSO_4$ transient phase or not? Many investigations have been performed on this system [9–18]. Barradas et al. [9] showed that the PbO crystals in the anodic film are β-PbO by the application of photoconduction spectroscopy. Bullock et al. [10] held that β-PbO is formed on lead at the beginning of the anodization and then converted gradually to α-PbO. By contrast, Buchanan and Peter [11] considered that α-PbO is the main composition of the film according to the absorption spectrum. The existence of $PbO \cdot PbSO_4$ is generally ignored. Recently, our group has obtained some new data on the phase composition of the anodic film.

He et al. [19] investigated the film using a photocurrent method and concluded that both α-PbO and β-PbO are photoactive components, and that a plot of $[-h\nu \ln(1-Y)]^{1/2}$ vs. $h\nu$ (Fig. 1) can be divided into two sections of lines a and b, in which $h\nu$ is the energy of photons and Y is the quantum yield of the photoelectrochemical current. It was suggested that section a ($2.0 \text{ eV} < h\nu < 2.6 \text{ eV}$) corresponds to the photocurrent effect of α-PbO and section b ($2.6 \text{ eV} < h\nu < 3.2 \text{ eV}$) is due to the total contribution of

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* Corresponding author. Fax: +86-21-6564-1740; E-mail: htliuk@online.sh.cn

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the β-PbO and α-PbO. The red shift of the spectral curves with increase in anodization time is due to an increase in the ratio of α-PbO to β-PbO [10,20–24] (Table 1) [23]. Han et al. [23] found that the curve of $[-h\nu \ln(1-Y)]^{1/2}$ vs. $h\nu$ became a straight line when the anodizing time was extended to 40 h, which indicates that for this time, the relative amount of β-PbO can be neglected.

Using photocurrent spectroscopy, linear sweep voltammetry and open-circuit decay curves, the phase composition of the anodic plumbous film formed on a lead electrode at 0.9 V in 4.5 M H_2SO_4 (25°C) can be determined as shown in Table 1 [23].

During the initial period of anodization, the amount of $PbO \cdot PbSO_4$ in the film cannot be ignored. This has been also demonstrated by Wei and Rajeshwar [25] using a quartz microbalance. The data in Table 1 show that the growth rate of the α-PbO film increases, while that of the β-PbO film decreases, with increasing amount of $PbO \cdot PbSO_4$ film. Burbank [26] reported that α-PbO is more stable than β-PbO at pH > 10.2. The formation of $PbO \cdot PbSO_4$ from the reaction of PbO with H_2SO_4 increases the pH value in the anodic film, which favours the growth of α-PbO.

The data in Table 1 also show that the growth rate of the $PbSO_4$ film is nearly zero after a short time [23,27,28]. If PbO is formed by:

$$Pb + H_2O = PbO + 2H^+ + 2e - \qquad (1)$$

Then H^+ will accumulate in the layer under the $PbSO_4$ film because the transference number of H^+ is always less than 1. On the other hand, PbO cannot exist without an alkaline condition, and such an environment may persist in the film by the following reactions:

$$2\alpha\text{-PbO} + 2H^+ + SO_4^{2-} = PbO \cdot PbSO_4 + H_2O \qquad (2)$$

$$4\alpha\text{-PbO} + 2H^+ + SO_4^{2-} = 3PbO \cdot PbSO_4 + H_2O \qquad (3)$$

Thus, the lead oxides are accompanied in the film by a certain quantities of basic lead sulfates.

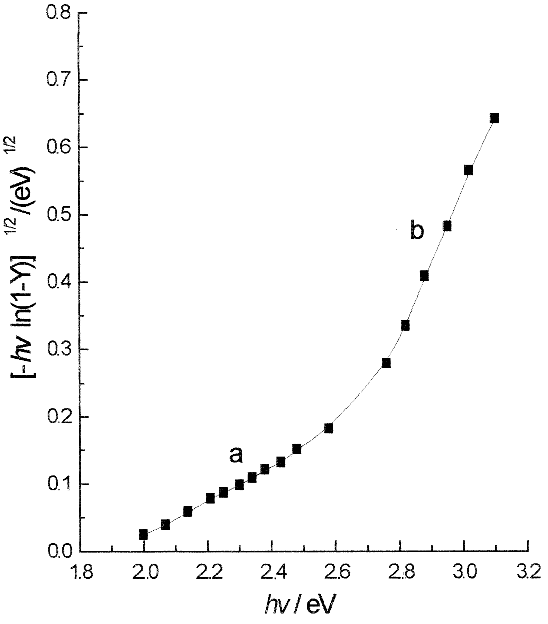

Fig. 1. $[-h\nu \ln(1-Y)]^{1/2}$ vs. $h\nu$ plot for the anodic film formed on Pb at 0.9 V (vs. Hg/Hg_2SO_4) in 4.5 M H_2SO_4 solution (25°C) for 3 h.

