

Resistance of the anodic PbO film formed in sulfuric acid solution

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The resistance of the anodic PbO film formed on lead at 0.9 V (vs. Hg/Hg₂SO₄) in 4.5 mol/dm³ H₂SO₄ was measured using alternating-current impedance method. The resistance of the anodic PbO film was found to be close to that of the interstitial liquid among the PbO particles in the film, suggesting that the interstitial liquid may serve as the major passage for ion transportation during the film growth.

Keywords Anodic PbO film, interstitial liquid, ac impedance

Introduction

The passivation of the positive grid using low antimony or antimony-free alloys is still one of the main reasons leading to the low charge acceptance, premature capacity loss and poor cycling life at deep charging/discharging cycles for maintenance-free lead/acid batteries. The passivation results from the poor conductance of lead monoxide (PbO) formed on the grid surface.¹ During the growth of the anodic Pb(II) film, the semipermeable PbSO₄ film is first formed. So the diffusion of SO₄²⁻ and Pb²⁺ ions through the PbSO₄ film is hindered, and only the diffusion of H⁺, OH⁻ and H₂O is allowed.² The selective migration of ions leads to a high pH of the solution in the anodic film, and the pH value of the solution in the anodic PbO film even reaches 9.³ The growth of the anodic PbO film has two possible mechanisms. One is a dissolution-precipitation process, the other is a solid-state process.⁴ In the solid-state process the growth of the anodic PbO film is controlled by the diffusion of oxygen through the anodic PbO film,⁵ but there are some experimental results which do not support this mecha-

nism. The diffusion coefficient of oxygen in the PbO crystal, for example, is very small, which is only 5×10^{-11} cm²/s at 500°C,⁶ and will be much smaller at room temperature. Therefore, the growth rate would be extremely small according to the solid-state mechanism. The Auger depth profiles of the different elements in the anodic film have been measured by our research group, and the oxygen concentration gradient is not found in the anodic PbO film.⁷ For an anodic PbO film, if the resistance of the solid phase (PbO particles) is much smaller than that of the liquid phase (interstitial solution among PbO particles), the film may grow via the solid-state process. Otherwise, the interstitial liquid among the PbO particles in the film may serve as the major passage for ion transportation during the film growth, and the film may grow via the dissolution-precipitation process. Hence, it is useful to study the resistance of the anodic PbO film for elucidating its growth mechanism. Recently our research group has obtained the thickness of the anodic PbO film from the photocurrent measurement.⁸ This makes us able to clarify the cause of the resistance of the anodic PbO film: whether it is mainly due to the resistance of the solid phase or the resistance of the liquid phase, which will be discussed in the present work.

Experimental

A section of lead (99.999%) rod, sealed with epoxy resin at lower part of an L-shaped glass tube and exposing a circular area of 0.234 cm² to the electrolyte, was used as the working electrode. A Pt plate served as

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the counter electrode. The reference electrode was the Hg/Hg₂SO₄ electrode containing the same electrolyte as that in the electrochemical cell. The electrolyte was a 4.5 mol/dm³ H₂SO₄ solution prepared from AR grade sulfuric acid and distilled water. All potentials reported here are referred to the Hg/Hg₂SO₄ reference electrode.

The surface of the lead electrode was mechanically polished with emery paper of successively decreasing grain size down to about 10 μm. The electrode was then rinsed with distilled water, and placed into the cell. Before anodizing, a cathodic polarization at -1.2 V for 20 min was performed to remove any oxidation products formed during the pretreatment. The anodic film studied in the present work was grown on the working electrodes in 4.5 mol/dm³ H₂SO₄ solution at 0.9 V, the potential near that of the positive grid of lead/acid batteries at deep-discharge.

The ac impedance measurements were carried out using a potentiostat/galvanostat (EG&G PARC 273), a two-phase lock-in analyzer (EG&G PARC 5208), and an ac impedance software (EG&G PARC 378). The amplitude of the ac signal was 5 mV. The frequency range was between 1 × 10³ Hz and 1 × 10⁵ Hz. The electrochemical impedance spectra were analyzed using an EG&G PARC EQUIVCRT impedance modelling software.

The chronoamperometry was carried out using the

EG&G PARC 273 potentiostat/galvanostat controlled by an EG&G PARC 270 software.

All experiments were carried out at 25 ± 1 °C.

