

Short communication

Oxygen evolution reaction on lead–bismuth alloys in sulfuric acid solution

W.S. Li^{a,*}, H.Y. Chen^a, X.M. Long^a, F.H. Wu^a, Y.M. Wu^a, J.H. Yan^{a,b}, C.R. Zhang^{a,b}

^a Department of Chemistry, South China Normal University, Guangzhou 510006, China

^b B.B. Battery Co. Ltd., Raoping, Guangdong 515700, China

Available online 10 January 2006

Abstract

Lead–bismuth alloys with bismuth from 0 to 8 wt.% were prepared. Oxygen evolution reaction on the alloys with lead dioxides was investigated by using linear voltammetry, electrochemical impedance spectroscopy, scanning electron spectroscopy, electron diffraction spectroscopy, oxygen collection experiments. The oxygen evolution reaction on the alloys with bismuth content <0.1% is not affected by the bismuth in the alloys. However, the rate of oxygen evolution reaction increases with increasing the bismuth content in the alloys. This is related to the dissolution of bismuth from the alloys to solution and the adsorption of bismuth ions from solution onto the surface of lead dioxide. Unlike lead, bismuth can dissolve into solution under anodic polarization. At the potentials where there is no oxygen evolution, lead–bismuth alloys are well passivated by lead sulfate or lead dioxide. The lead dioxide on the alloys becomes porous when oxygen evolution takes place on it, thus bismuth in the alloys dissolves. The amount of dissolved bismuth increases with the bismuth content in the alloys and the adsorption of bismuth ions onto lead dioxide takes place when bismuth ion concentration near the oxide surface is high enough. The lead dioxide with adsorbed bismuth ions can accelerate oxygen evolution reaction and oxygen evolution increases with increasing the amount of adsorbed bismuth ions.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Oxygen evolution reaction; Lead–bismuth alloy; Sulfuric acid

1. Introduction

The successful application of valve-regulated lead–acid (VRLA) batteries depends to a great extent on the limitation of water decomposition, i.e. hydrogen evolution on negative electrodes and oxygen evolution on positive electrodes. Understanding the factors that influence hydrogen and oxygen evolution reactions in VRLA batteries is necessary to improve battery performances. It is found that some of minor alloy elements can inhibit or improve hydrogen and oxygen evolution reactions [1,2]. Among the minor elements concerned, bismuth has attracted the most investigations because it is costly to separate bismuth from lead due to their similarity in physical and chemical performances. Lead industry hopes bismuth produces benefit but detrimental effect on lead acid battery performance so that it does not need to be removed from lead.

Much work has been done on the effect of bismuth on hydrogen evolution reaction on lead and the mechanism is well

understood [3–5]. Bismuth accelerates the hydrogen evolution reaction on lead whether it enters the lead crystals in the form of lead alloys or is deposited on the lead surface from solution by displacement reaction with lead. By contrast, the hydrogen evolution reaction is less dependent on bismuth in lead–bismuth alloys than on bismuth that is chemically deposited on lead. The effect of bismuth can be neglected if the alloy electrode is not taken to a very negative potential. In this case, bismuth is not detrimental to the battery performance.

Compared with the effect of bismuth on hydrogen evolution, less work has been conducted to study the effect of bismuth on oxygen evolution reaction on lead. It has been reported that the oxygen evolution reactions on lead oxides are accelerated by doping bismuth in the oxides. The oxides used in these reports were prepared by anodic oxidation of Pb^{2+} in the solution containing Bi^{3+} [6–11] or by mixing lead oxide with bismuth oxide [12–14]. The mechanism for the oxygen evolution on the lead oxide formed on pure lead has been understood [15,16], but that on lead containing bismuth is not available. In this paper, oxygen evolution reaction on lead alloys with 0–8% bismuth is studied by linear potential sweep, potentiostat electrolysis, alternative

* Corresponding author. Tel.: +86 20 85211368; fax: +86 20 85216890.
E-mail address: liwsh@scnu.edu.cn (W.S. Li).

current impedance, oxygen evolution collection, and scan electron microscopy.