Table 1
Various quantities of electricity for forming anodic films at different anodizing times t (25°C) [23]

t (h)	$Q_{\alpha\text{-PbO}}$ (mC cm^{-2})	$Q_{\beta\text{-PbO}}$ (mC cm^{-2})	Q_{PbSO_4} (mC cm^{-2})	$Q_{PbO \cdot PbSO_4}$ (mC cm^{-2})
1	25	50	201	278
2	63	76	216	402
3	106	106	226	621
4	166	119	226	728

It is rather difficult to detect the photocurrent of $PbO \cdot PbSO_4$ because its bandgap is over 3.5 eV. The results of electrochemical impedance spectroscopy (EIS) and X-ray diffraction (XRD) provide evidence for the existence of $PbO \cdot PbSO_4$. Pu et al. [29] measured the space-charge region capacitance (C_{sc}) of the anodic film in the potential range between −0.3 and −0.7 V. The curve of C_{sc}^{-2} vs. E is in agreement with the Mott–Schottky equation and the flatband potential (E_{fb}) is −0.95 V. This cannot be due to the contribution of a α-PbO or β-PbO film, for the flatband potential of both α-PbO and β-PbO is about −0.3 V according to the photocurrent method [30,31]. Therefore, the flatband potential of −0.95 V measured by EIS provides further evidence for the existence of $PbO \cdot PbSO_4$.

Xia and Zhou [32] used XRD to analyze the change in phase composition of the anodic film during reduction at −0.91 V (i.e., at a potential which is slightly more positive than the reduction potential of $PbSO_4$). It was found that $PbO \cdot PbSO_4$ is reduced first. After the reduction of $PbO \cdot PbSO_4$ is completed, α-PbO begins to be reduced to Pb. In a high pH environment, α-PbO rather than $PbO \cdot PbSO_4$ is stable, as shown by Eq. (2). Hence, α-PbO cannot convert to $PbO \cdot PbSO_4$ during the cathodic reduction of α-PbO, which is a pH-increase process (Eq. (1)). This is in accordance with the results of XRD.

3. Reduction peak around −0.9 V in the negative LSV for the anodic film

Two peaks are found in the negative LSV for the anodic film formed on lead in H_2SO_4 at 0.9 V. One is recognized as the reduction of $PbSO_4$ to Pb. The other is at a more positive potential (around −0.9 V) and has not been assigned properly since the potential deviates considerably from the thermodynamic values for relevant lead compounds [12–18].

Han et al. [23] studied the open-circuit decay curve of the anodic film formed on lead at 0.9 V in 4.5 M H_2SO_4 (25°C) for 1 h, followed by cathodic reduction using LSV to -0.85 V (the potential of the peak), then standing at open circuit. The steady potential was -0.443 V and was very close to the thermodynamic potential of $PbO \cdot PbSO_4/Pb$ covered with a semi-permeable $PbSO_4$ membrane, viz., -0.434 V. This indicates that the current peak corresponds to the reduction of $PbO \cdot PbSO_4$ to Pb, followed by the reduction of PbO (α-PbO and β-PbO) to Pb.

It can be concluded from the XRD patterns that the anodic film formed on Pb in the potential region of oxygen evolution is composed of α-PbO_2, β-PbO_2, and Pb(II) compounds [33,34]. Cai et al. [34] investigated the reduction process of the film using LSV, XRD and photocurrent methods. The results showed that α-PbO_2 can be converted to α-PbO in an anodic film reduced at potentials lower than 0.8 V ($E \leq 0.8$ V). Thus, the cathodic peak at about -0.9 V in the LSV for the anodic film formed on Pb at high potential indicates that the reduction process includes not only the reduction of α-PbO, β-PbO and $PbO \cdot PbSO_4$ to Pb, but also the reduction of the reduction product of α-PbO_2 in the LSV process. It is unlikely that most of the α-PbO_2 would be reduced at the cathodic peak in the LSV as proposed by Panesar [15].