Results and discussion

Impedance measurements

When the potential of the anodic oxidation for lead in sulfuric acid solution is in the PbO potential region (-0.40 V—0.95 V),⁹ a complex composition of the anodic film on the lead electrode will be obtained, *i. e.*, PbO/3PbO·PbSO₄·H₂O/PbO·PbSO₄/PbSO₄, with PbO, PbO·PbSO₄, and PbSO₄ as the major components.^{8,10}

The equivalent circuit for analysis of the impedance data is shown in Fig. 1, where *R*1 stands for the resistance of the electrolyte, *R*2 and *C*3 are the resistance and capacitance of the anodic film containing PbSO₄ and PbO·PbSO₄ respectively, *R*5 and *C*4 are the resistance and capacitance of the anodic PbO film respectively, *R*6 stands for the polarization resistance, and *C*7 is the capacitance of the double layer. In this equivalent circuit the resistance and capacitance of the anodic PbO film are separated from those of the other components of the anodic film.

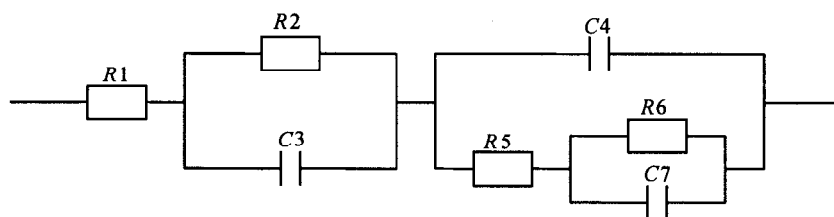


Fig. 1 Equivalent circuit of the anodic film.

The Nyquist plots for the anodic film are depicted in Fig 2. It can be found that the simulated plots fit the experimental plots well.

Table 1 lists the parameters in the equivalent circuit.

Table 1 *R*1, *R*2, *C*3, *C*4, *R*5, *R*6, and *C*7 versus anodizing time

Anodizing time (h)	<i>R</i> 1 (Ω·cm ²)	<i>R</i> 2 (Ω·cm ²)	<i>C</i> 3 (μF/cm ²)	<i>C</i> 4 (μF/cm ²)	<i>R</i> 5 (Ω·cm ²)	<i>R</i> 6 (Ω·cm ²)	<i>C</i> 7 (μF/cm ²)
1	1.5	38	1.1	0.30	34	1.3 × 10 ³	0.26
2	3.3	80	0.52	0.17	61	2.1 × 10 ³	0.17
3	4.5	122	0.38	0.12	95	2.7 × 10 ³	0.14
4	5.2	153	0.31	0.099	110	3.1 × 10 ³	0.12

