

Effects of Samarium on the Properties of the Anodic Pb(II) Oxides Film Formed on Pb in Sulfuric Acid Solution

LIU, Hou-Tian* (柳厚田) YANG, Chun-Xiao(杨春晓) ZHANG, Xin-Hua(张新华)
ZHOU, Yan-Bao(周彦葆) ZHOU, Wei-Fang(周伟妨)

Department of Chemistry, Fudan University, Shanghai 200433, China

The effects of samarium on the properties of the anodic Pb(II) oxides films formed on lead at 0.9 V (vs. Hg/Hg₂SO₄) in 4.5 mol/L H₂SO₄ solution were studied using linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS) and scanning electron micrographs (SEM). The experimental results show that adding Sm to lead metal can inhibit the growth of the Pb(II) oxides film effectively, and reduce the resistance of the PbO oxides film obviously. The addition of Sm increases the porosity of the anodic film, which may cause the increase of the ionic conductance produced by the interstitial liquid among the PbO particles in the film and lead to the decrease of the resistance of the anodic film.

Keywords lead, samarium, anodic Pb(II) oxides film

Introduction

Antimony-free Pb-Ca alloys have commonly been used in the manufacture of grids in order to minimize gassing in either low-maintenance or valve-regulated lead acid batteries. However, these alloys can cause other problems such as premature capacity loss, low charge-acceptance and poor deep charge-discharge cycle performance.^{1,2} These problems are associated with the poor conductance of t-PbO layer formed on the grid surface for the antimony-free alloys.³⁻⁶ The formation of t-PbO is caused by the presence of a lead sulfate layer with a semi-permeable membrane and it increases the local pH at the grid/PbO interface to a value of close to 9.^{4,7-9}

Owing to the mentioned detrimental influences of the antimony-free Pb-Ca alloys, some metal elements, such as Sr or Li, whose electrode potential is close to or more

negative than that of calcium, have been added into lead metal or lead alloys to increase the hydrogen over-potential and improve the crystal grain structure of the alloys.¹⁰⁻¹²

Recently, we have discovered that Ce added to the Pb-Ca-Sn alloy can decrease the resistivity of the anodic Pb(II) oxides (PbO + PbO·PbSO₄) film remarkably, but inhibit the growth of the film only slightly.¹³

Samarium and cerium are of the same group of the rare earth elements, and samarium also has the value of the electrode potential close to that of calcium. Samarium has higher hardness and better mechanical performance than lead, calcium, strontium and lithium. However, it has not been reported that there is any lead alloy containing Sm to improve the performance of the grid materials for lead acid batteries.

In this work, the growth rate and the impedance behavior of the anodic Pb(II) oxides film formed on Pb-1.0 at. % Sm alloy at 0.9 V (vs. Hg/Hg₂SO₄) in H₂SO₄ (4.5 mol/L) solution were studied using linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS) and scanning electron microscope (SEM).

Experimental

A Pb rod and a Pb-1.0 at. % Sm alloy (Pb-Sm) rod were used as working electrodes. The alloy was prepared with lead (99.994%) and samarium (99.9%). The rods were sealed with epoxy resin in the lower part of an L-shaped glass tube, so that a cross sectional area of 0.3

* E-mail: htliu@fudan.edu.cn; Tel: +86-21-65643975; Fax: +86-21-65641740

Received October 8, 2001; revised January 14, 2002; accepted January 24, 2002.

Project supported by the National Natural Science Foundation of China (Nos. 29873013 and 20173013).

cm² was exposed in the electrolyte. A flat working-electrode surface was obtained by mechanical polishing with emery paper of successively decreasing grain size down to about 10 μm. The working electrode was then washed with double-distilled water before immersed in the electrolyte. Before experiment, the electrode was cathodically polarized at -1.2 V for 20 min in order to remove any oxidation products formed by aerial oxidation during preliminary treatment. The electrolyte was 4.5 mol/L H₂SO₄ solution prepared from A. R. H₂SO₄ and double-distilled water. A platinum plate served as a counter electrode. An Hg/Hg₂SO₄ electrode containing the same solution in the electrochemical cell was used as the reference electrode. All potentials reported here are referred to this electrode.

The LSV was performed using an EG&G PARC 273 Potentiostat-Galvanostat controlled by EG&G PARC Model 270 software. The working electrode was polarized at 0.9 V for 1–4 h, then the potential was swept from 0.9 V to -1.2 V at a rate of 1 mV/s.