2. Experimental

Lead (99.99 wt.%) and bismuth (99.999 wt.%) were used to prepare alloys. The content of bismuth in prepared lead–bismuth alloys was determined with ICP (P-4010, Hitachi). Four alloys were used, as shown in Table 1. Alloy electrodes were prepared as follows: metals, single or double, were melted at 460 °C, mixed by stirring, cast as cylinder and sealed with epoxy resin leaving a disk working surface with a diameter of 6.18 mm.

Electrochemical experiments were performed with PGSTAT-30 (Autolab, Eco Chemie B.V. Company) and a three electrode cell. The prepared electrodes were used as working electrodes. A platinum electrode with a large area was used as auxiliary electrode. The reference electrode was Hg/Hg₂SO₄/4.79 M H₂SO₄. All the potential values in this paper are reported with respect to this reference electrode. Before each experiment, the working electrode was polished with a silicon carbide paper of 1200 grit, washed with deionized and double-distilled water, degreased with ethanol and pre-polarized at –1.2 V for 10 min to remove oxide formed in air. The working surface was perpendicular to the solution surface during experiment to prevent the gas bubble from adhesion on the electrode. In the measurement of alternative current impedance, frequencies used were from 10⁵ to 0.5 Hz and the amplitude of the ac voltage was 10 mV. In the application of equivalent circuit, a constant phase element (CPE) was used. The impedance (*Z*) of a CPE can be obtained with the following relationship [17–19]:

$$Z = [Q(j\omega)]^{n-1} \quad (1)$$

where ω is the frequency of alternative current, *Q* the combination of properties related to both the surface and the electroactive species, and exponent *n* is the slope of the impedance-frequency Bode plot. CPE has the properties of a capacitance when 0.5 < *n* < 1. With the values of *Q* obtained by fitting experimental data with a Randle equivalent circuit, the double layer capacitance (*C*) at different potentials can be obtained by [20–22]:

$$C = Q(\omega'')^{n-1} \quad (2)$$

where ω'' is the frequency at which the imaginary part of impedance has a maximum.

Oxygen collection experiments were performed at constant potentials with a potentiostat/galvanostat (Model 363, EG and G) in the three electrode cell. The auxiliary electrode and the reference electrode were the same as in electrochemical mea-

surements. Hydrogen evolved on the working electrode was collected and its volume was measured. The electrolyte used in this paper was 4.79 M H₂SO₄ solution. Solution was prepared with de-ionized and double-distilled water and analytic grade H₂SO₄. All the experiments were conducted at ambient temperature.

3. Results and discussion

To get the anodic behavior of oxygen evolution on the alloys, the anodic polarization curves was measured by sweeping potential negatively after electrolyzing the alloys at 1.7 V for 40 min in 1.28 g cm⁻³ sulfuric acid solution to form a layer of lead oxide. The results are shown in Fig. 1. It can be seen from the curves a–c in Fig. 1 that the anodic polarization curves are almost the same for the alloys with bismuth content <0.1%. This suggests that the bismuth in the alloys hardly affects the oxygen evolution reaction when its content is <0.1%. However, the current on the alloys with higher amount of bismuth increases with increasing bismuth content at the same potential. This indicates that the bismuth in the alloys accelerates the oxygen evolution reaction when its content is >0.1%.

Fig. 2 shows the electrochemical impedance spectra of lead alloys obtained at 1.55 V. The electrode was pre-treated as those used in Fig. 1. It can be seen that the electrochemical impedance spectra on the alloys with different bismuth content are characteristic of the reaction limited by charge transfer step. This means that the oxygen evolution reaction on the alloys is limited by charge transfer step. The reaction resistance and the double layer capacitance obtained by fitting with a Randle equivalent circuit and calculating with Eqs. (1) and (2) are listed in Table 2. It can be seen that the impedance behavior is hardly influenced by the bismuth when its content lower than 0.1 but the impedance decreases with increasing bismuth content on the alloys with higher amount of bismuth.