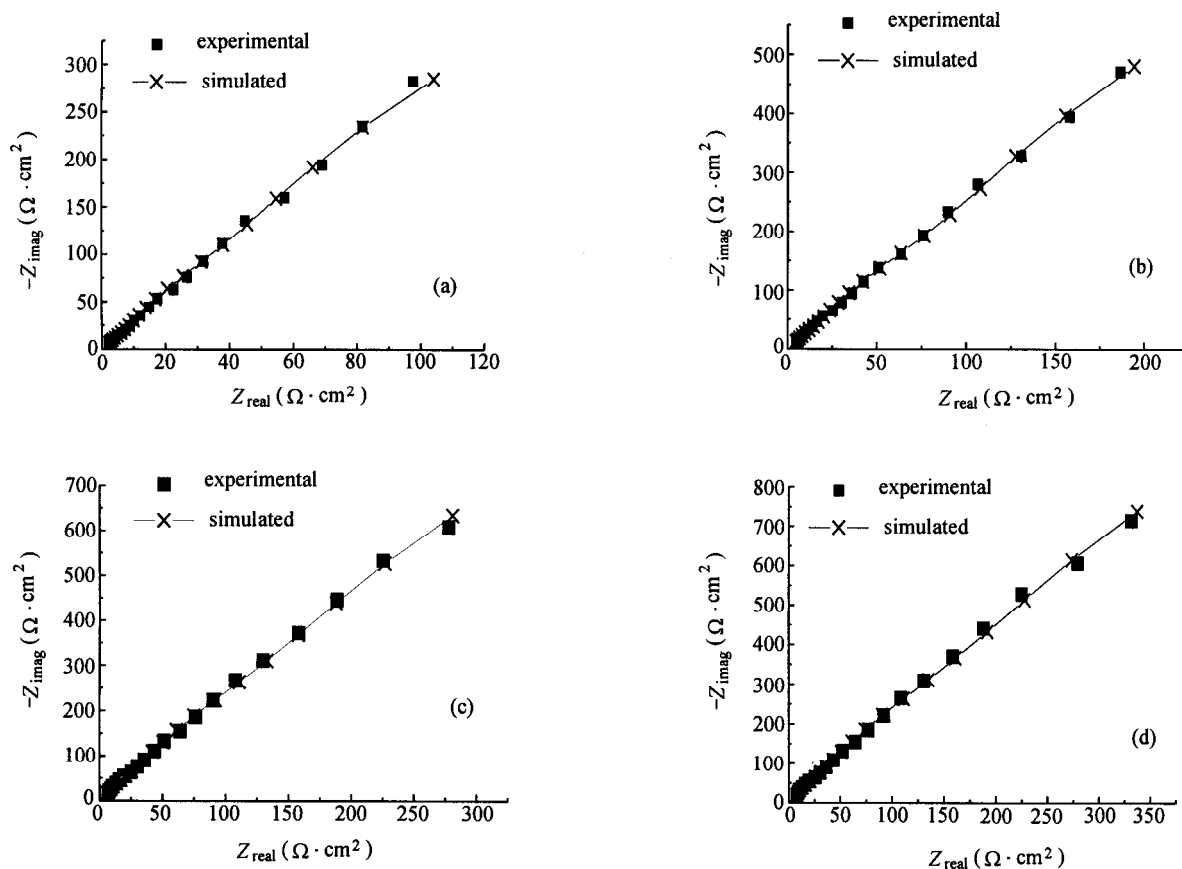


Fig. 2 Nyquist plots for the anodic films formed on lead at 0.9 V in 4.5 mol/dm³ H₂SO₄ for different growth time at 25°C: (a) 1 h, (b) 2 h, (c) 3 h, (d) 4 h.

Interstitial solution resistance in PbO film

The resistance of the interstitial solution among the PbO particles in the anodic PbO film (R_i) may be calculated from Eq. (1),¹¹

$$R_i = \rho \times \beta^2 \times d/P \quad (1)$$

where ρ is the specific resistance of the interstitial solution, β and P are the tortuosity factor and porosity of the anodic PbO film respectively, and d is the thickness of the anodic PbO film, which has been obtained from the photocurrent measurements and listed in Table 2.⁸ The concentrations of H⁺, OH⁻, Pb²⁺, and SO₄²⁻ (C_{H^+} , C_{OH^-} , $C_{Pb^{2+}}$, and $C_{SO_4^{2-}}$) in the interstitial solution in the anodic PbO film are 1×10^{-9} , 1×10^{-5} , 5.0×10^{-6} , and 6.3×10^{-12} mol/dm³,³ respectively. C_{H^+} and $C_{SO_4^{2-}}$ may be neglected owing to their much smaller values. The limiting molar conductivities of 1/2 Pb²⁺ and OH⁻

are 70 and 197.6 cm²/(Ω·mol) at 25°C, respectively.¹² Hence ρ can be calculated as follows:

$$\rho_{OH^-} = (1 \times 10^{-8} \times 197.6)^{-1} = 5.06 \times 10^5 \quad (\Omega \cdot \text{cm})$$

$$\rho_{Pb^{2+}} = (1.0 \times 10^{-9} \times 70)^{-1} = 1.43 \times 10^6 \quad (\Omega \cdot \text{cm})$$

$$1/\rho = 1/\rho_{OH^-} + 1/\rho_{Pb^{2+}}$$

Thus, $\rho = 3.74 \times 10^5 \quad (\Omega \cdot \text{cm})$.

We assume that the anodic PbO film is composed of the closest packing of the PbO particles, so P and β are taken to be 26% and $\sqrt{2}$ respectively.¹³ Thus, the values of R_i can be obtained through Eq. (1), being very close to those of R_5 as shown in Table 2.

Moreover, C_4 may be calculated from Eq. (2),

$$C_4 = \epsilon_0 \times [\epsilon_{PbO} \times (1 - P) + \epsilon_{H_2O} \times P] / d \quad (2)$$

Table 2 R_5 , R_i , R_{PbO} , C_4 and d versus anodizing time

Anodizing time (h)	R_5 ($\Omega \cdot \text{cm}^2$)	R_i ($\Omega \cdot \text{cm}^2$)	R_{PbO} ($\Omega \cdot \text{cm}^2$)	C_4 ($\mu\text{F}/\text{cm}^2$)		d (μm) ⁸
				Exp.	Calcd. from Eq. (2)	
1	34	32	1.03×10^5	0.30	0.34	0.103
2	61	58	1.85×10^5	0.17	0.19	0.185
3	95	91	2.82×10^5	0.12	0.12	0.282
4	110	105	3.73×10^5	0.099	0.094	0.373

with the same values of P and d as used above, where $\epsilon_0 = 8.854 \times 10^{-14}$ (F/cm) is the permittivity of vacuum, $\epsilon_{PbO} = 26$ and $\epsilon_{H_2O} = 78$ are the dielectric constants of PbO and H₂O, respectively.¹⁴ The values of the calculated C_4 are also very close to those of the experimental C_4 as shown in Table 2. This indicates that the values of P and d used here are reasonable, and the conductance due to the liquid phase cannot be neglected.