4. Conditions for the growth of different phases in anodic Pb(II) films

4.1. Formation of an alkaline environment

When lead is anodized in sulfuric acid solution, a semipermeable membrane of $PbSO_4$ is formed on the surface by:

$$Pb + SO_4^{2-} = PbSO_4 + 2e^- \qquad (4)$$

The membrane allows H^+, OH^- and H_2O to transfer through the $PbSO_4$ layer, but not Pb^{2+} or SO_4^2. Thus, the consumption of SO_4^{2-} ions in reaction (4) should be compensated by OH^- ions by virtue of the principle of electroneutrality, and the pH value at the inside of the membrane rises for the formation of $PbSO_4$ through reaction (4) [35].

Our experiments were carried out in 4.5 M H_2SO_4 solution at 25°C, so the equilibrium potential (E) for $Pb/PbSO_4/4.5$ M H_2SO_4 should be:

$$E = -0.956 - 0.0296\log a_{SO_4^{2-}} + E_m \qquad (5)$$

where E is in volts vs. a Hg/Hg_2SO_4, 4.5 M H_2SO_4 reference electrode at 25°C. E_m is the membrane potential of $PbSO_4$,

$$E_m = 0.0592(pH_i - pH_o) \qquad (6)$$

where pH_i and pH_o are the pH values inside and outside the membrane, respectively. When the following two reactions reach equilibrium

$$2PbSO_4 + H_2O = PbO \cdot PbSO_4 + 2H^+ + SO_4^{2-}$$

$$K = 2.82 \times 10^{-16} \qquad (7)$$

$$2Pb^{2+} + SO_4^{2-} + H_2O = PbO \cdot PbSO_4 + 2H^+$$

$$K = 1.60 \times 10^{-2} \qquad (8)$$

the pH_i and $a_{SO_4^{2-}}$ are 6.04 and 3.75×10^{-4}, respectively, and the pH_o in the bulk solution is -0.52, so E is -0.47 V.

4.2. Growth of basic lead sulfates and lead oxide in anodic film and source of SO_4^{2-} ions

4.2.1. Growth of $PbO \cdot PbSO_4$ film

For reactions (7) and (8) in the film, if the pH_i value is more than 6.04, the reactions will favour the growth of a $PbO \cdot PbSO_4$ film. The $PbSO_4$ film will become thinner with the growth of the $PbO \cdot PbSO_4$ film and the semipermeable properties of the $PbSO_4$ film vanish somewhat, which may favour thickening of the thinner $PbSO_4$ film through reaction (4) to the previous thickness. Our group has proved that the thickness of the $PbSO_4$ film will be almost constant when the anodic Pb(II) film grows to a certain degree [23]. In reaction (7), the consumption of 1 mol $PbSO_4$ produces 1 mol H^+, and in reaction (4) the consumption of 2 mol H^+ forms 1 mol $PbSO_4$. Thus, the value of pH in the film will be increased by the growth of a $PbO \cdot PbSO_4$ film.

$PbO \cdot PbSO_4$ can also be formed as follows:

$$2Pb + H_2O + SO_4^{2-} = PbO \cdot PbSO_4 + 2H^+ + 4e^- \qquad (9)$$

and the equilibrium potential of $PbO \cdot PbSO_4$ covered with $PbSO_4$ film should be

$$E = -0.713 - 0.0296pH_i - 0.0148\log a_{SO_4^{2-}} + E_m \qquad (10)$$

Using the equilibrium constant of Eq. (7), we can obtain $E = -0.45$ V. If the potential is more positive than -0.45 V, a $PbO \cdot PbSO_4$ film will develop as described by Eq. (9) and can be inferred that 4 mol of OH^- ions would migrate into the film to form 1 mol $PbO \cdot PbSO_4$, which increases the pH in the film.

In brief, to maintain electrical neutrality during the consumption of SO_4^{2-} or the formation of Pb^{2+} inside the semipermeable membrane, an equal equivalent amount of OH^- increases, with increase of pH value in the film. The formation of other basic lead sulfates inside the semipermeable film of $PbSO_4$ will also improve the alkalization of the film.