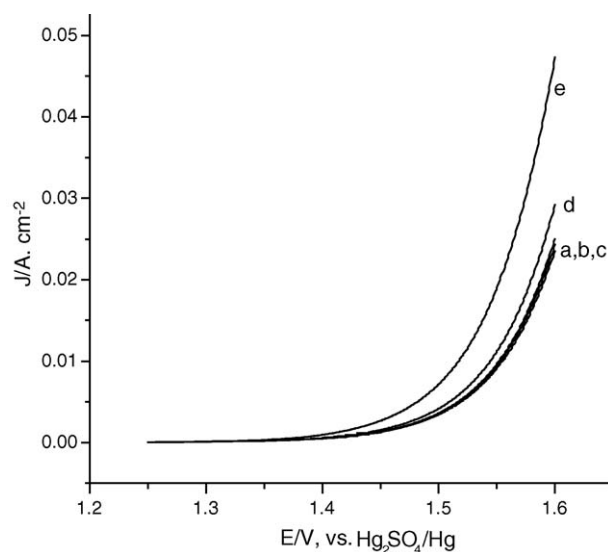


Fig. 1. Anodic polarization curves of lead alloy electrodes in 1.28 g cm⁻³ sulfuric acid solution, with (a) 0 wt.%, (b) 0.035 wt.%, (c) 0.103 wt.%, (d) 0.83 wt.%, (e) 7.33 wt.% Bi in the alloys, scan rate: 2 mV s⁻¹.

Table 1
Bismuth contents in lead alloys

Alloy	Bismuth content (wt.%)
a	0.00
b	0.033
c	0.103
d	0.83
e	7.33

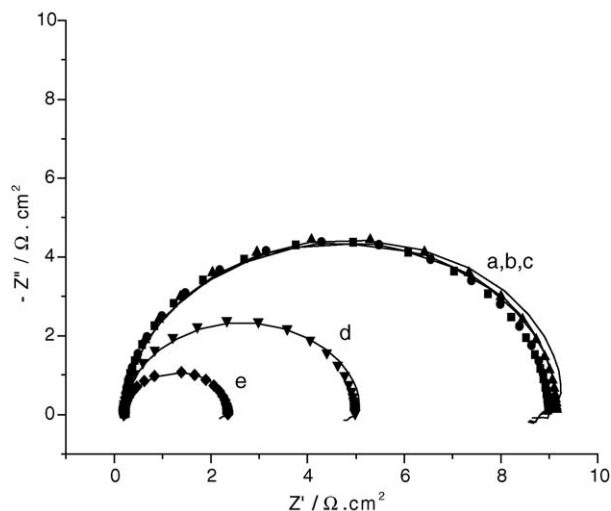


Fig. 2. Electrochemical impedance spectra of lead–bismuth alloy electrodes at 1.55 V in 1.28 g cm^{-3} sulfuric acid solution, with (a) 0 wt.%, (b) 0.035 wt.%, (c) 0.103 wt.%, (d) 0.83 wt.%, (e) 7.33 wt.% Bi in the alloys.

Table 2

Resistance and double layer capacitance for oxygen evolution reaction on the lead bismuth alloys at 1.55 V

Alloy	Bismuth content (wt.%)	Resistance ($\Omega \text{ cm}^2$)	Capacitance
a	0	8.8	0.95
b	0.033	8.8	1.08
c	0.103	8.9	1.13
d	0.83	4.8	0.93
e	7.33	2.2	1.67

Fig. 3 shows the variation of oxygen evolution volume with bismuth content for the lead alloys at 1.55 V in 1.28 g cm^{-3} sulfuric acid solution. It can be found that there is the same behavior of the effect of bismuth on oxygen evolution with that on anodic polarization and electrochemical impedance. It is obvious that oxygen evolution reaction is almost not affected by bismuth when its content is $<0.1\%$ but is accelerated on the alloys with higher content of bismuth.

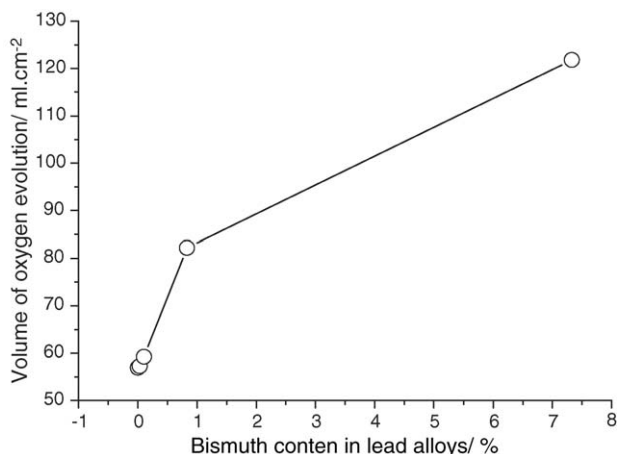


Fig. 3. The variation of oxygen evolution volume with bismuth content for the lead alloys at 1.55 V in 1.28 g cm^{-3} sulfuric acid solution.