If the resistance of the anodic PbO film is mainly due to the PbO crystals, the resistance of the anodic PbO film (R_{PbO}) may be calculated by adopting the specific resistance of the PbO crystal to be $1.0 \times 10^{10} \Omega \cdot \text{cm}$,^{15,16} see Table 2. Since R_{PbO} is much larger than R_5 , as shown in Table 2, we can infer that the smaller values of R_5 can be only attributed to the interstitial solution among the PbO particles in the film, which may serve as the major passage for ion transportation during the film growth.

Verification of the equivalent circuit

(1) Estimation of the interstitial solution resistance in PbO·PbSO₄ film

The resistance of the interstitial solution among the PbO·PbSO₄ particles in the anodic film (R_j) could also be estimated by Eq. (1), where ρ is the specific resistance of the interstitial solution, β and P are the tortuosity factor and porosity of the PbO·PbSO₄ film, respectively, and d is the thickness of the PbO·PbSO₄ film. The concentrations of ions in the interstitial solution in the PbO·PbSO₄ film are assumed to be close to those at the interface of $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}/\text{PbO} \cdot \text{PbSO}_4$ (*vide infra*). So C_{H^+} , C_{OH^-} , $C_{Pb^{2+}}$, and $C_{SO_4^{2-}}$ in the interstitial solution are 4.47×10^{-8} , 2.24×10^{-7} , 3.16×10^{-5} , and 3.16×10^{-5} mol/dm³, respectively.³ C_{H^+} and C_{OH^-} may be neglected owing to their much smaller val-

ues. The limiting molar conductivities of $1/2 \text{Pb}^{2+}$ and $1/2\text{SO}_4^{2-}$ are 70 and 80 cm²/($\Omega \cdot \text{mol}$) at 25°C, respectively.¹² Hence ρ can be calculated as follows:

$$\rho_{Pb^{2+}} = (6.32 \times 10^{-8} \times 70)^{-1} = 2.26 \times 10^5 \text{ } (\Omega \cdot \text{cm})$$

$$\rho_{SO_4^{2-}} = (6.32 \times 10^{-8} \times 80)^{-1} = 1.98 \times 10^5 \text{ } (\Omega \cdot \text{cm})$$

$$1/\rho = 1/\rho_{Pb^{2+}} + 1/\rho_{SO_4^{2-}}$$

$$\text{Thus, } \rho = 1.05 \times 10^5 \text{ } \Omega \cdot \text{cm}.$$

We also assume that the anodic PbO·PbSO₄ film is composed of the closest packing of the PbO·PbSO₄ particles, so P and β are also taken to be 26% and $\sqrt{2}$, respectively.¹³ The electric charge required to form PbO·PbSO₄ ($Q_{PbO \cdot PbSO_4}$) has been obtained by our research group.⁸ It comes from Eq. (3),⁸

$$Q_{PbO \cdot PbSO_4} = Q - Q_{PbSO_4} - Q_{PbO} - Q_S \quad (3)$$

where Q is the total electric charge consumed at the Pb electrode during the growth of the anodic film, Q_{PbSO_4} is the electric charge required to reduce the PbSO₄ film, Q_{PbO} is the electric charge required to form the PbO film and is calculated using the thickness of the PbO film and its molar volume. The thickness d is shown in Table 2. Q_S is the electric charge corresponding to the Pb(II) species dissolved in the bulk solution from the film. However, the porosity of the anodic PbO film ($P = 26\%$) has not been considered in the literature⁸ for calculating the Q_{PbO} . So $Q_{PbO \cdot PbSO_4}$ is corrected with Eq. (4) and the corrected $Q_{PbO \cdot PbSO_4}$ ($Q_{PbO \cdot PbSO_4(c)}$) is thus obtained,

$$Q_{PbO \cdot PbSO_4(c)} = Q_{PbO} \times 0.26 + Q_{PbO \cdot PbSO_4} \quad (4)$$

where both Q_{PbO} and $Q_{PbO \cdot PbSO_4}$ come from the literature⁸.