4.2.2. The growth of $3PbO \cdot PbSO_4 \cdot H_2O$ film

The following equilibrium may exist in the film,

$$2PbO \cdot PbSO_4 + 2H_2O$$

$$= 3PbO \cdot PbSO_4 \cdot H_2O + SO_4^{2-} + 2H^+$$

$$K = 3.72 \times 10^{-19} \quad (11)$$

$$4Pb^{2+} + SO_4^{2-} + 4H_2O = 3PbO \cdot PbSO_4 \cdot H_2O + 6H^+$$

$$K = 9.51 \times 10^{-23} \quad (12)$$

When $pH > 7.13$, reactions (11) and (12) will shift to the right and a $3PbO \cdot PbSO_4 \cdot H_2O$ film will develop.

The equilibrium potential, E, of the film of $3PbO \cdot PbSO_4 \cdot H_2O$ covered by $PbSO_4$ on lead could be:

$$4Pb + SO_4^{2-} + 4H_2O = 3PbO \cdot PbSO_4$$

$$\cdot H_2O + 8e^- + 6H^+ \quad (13)$$

$$E = -0.570 - 0.044pH_i - 0.0074\log a_{SO_4^{2-}} + E_m \quad (14)$$

Using the equilibrium constant of Eq. (11), E is calculated as -0.40 V.

4.2.3. Growth of α-PbO film

The following three reactions may exist in the film

$$H^+ + HPbO_2^- = \alpha\text{-}PbO + H_2O \quad K = 2.24 \times 10^{15} \quad (15)$$

$$Pb^{2+} + H_2O = \alpha\text{-}PbO + 2H^+ \quad K = 2.26 \times 10^{-13} \quad (16)$$

$$3PbO \cdot PbSO_4 \cdot H_2O = 4\alpha\text{–}PbO + SO_4^{2-} + 2H^+$$

$$K = 2.75 \times 10^{-29} \quad (17)$$

When $pH > 8.98$, it will favour the growth of α-PbO by Eqs. (15)–(17). The α-PbO film may be formed by the anodic reaction,

$$Pb + H_2O = \alpha\text{-}PbO + 2H^+ + 2e^- \quad (18)$$

and the equilibrium potential of an α-PbO film covered by a $PbSO_4$ film on lead should be as follows:

$$E = -0.352 - 0.0592pH_i + E_m \quad (19)$$

$$E = -0.352 - 0.0592pH_o$$

$$E = -0.32 \text{ V}$$

Since SO_4^{2-} does not participate in Eq. (18), it seems that the reaction will not effect the pH value. The semipermeability of the $PbSO_4$ film is, however, not perfect and the sum of the transference numbers of H^+ and OH^- is less than unity. Thus, the pH value in the film will decrease accordingly. In order to maintain the pH value, basic lead sulfates continue to grow even after the formation of PbO begins.

4.2.4. Growth of PbO_x ($1 < x < 2$)

The equilibrium potential of Pb/α-PbO/α-PbO_2/$PbSO_4$ can be shown as:

$$\alpha\text{-}PbO + H_2O = \alpha\text{-}PbO_2 + 2H^+ + 2e^- \quad (20)$$

$$E = 0.507 - 0.0592pH_i + E_m$$

$$= 0.0507 - 0.0592pH_o = 0.54 \quad (21)$$

When the potential is more positive than 0.54 V, α-PbO_2 may grow by Eq. (20). α-PbO can also grow by Eq. (18), but there is no evidence of the formation of the α-PbO_2 phase when lead is anodized at 0.9 V. This suggests that Eqs. (18) and (20) take place at the Pb/PbO interface. The result of reactions (18) and (20) is the formation of PbO_x ($1 < x < 2$). The value of x is closer to 2 if the potential is higher. When the potential is even higher, viz., 1.3 V, transformation to β-PbO_2 takes place, i.e.,

$$PbSO_4 + 2H_2O = \beta\text{-}PbO_2 + 4H^+ + 2e^- \quad (22)$$

4.3. Position of charge transfer in anodic film during anodization

The electrochemical potential ($\bar{\mu}_i$) of species i in the film is the same everywhere and the net current is zero when the anodic film is in the state of equilibrium. At equilibrium, although the concentrations of ions in the phases in the film differ, there is no diffusion of H^+ ions and other ions because of the effect of the electric field in the film. If an applied potential causes the anodic film to grow, a gradient of the $\bar{\mu}_i$ of the relevant ions will be produced in the film, as well as the ion current formed by them. For example, in the film where Eq. (18) proceeds, the $\bar{\mu}_{H^+}$ should be higher than that in other places and a H^+-ion current should be formed. If the reaction given by Eq. (18) occurs at the Pb/PbO interface, then the ion current should decrease because the $\bar{\mu}_{H^+}$ gradient is reduced with increase in the thickness of the PbO film. Thus, there should be a linear relationship between i and $t^{-1/2}$. If the charge transfer of Eq. (18) takes place at other interfaces, such as the interface between α-PbO and basic lead sulfate, Eq. (18) may proceed as:

$$H_2O = 2H^+ + O_{ad} + 2e^- \quad (23a)$$

$$O_{ad} \xrightarrow{\text{PbO film}} \text{O (lead metal surface)} \quad (23b)$$

$$\text{O (lead metal surface)} + \text{Pb (lead metal surface)} = \text{PbO} \quad (23c)$$

Reaction (23) is controlled by oxygen diffusion. Hence, there is also a linear relationship between i and $t^{-1/2}$. There should be a gradient of oxygen concentration in the PbO film according to this oxygen-diffusion mechanism. We have analyzed the element depth distribution in the anodic film by Auger electron spectroscopy (AES) [36], but the existence of an oxygen concentration gradient in the film has not been confirmed. The diffusion coefficient of oxygen is very small in the PbO crystal (D/cm^2 s^{-1} = $5.4 \times 10^{-5} \exp(-0.93\ \text{eV}/RT)$ at 500–650°C) [37], e.g., $D = 4.7 \times 10^{-11}$ cm^2 s^{-1} at 500°C. Thus, at room temperature, the rate of growth of the PbO film, which is controlled by oxygen diffusion, is very small; the mechanism of reaction (23) for the growth of PbO film may not be true.

Zhai [38] studied the reduction of the PbO film formed at 0.6 V (vs. Hg/Hg_2SO_4, 35% H_2SO_4) in 35% H_2SO_4 for 10 h, using X-ray photoelectron spectroscopy (XPS) and Ar^+-ion corrosion depth analysis at a reduction potential of -0.7 V. The results indicated that the reduction of PbO proceeded at the interface of the Pb/PbO film.

If the electronic current resistance in the PbO film is larger than the ion current resistance then reaction (18) at the interface of Pb/PbO would be more possible. The PbO film consists of PbO particles, and the interstitial liquid film between the particles in the PbO layer may provide the major passages for ion transportation. Hence, the resistivity of the anodic film may be much smaller than that of the PbO crystal. Zhai et al. [39], found that the resistance of the anodic film is 5×10^2 Ω for Pb anodized at 0.6 V (vs. Hg/Hg_2SO_4, 35% H_2SO_4) in 35% H_2SO_4 for 20 min. This low value of the resistance is obviously due to the migration of ions in the interstitial liquid film.

5. Effect of antimony on growth of anodic Pb(II) oxide film

The addition of antimony to the positive grid alloy can increase the deep-discharge life-cycle of lead–acid batteries, but the mechanism has still to be clarified [30]. Using a.c. impedance [31] and photocurrent methods [29], we have studied the growth rate and semiconductor properties of the anodic Pb(II) oxide film formed on Pb–Sb alloy in sulfuric acid solution. The film is found to be an n-type semiconductor. The donor density of the anodic film formed on Pb–Sb alloy is more than that of the film formed on lead metal, and increases with antimony content. The growth rate of the former film, however, is less than that of the latter, and decreases with antimony content. It is possible that in the Pb(II) oxide lattice Sb^{3+} replaces Pb^{2+}, and the density of free-electrons increases accordingly. According to Hauffe's valency rules [40], for a metal oxide n-type semiconductor, if the valency of the additive metal in an alloy is higher than that of the basic metal, then the free-electron density will increase, but the density of lattice defects (i.e., oxygen anion vacancies in the present case) will decrease. Thus, the rate of diffusion of oxygen anions in the anodic film via oxygen vacancies will also decrease, and so will the growth rate of the anodic film according to the oxygen diffusion mechanism. If, however, the additive element in the alloy is arsenic or bismuth, which are Group V elements of the Periodic table like antimony, the growth rate of the anodic Pb(II) oxide film is close to that formed on lead metal and there is no conformation with the Hauffe's rules, especially when the additive content is rather high [36,41–43].