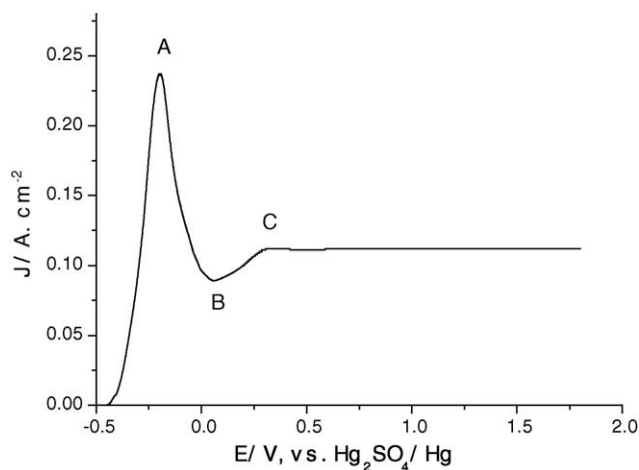


Fig. 4. Anodic polarization curves of bismuth electrodes in 1.28 g cm^{-3} sulfuric acid solution, 20 mV s^{-1} .

To understand the mechanism on the effect of bismuth in the alloys on oxygen evolution, the anodic polarization behavior of bismuth was studied. Fig. 4 shows the result obtained for the bismuth (99.999 wt.%) electrode in 1.28 g cm^{-3} sulfuric acid solution. It can be seen that the potential for bismuth to begin to be oxidized at -0.45 V . The current for the oxidation of bismuth increases with increasing potential before -0.2 V . This can be ascribed to the dissolution of bismuth into solution. Fig. 5 shows the surface morphology of bismuth before and after anodic polarization. Fig. 5A shows the surface of bismuth as it is polished with silicon carbide paper. Fig. 5B is completely different from Fig. 5A, which shows crystal grains of bismuth without any coverage. It is obvious that active dissolution reaction of bismuth takes place when bismuth is polarized at the potentials from -0.45 to 0.2 V .

When the potential shifts positively further, as shown in Fig. 4, the current reaches its maximum (A) at about -0.2 V , decreases to a valley (B) at about 0 V and then increases again, and finally keeps almost constant after 0.3 V (C). The appearance of current peak (A) can be ascribed to the deposition of bismuth compound from solution, which hinders the further dissolution of bismuth. The deposited bismuth compound should be bismuth sulfate because the solution contains only sulfate anion. Bismuth sulfate has a better solubility and naked bismuth can be available when anodic polarization current is low. However, the deposition of bismuth sulfate will take place when anodic polarization current is high enough and the concentration of bismuth near the electrode surface reaches its saturation concentration. At higher potential, a bismuth sulfate film with a certain thickness is obtained due to the balance between the formation of new bismuth ions from the anodic dissolution of bismuth electrode and their diffusion from the electrode surface to the bulk solution, resulting in a constant current independent of potential. Note that no oxygen evolution reaction occurs on this electrode surface covered with bismuth sulfate even if the potential is over 1.8 V . This suggests that bismuth oxide cannot be formed on the electrode surface because it favors the oxygen evolution reaction.

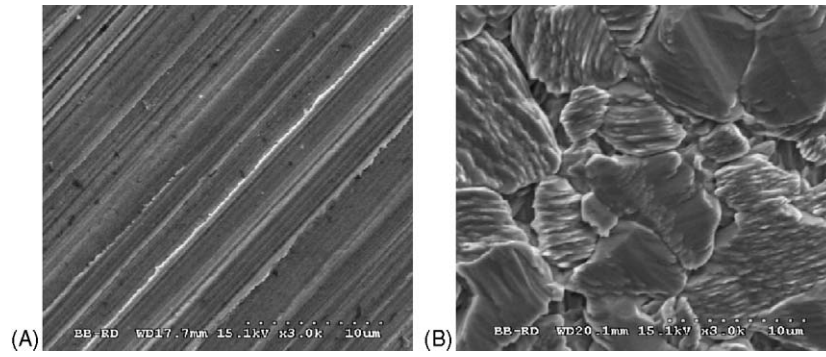


Fig. 5. Morphology of bismuth electrodes before (A) and after (B) anodic polarization at -0.4 V in 1.28 g cm^{-3} sulfuric acid solution.