The thickness of the $\text{PbO} \cdot \text{PbSO}_4$ film (d) can be obtained from the $Q_{\text{PbO} \cdot \text{PbSO}_4(c)}$, the molar volume of $\text{PbO} \cdot \text{PbSO}_4$, $V_m = 76.1 \text{ cm}^3$,¹⁷ and its porosity $P = 26\%$. $Q_{\text{PbO} \cdot \text{PbSO}_4}$, $Q_{\text{PbO} \cdot \text{PbSO}_4(c)}$ and d are shown in Table 3.

The specific resistance of the interstitial solution in the PbSO_4 film is small for the large values of the concentrations of the ions in the PbSO_4 film, so the resistance of the PbSO_4 film can be neglected.

R_j is close to R_2 except at 1 h as shown in Table 3. This may be explained as follows. The values of the pH at the interfaces of $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O} / \text{PbO} \cdot \text{PbSO}_4$ and $\text{PbO} \cdot \text{PbSO}_4 / \text{PbSO}_4$ are 7.35 and 6.45, respectively,³ so concentration gradients of the ions are formed in the $\text{PbO} \cdot \text{PbSO}_4$ film. However, the consumed SO_4^{2-} ion

for the growth of the $\text{PbO} \cdot \text{PbSO}_4$ film could not be made up from the bulk solution owing to the semipermeable PbSO_4 film. Then an equivalent amount of OH^- ions, whose negative charges can substitute those of the diminished SO_4^{2-} ions in order to keep the electroneutrality, will be produced, and the pH value of the interstitial solution in the $\text{PbO} \cdot \text{PbSO}_4$ film will be increased accordingly. Thus, after a certain time of the anodic oxidation, the pH value in the $\text{PbO} \cdot \text{PbSO}_4$ film will be close to that at the interface of $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O} / \text{PbO} \cdot \text{PbSO}_4$, and so will be those of the relevant ions. Hence, the significant deviation of R_j from R_2 at 1 h may be due to the large concentration gradients of the ions in the $\text{PbO} \cdot \text{PbSO}_4$ film at this initial period.

The agreement of R_j and R_2 may show that the equivalent circuit is reasonable.

Table 3 Values of R_2 , R_j , $Q_{\text{PbO} \cdot \text{PbSO}_4}$, and d versus anodizing time

Anodizing time (h)	R_2 ($\Omega \cdot \text{cm}^2$)	R_j ($\Omega \cdot \text{cm}^2$)	$Q_{\text{PbO} \cdot \text{PbSO}_4}$ (mC/cm^2)	$Q_{\text{PbO} \cdot \text{PbSO}_4(c)}$ (mC/cm^2)	d (μm)
1	38	64	278	298	0.794
2	80	95	402	438	1.17
3	122	116	482	537	1.43
4	153	140	572	646	1.72

(2) Estimation of the polarization resistance (R_p)

Because the polarization is large enough, the value of the R_p may be estimated by Eq. (5),¹⁸

$$R_p = \frac{d\eta}{di} = \frac{b_a}{2.303i} = \frac{RT}{(1-\alpha)nF} \quad (5)$$

where $T = 298 \text{ K}$, $R = 8.314 \text{ J}/(\text{K} \cdot \text{mol})$, α is the cathodic transfer coefficient, $F = 9.65 \times 10^4 \text{ C}/\text{mol}$, and i is the current density as shown in Fig. 3.

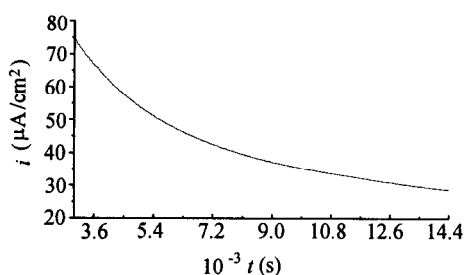


Fig. 3 Current-time plot for a lead electrode at 0.9 V in 4.5 mol/dm³ H₂SO₄ solution at 25°C.

For the electrode reaction $\text{Pb}^{2+} + 2e = \text{Pb}$, $n = 2$ and $\alpha = 0.85 \pm 0.05$ ¹⁹ ($\alpha = 0.85$ is taken here), the estimated i , R_p and R_6 are shown in Table 4. It can be seen that the values of the estimated R_p are quite close to those of the experimental R_6 . The agreement of R_p and R_6 also indicates that the equivalent circuit suggested in the present work is reasonable.

Table 4 R_p , R_6 and i vs. the growth time of the anodic film

Anodizing time (h)	i ($\mu\text{A}/\text{cm}^2$)	$10^3 R_p$ ($\Omega \cdot \text{cm}^2$)	$10^3 R_6$ ($\Omega \cdot \text{cm}^2$)
1	67	1.3	1.3
2	42	2.0	2.1
3	34	2.5	2.7
4	29	2.9	3.1

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