The EIS was 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 388). The amplitude of the ac signal was 5 mV. The frequency was in the range of 1 × 10³–1 × 10⁵ Hz. The electrochemical impedance spectra were analyzed using an EG&G PARC EQUIVCRT impedance modeling software.

The scanning electron micrographs of the surfaces for the anodic films were obtained using XL30 D6716 scanning electron microscope.

All electrochemical measurements were performed at (25 ± 1) °C.

Results and discussion

LSV

The potentials of the Pb and Pb-Sm electrodes were kept at 0.9 V for 1, 2, 3 and 4 h separately and then swept in the negative direction to -1.2 V at a rate of 1 mV/s in H₂SO₄ (4.5 mol/L) solution.

The typical voltammograms obtained for Pb and Pb-Sm electrodes are shown in Fig. 1, where the peaks a correspond to the reduction of Pb(II) oxides to Pb and the peaks b correspond to the reduction of PbSO₄ to Pb. The reduction potentials of the peak a and the peak b for

Pb electrode are -0.91 V and -0.97 V, respectively, and those for Pb-Sm electrode are -0.90 V and -0.98 V, respectively. It can be found in Fig. 1 that the current of the peak a for Pb-Sm electrode is lower than that for Pb. This suggests that adding Sm can inhibit the growth of the anodic Pb(II) oxides film.

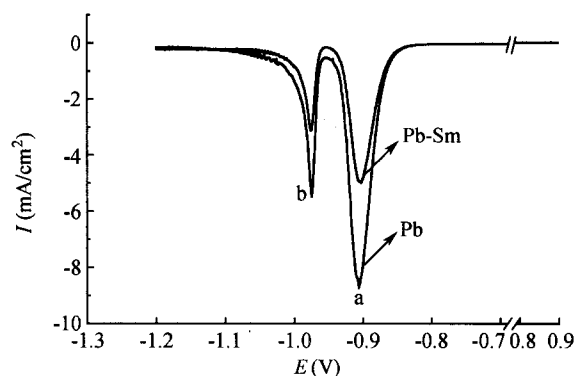


Fig. 1 Voltammograms for the anodic films formed on Pb and Pb-Sm at 0.9 V for 2 h in H₂SO₄ (4.5 mol/L), $\nu = 1$ mV/s, (a) reduction of Pb(II) oxides to Pb; (b) reduction of PbSO₄ to Pb.

Table 1 lists the reduction charges of peaks a and peaks b, $Q_{\text{Pb(II)/Pb}}$ and $Q_{\text{PbSO}_4/\text{Pb}}$, for Pb and Pb-Sm electrodes. It can be observed from Table 1 that the growth rates of the $Q_{\text{PbSO}_4/\text{Pb}}$ for the two electrodes are much less than those of the $Q_{\text{Pb(II)/Pb}}$, and that of the $Q_{\text{PbSO}_4/\text{Pb}}$ does not vary significantly with the anodization time, therefore, $Q_{\text{PbSO}_4/\text{Pb}}$ may be neglected while the growth rate of the anodic film is calculated. Fig. 2 shows the plots of $Q_{\text{Pb(II)/Pb}}$ versus the oxidation time for Pb and Pb-Sm electrodes. From Fig. 2, the growth rates of the anodic Pb(II) oxides films for Pb and Pb-Sm electrodes were obtained as 0.082 C·cm⁻²·h⁻¹ and 0.047 C·cm⁻²·h⁻¹, respectively. It suggests that adding Sm may decrease the growth rate of anodic the Pb(II) oxides film.

EIS

When the potential of anodic oxidation for lead in sulfuric acid solution is in the PbO potential region (-0.40–0.95 V),¹⁴ a complex composition of the anodic film on the lead electrode will be obtained, *i. e.*, Pb/PbO/3PbO·PbSO₄·H₂O/PbO·PbSO₄/PbSO₄, with PbO, PbO·PbSO₄ and PbSO₄ as the major components.¹⁵

Our research group has obtained the thickness of the anodic PbO film on Pb from the photocurrent measurement and proved that the resistance of the anodic PbO film is close to that of the interstitial liquid among the PbO particles in the film, from which it was inferred that the anodic PbO film grows via the dissolution-precipitation mechanism.¹⁶