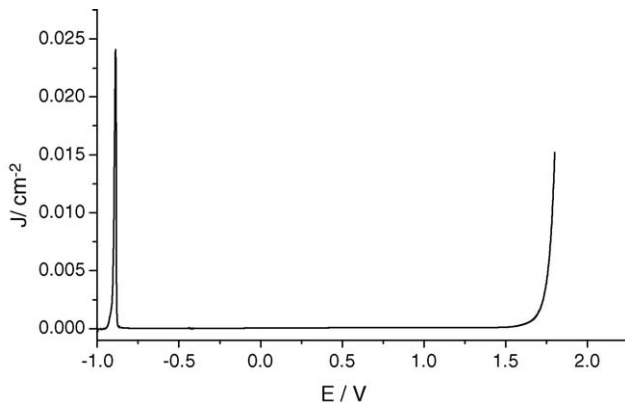


Fig. 6. Anodic polarization curves of lead electrodes in 1.28 g cm^{-3} sulfuric acid solution, 20 mV s^{-1} .

Fig. 6 shows the anodic polarization curve of lead electrode in 1.28 g cm^{-3} sulfuric acid solution. It can be seen that lead begins to be oxidized at about -1.0 V, far more negative than that for bismuth, indicating that the oxidation of lead in lead–bismuth alloys takes place first. Unlike bismuth sulfate, lead sulfate has a poor solubility. Thus sharp current peak appears for the formation of lead sulfate on the electrode surface and the lead is well passivated (without current) after the peak potential till the potential for the conversion of lead sulfate to lead dioxide and the oxygen evolution.

Based on the anodic polarization of bismuth and lead in sulfuric acid solution, the bismuth in the lead–bismuth alloys is

hardly oxidized because compact lead sulfate film on the alloys is formed before the oxidation of bismuth. Fig. 7 shows the surface morphology of lead and lead–bismuth alloy after oxidation at -0.9 V for 1 h. It can be observed that deposited lead sulfate is formed on both lead and lead–bismuth electrodes and the deposited layer on lead–bismuth electrode is more compact than that on lead electrode.

Figs. 8 and 9 show the morphology of lead and lead–bismuth electrodes after anodic polarization at the potentials before and after oxygen evolution, respectively. The formation of lead dioxide from lead sulfate can be observed for lead and lead–bismuth electrodes at the potential lower than that for oxygen evolution and the formed lead dioxide is compact, as shown in Fig. 8. At the potential where oxygen evolution occurs, however, porous lead oxide is formed on lead and lead–bismuth electrodes and the pore on the lead–bismuth is far bigger than that on lead, as shown in Fig. 9. At this moment, bismuth in the alloys should be oxidized and dissolve into solution.

With results and discussion above, the mechanism on the effect of bismuth in alloys can be inferred as follows. Bismuth in the alloys dissolve into solution at high potentials because the formation of porous lead dioxide due to oxygen evolution. The dissolved bismuth ions in the solution are adsorbed on lead dioxide when their concentration near the oxide surface is high enough. The lead dioxide with adsorbed bismuth has a quicker kinetics than that without adsorbed bismuth. The oxygen evolution reaction becomes quicker as the bismuth content increases in the alloys. On the alloys with bismuth content $<0.1\%$, the