It is difficult to explain the effects of Group V elements on the growth of the anodic Pb(II) oxide film using the conventional oxygen-diffusion mechanism [44–46]. This is due to the following two reasons. First, the charge-transfer position would occur at the interface of Pb and the Pb(II) oxide film, and not at the interface of the Pb(II) oxide and the $PbSO_4$ film. This is confirmed by a comparison between the electronic current resistance and the ionic current resistance during growth of the anodic Pb(II) oxide film. Second, the diffusion coefficient of oxygen in the Pb(II) oxide crystal is so small that it cannot maintain the proper growth rate of the anodic film. Moreover, the oxygen concentration gradients in the anodic film on lead have not been observed in our analysis of the element depth distribution in the anodic film by the AES method. Thus, in the charge-transfer step for the growth of anodic film, the ion current in the Pb(II) oxide film mainly flows through the interstitial liquid film among the particles. It is quite obvious that the formation or the consumption of ions in the charge-transfer step will result in a concentration gradient in the film. Hence, the relationship between current density and time has the characteristics of a diffusion process.

Studies on the growth rate of the anodic Pb(II) oxide film formed on Pb–Sn, Pb–As, Pb–Sb, Pb–Bi, Pb–Cd and Pb–Cu binary alloys reveal that only the addition of tin or antimony hinders the growth of the film [47,48]. Table 2 lists the concentrations of various oxygen-containing complex anions in equilibrium with their relevant oxides at pH = 9 and 25°C [45,49–54]. It is assumed that the charge-transfer step takes place on the substrate surface where the pH value is about 9.

From the comparison of the concentrations of various anions in Table 2, an explanation can be obtained of the effects of alloy additives in inhibiting the growth of the anodic Pb(II) oxide film.

Three cases are discussed as follows.

(1) The saturated solubility values of the oxygen-containing complex anions of the additives in the alloys are close to that of $PbOOH^-$.

Table 2
Concentrations of various oxygen-containing complex anions in equilibrium with their relevant oxides at pH 9 and 25°C

Oxide	Ion	
	Species	Concentration/M
ortho-Sb_2O_3	SbO_2^-	6.6×10^{-6}
As_2O_3	AsO_2^-	0.13
Bi_2O_3	–	–
$Sn(OH)_2$	$SnOOH^-$	4.2×10^{-6}
$Cd(OH)_2$	$CdOOH^-$	1.1×10^{-10}
$Cu(OH)_2$	$CuOOH^-$	2.4×10^{-9}
PbO	$PbOOH^-$	4.3×10^{-7}

For example, the saturated solubility of SbO_2^- and $SnOOH^-$ is nearly the same as that of $PbOOH^-$ (Table 2). When Pb–Sb or Pb–Sn alloy is anodized, oxygen-containing complex anions are produced. In the case of antimony, for example, the following reactions take place [55]:

$$Sb + H_2O = SbOH_{ads} + H^+ + e^- \quad (24a)$$

$$SbOH_{ads} = SbO_{ads} + H^+ + e^- \quad (24b)$$

$$SbO_{ads} + H_2O = HSbO_2 + H^+ + e^- \quad (24c)$$

$$HSbO_2 = SbO_2^- + H^+ \quad (24d)$$

After the concentrations of the oxygen-containing complex anions formed during anodization reach over-saturation, co-precipitation takes place on the surface of the substrate. The active surface of the substrate will be passivated, or the ion of the relevant additive metal will occupy the lattice of Pb(II) oxide and change the semiconductor properties of the anodic film. Accordingly, the growth of the anodic Pb(II) oxide film will be retarded.

(2) The saturated solubility values of the oxygen-containing complex anions of the additives for the alloys are much greater than that of $PbOOH^-$.

AsO_2^- is a good example. The concentration of AsO_2^- is much larger than that of $PbOOH^-$. Using AES to analyze the element depth distribution of the anodic Pb(II) oxide film formed on Pb–6 at.% As alloy, it is found [36] that the concentration of As in the outer layer is 12 at.%, i.e., much higher than that in the substrate. For the anodic Pb(II) oxide film formed on Pb–3 at.% Sb alloy, however, the distribution of antimony in the film is homogeneous and is similar to that in the substrate [56].

The concentration of AsO_2^- in equilibrium with As_2O_3 increases with pH. The pH in the inner layer of the anodic film is higher than that in the outer layer, and AsO_2^- in the inner layer diffuses to the outer layer, thus As_2O_3 will be precipitated. It is impossible for arsenic to assist co-precipitation at the substrate surface. Thus, addition of arsenic will not inhibit the growth of the anodic Pb(II) oxide film.