Table 1 Reduction charges of different components in anodic films formed on Pb and Pb-Sm electrodes for various growth time

Anodization time (h)		1	2	3	4
Pb	$Q_{\text{Pb(II)/Pb}}$ (C/cm ²)	0.23	0.32	0.42	0.47
	$Q_{\text{PbSO}_4/\text{Pb}}$ (C/cm ²)	0.14	0.16	0.17	0.18
Pb-Sm	$Q_{\text{Pb(II)/Pb}}$ (C/cm ²)	0.17	0.22	0.27	0.31
	$Q_{\text{PbSO}_4/\text{Pb}}$ (C/cm ²)	0.13	0.10	0.11	0.10

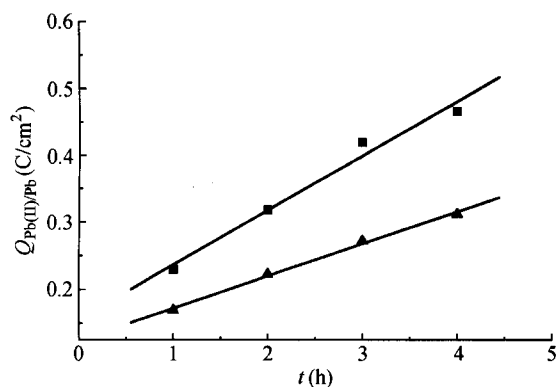


Fig. 2 Plots of the reduction charges of Pb(II) film ($Q_{\text{Pb(II)/Pb}}$) versus growth time for Pb and Pb-Sm electrodes. (■ Pb; ▲ Pb-Sm).

Fig. 3 shows the equivalent circuit for analysis of the impedance data of Pb electrode. R1 stands for the resistance of the electrolyte and the contacting resistance between the anodic film and lead substrate. R2 and C3 are the resistance and capacitance of the anodic film containing PbSO₄ and PbO·PbSO₄, respectively. R5 and C4 are the resistance and capacitance of the anodic PbO film, respectively. R6 stands for the polarization resistance. C7 is the capacitance of the double layer.

The quantity of Sm is much less than that of Pb in the alloy, and the major components of the anodic films formed on Pb-Sm are the same as that on Pb, therefore the equivalent circuit presented in Fig. 3 is also applied

for the Pb-Sm electrode.

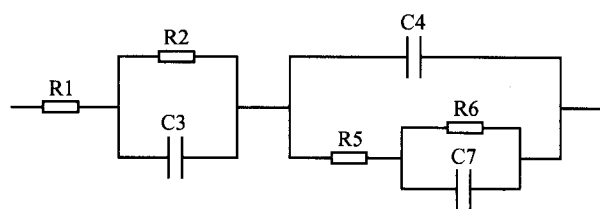


Fig. 3 Equivalent circuit of the anodic film.

The typical Nyquist plots of the anodic films for the Pb and Pb-Sm electrodes are depicted in Fig. 4. It can be found that the simulated plots fit the experimental plots well.

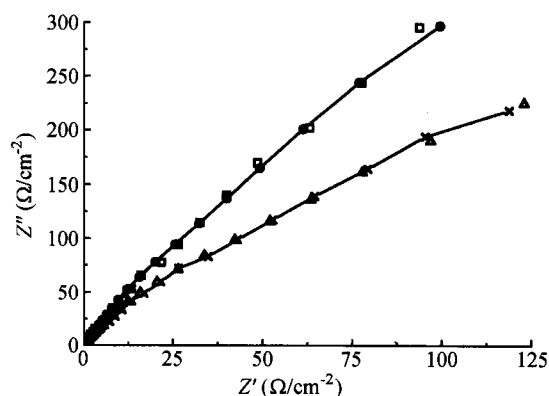


Fig. 4 Nyquist plots for the anodic films formed on Pb and Pb-Sm electrodes at 0.9 V in H₂SO₄ (4.5 mol/L) for 1 h at 25 °C, □— experimental for Pb; ●— simulated for Pb; △— experimental for Pb-Sm; ×— simulated for Pb-Sm.

Tables 2 and 3 list the parameters in the equivalent circuit.

By comparing the values of the parameters in Tables 2 and 3, it can be found that R5, R6 and C7 of the film on Pb-Sm all differ significantly from those on Pb. This is due to the larger porosity of the film on Pb-Sm. In the present work, the smaller value of R6 and the larger value of C7 for Pb-Sm both indicate larger wetted area on the surface of the Pb-Sm substrate, and larger porosity of the film, thus it makes the ionic conductance of the interstitial liquid among the PbO particles in the film higher, and the resistance of PbO film R5 lower.

Table 2 R1, R2, C3, C4, R5, R6, and C7 for Pb-Sm electrode versus anodizing time

Anodizing time (h)	R1 ($\Omega \cdot \text{cm}^2$)	R2 ($\Omega \cdot \text{cm}^2$)	C3 ($\mu\text{F} \cdot \text{cm}^{-2}$)	C4 ($\mu\text{F} \cdot \text{cm}^{-2}$)	R5 ($\Omega \cdot \text{cm}^2$)	R6 ($\Omega \cdot \text{cm}^2$)	C7 ($\mu\text{F} \cdot \text{cm}^{-2}$)
1	0.80	49	0.89	0.37	28	679	0.32
2	1.5	87	0.46	0.22	40	780	0.32
3	2.9	117	0.35	0.18	57	834	0.32
4	3.9	147	0.30	0.15	69	884	0.35

Table 3 R1, R2, C3, C4, R5, R6, and C7 for Pb electrode versus anodizing time

Anodizing time (h)	R1 ($\Omega \cdot \text{cm}^2$)	R2 ($\Omega \cdot \text{cm}^2$)	C3 ($\mu\text{F} \cdot \text{cm}^{-2}$)	C4 ($\mu\text{F} \cdot \text{cm}^{-2}$)	R5 ($\Omega \cdot \text{cm}^2$)	R6 ($\Omega \cdot \text{cm}^2$)	C7 ($\mu\text{F} \cdot \text{cm}^{-2}$)
1	0.51	39	1.2	0.35	47	1.4×10^3	0.19
2	6.0	82	0.58	0.21	72	1.9×10^3	0.18
3	1.2	111	0.43	0.16	94	2.3×10^3	0.16
4	1.6	129	0.37	0.13	113	2.7×10^3	0.15

Fig. 5 shows the plots of R5 versus time for Pb and Pb-Sm electrodes. It could be seen that R5 increases with the increasing of the oxidation time. The growth rates of the values of R5 for Pb and Pb-Sm electrodes obtained from Fig. 5 are $22.0 \Omega \cdot \text{cm}^2 \cdot \text{h}^{-1}$ and $14.0 \Omega \cdot \text{cm}^2 \cdot \text{h}^{-1}$, respectively. So, the results also demonstrate that adding Sm may reduce the growth of the resistance of PbO film.

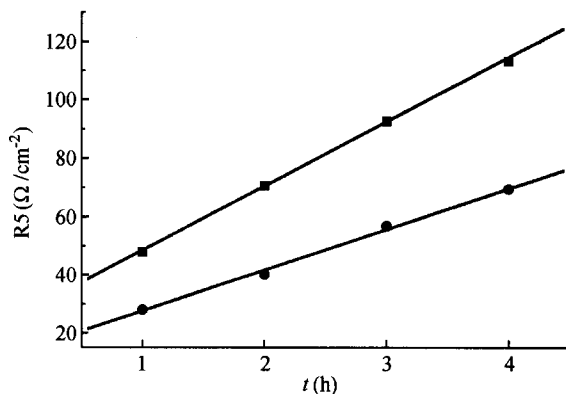


Fig. 5 Plots of the values of the resistance of the PbO film (R5) versus growth time for Pb and Pb-Sm electrodes (■—Pb; ●—Pb-Sm).

Although the value of $Q_{\text{Pb(II)/Pb}}$ for Pb-Sm is significantly less than that for Pb, the thickness of the film on

Pb-Sm would differ only slightly from that on Pb. This is due to the larger porosity of the film on Pb-Sm, which increases the thickness of the film. Hence the value of the capacitance of PbO film (C4) on Pb-Sm, which varies with the thickness of the film, also differs slightly from that on Pb (Tables 2 and 3).

SEM

Fig. 6 (a) and (b) Show the *ex-situ* SEM photographs for the surfaces of the anodic films formed on Pb and Pb-Sm electrodes respectively at 0.9 V for 2 h. Comparing this two photographs, obvious difference can be found that there is a looser pile of the particles in the anodic film on the Pb-Sm electrode than that on the Pb electrode, which indicates a possible significant difference between the porosities of the films on this two electrodes.