(3) Saturated solubility values of the oxygen-containing complex anions of the additives for the alloys are much less than that of PbOOH.

In this case, the precipitation of the oxide of the additive on the surface of the substrate occurs earlier than that of Pb(II) oxides, hence, co-precipitation is difficult. Retardation of the growth of the anodic Pb(II) film, as in the case 1, cannot occur. The existence of oxygen-containing anions of Bi has not been reported; the saturated solubility of $Bi(OH)_3$ in concentrated NaOH is merely 10^{-4} M [57]. Thus, the concentration of Bi(III) is too low to co-precipitate with Pb(II) at $pH = 9$. The addition of bismuth will not inhibit the growth of the anodic Pb(II) oxide film.

Using a photocurrent method, we studied the relationship between anodizing time and the quantum yield of the anodic Pb(II) oxide film formed on Pb, Pb–3 at.% As, Pb–3 at.% Sb, Pb–3 at.% Bi in 4.5 M H_2SO_4 solution at 0.6 V within 36 h [48]. The quantum yields of β-PbO and α-PbO can be obtained from analysis of the total quantum yield [23,35]. The induction period, t_0, of the growth of β-PbO and α-PbO can be obtained by extrapolation of the linear relationship between the quantum yield and the square root of time. The data (Table 3) show that the addition of antimony to the lead alloy decreases the induction period of β-PbO. This shows that the crystal of Sb_2O_3 in co-precipitation is orthorhombic, and acts as a crystal nucleus.

Owing to the overlap of the main characteristic line observed by XRD for *o*-Sb_2O_3 and α-PbO, it is very difficult to use XRD to determine the amount of Sb_2O_3 in the anodic Pb(II) film formed in H_2SO_4 solution. Using XRD, it is found that the crystal form of Sb_2O_3 produced on Pb–3 at.% Sb in 0.1 M NaOH solution is orthorhombic [58], i.e., the same as that produced on antimony in a solution with $pH = 1.5$ [56].

The crystal of As_2O_3 in the anodic Pb(II) film formed on Pb–6 at.% As is amorphous [36], and the crystal of Bi_2O_3 in the anodic Pb(II) formed on Pb–9 at.% Bi is not orthorhombic, but monoclinic or tetragonal [43]. Thus, As_2O_3 and Bi_2O_3 cannot contribute to the nucleation of β-PbO.

The growth of basic lead sulfate in the film does not cease even when the electrode is anodized for a rather long time. For example, the growth rate of basic lead sulfate in the anodic Pb(II) film does not decrease significantly when lead is anodized at 0.9 V for 4 h [23]. The growth of basic lead sulfate will consume SO_4^{2-} which will increase the pH of solution. If the pH exceeds 12, it will favour the growth of α-PbO, instead of β-PbO [26]. The XRD results show that only α-PbO exists in the anodic Pb(II) oxide film formed on lead in 0.1 M NaOH solution, β-PbO is not detected [58]. Both α-PbO and β-PbO exist in the anodic film formed on Pb–3 at.% Sb, the possible explanation is that the crystal of Sb_2O_3 in the anodic film is also orthorhombic.

The growth of β-PbO ceases when Pb, Pb–3 at.% As and Pb–3 at.% Bi are anodized for 9, 7 and 16 h, respectively, while the growth of β-PbO in the anodic film formed on Pb–3 at.% Sb continues for at least 36 h. The growth of β-PbO in the latter case may be assisted by the contribution of *o*-Sb_2O_3.

The saturated solubility values of As_2O_3 and Bi_2O_3 in acid solution are larger than that of Sb_2O_3; Bi_2O_3 has the greatest value [49–51]. It has been observed [32] that Bi_2O_3 is contained in the $PbSO_4$ film in the outer layer of

Table 3
Induction period (min) for the growth of β-PbO and α-PbO in anodic Pb(II) films

	Pb	Pb–3 at.% As	Pb–3 at.% Sb	Pb–3 at.% Bi
β-PbO	3	16	< 1	12
α-PbO	8	21	8	24

the anodic Pb(II) film formed on Pb–9 at.% Bi alloy in acid media [32]. Using scanning electron microscopy (SEM), it is also found that the semipermeability of the $PbSO_4$ film is not good and it therefore takes longer to increase the pH in the inner layer which delays the growth of PbO, as shown in Table 3.

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