Conclusion

Sm as an additive to lead alloy may obviously inhibit the growth of the anodic Pb(II) oxides film. Moreover, it can reduce the resistance of the anodic PbO film significantly, which is due to the larger porosity of the film on Pb-Sm alloy.

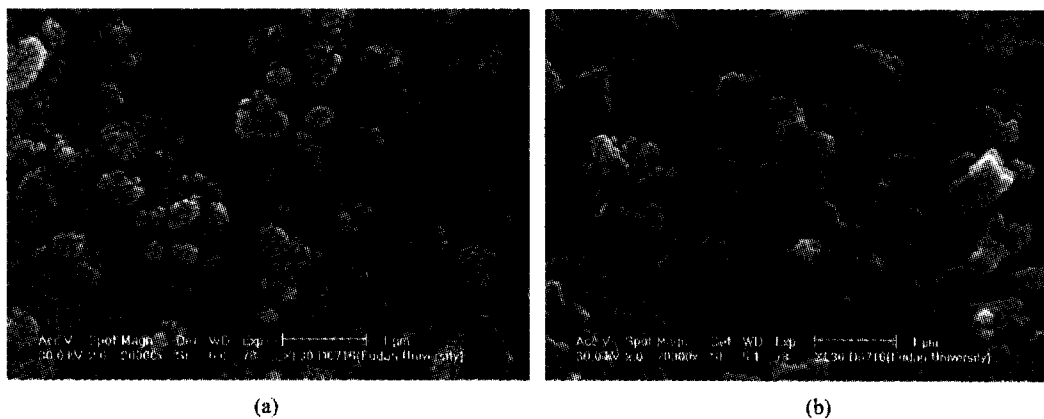


Fig. 6 *Ex-situ* SEM photographs for the surfaces of the anodic films formed on Pb and Pb-Sm electrodes at 0.9 V for 2 h, (a) Pb electrode; (b) Pb-Sm electrode.

References

- Bullock, K. R.; Butler, M. A. *J. Electrochem. Soc.* **1986**, *133*, 1085.
- Burbank, J. B. *J. Electrochem. Soc.* **1959**, *106*, 369.
- Pavlov, D.; Monahov, B.; Maja, M.; Penazzi, N. *J. Electrochem. Soc.* **1989**, *136*, 27.
- Ruetschi, P. *J. Electrochem. Soc.* **1973**, *120*, 331.
- Pavlov, D.; Popova, R. *Electrochim. Acta* **1970**, *15*, 1483.
- Pavlov, D.; Iordanov, N. *J. Electrochem. Soc.* **1970**, *117*, 1103.
- Ruetschi, P.; Angstadt, R. T. *J. Electrochem. Soc.* **1964**, *111*, 1323.
- Stein, N.; Rocca, E.; Kleim, R.; Lecuire, J. M.; McRae, E. *Electrochim. Acta* **1998**, *44*, 445.
- Liu, H.-T.; Wang, Q.-Z.; Wang, Y.-Q.; Zhou, W.-F.; Cai, W.-B. *Electrochemistry* **1996**, *2*, 123 (in Chinese).
- Bagshaw, N. E. *J. Power Sources* **1991**, *33*, 3.
- Liu, H.-T.; Wang, F.-W.; Xu, P.-D.; Zhou, W.-F. *J. Fudan Univ. (Nat. Sci.)* **1995**, *34*, 25 (in Chinese).
- Mao, G. W.; Wilson, T. L.; Larson, J. G. *J. Electrochem. Soc.* **1970**, *117*, 1323.
- Liu, H.-T.; Yang, J.; Liang, H.-H.; Zhuang, J.-H.; Zhou, W.-F. *J. Power Sources* **2001**, *93*, 230.
- Pavlov, D.; Puliev, Kh. N.; Klaya, E.; Iordanov, N. *J. Electrochem. Soc.* **1969**, *116*, 316.
- Han, J.; Pu, C.; Zhou, W.-F. *J. Electroanal. Chem.* **1994**, *368*, 43.
- LIU, H.-T.; LIANG, H.-H.; YANG, J.; ZHOU, W.-F. *Chin. J. Chem.* **2000**, *18*, 489.

(E0110083 SONG, J. P.; ZHENG, G. C.)