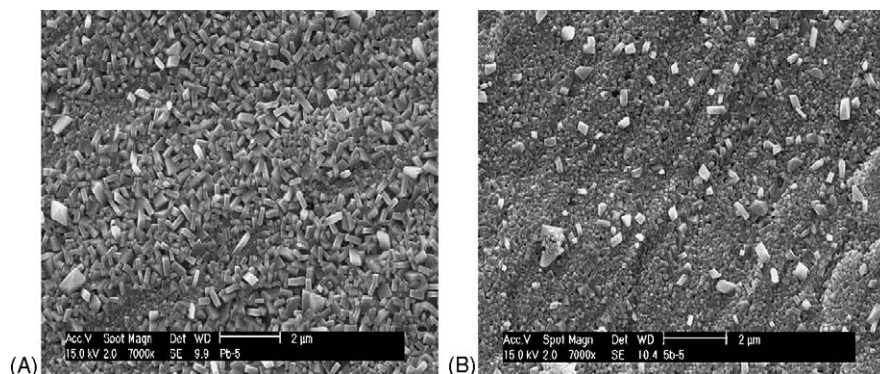


Fig. 7. Morphology of lead (A) and lead–bismuth (7.33%, B) electrodes after anodic polarization at -0.9 V for 1 h in 1.28 g cm^{-3} sulfuric acid solution.

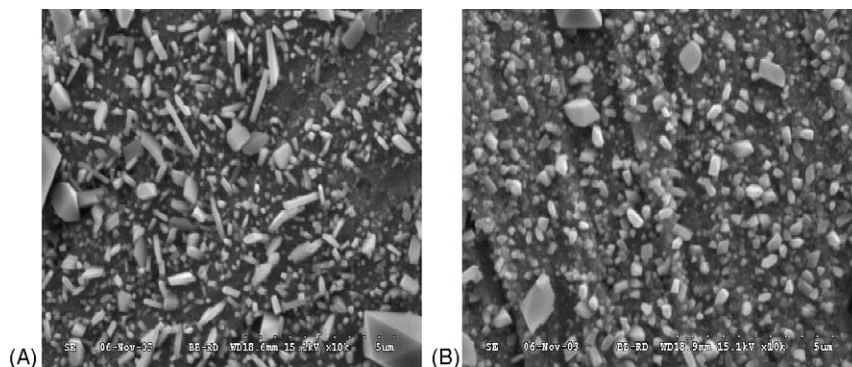


Fig. 8. Morphology of lead (A) and lead–bismuth (7.33%, B) electrodes after anodic polarization at 0.9 V for 1 h in 1.28 g cm^{-3} sulfuric acid solution.

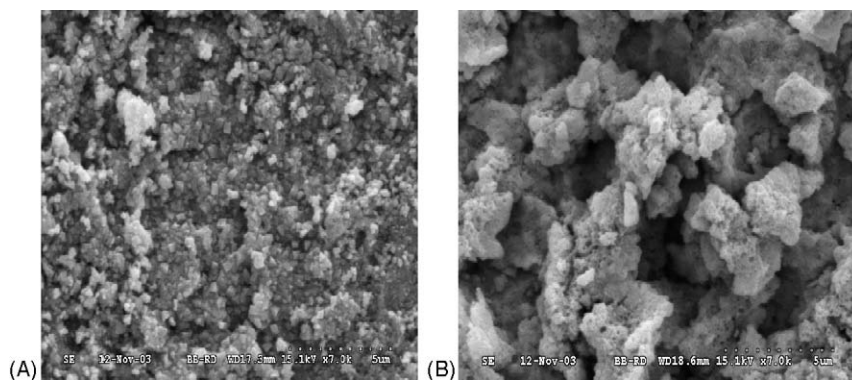


Fig. 9. Morphology of lead (A) and lead–bismuth (7.33%, B) electrodes after anodic polarization at 1.9 V for 1 h in 1.28 g cm^{-3} sulfuric acid solution.

dissolved bismuth in solution is too low to be adsorbed on the lead dioxide. Thus, there is no significant effect of bismuth on the oxygen evolution reaction when bismuth content in the alloy is $<0.1\%$.

4. Conclusion

Oxygen evolution reaction on the alloys is affected to different extent when the content of bismuth in alloys is lower and larger than 0.1% . The alloys with $<0.1\%$ bismuth have similar oxygen evolution behaviors to pure lead, almost same anodic polarization curve, same electrochemical impedance spectroscopy and same amount of oxygen evolution with pure lead. However, when the content of bismuth in alloys is $>0.1\%$, at the same potential the current and the amount of oxygen evolution increases but the reaction resistance decreases with increasing the content of bismuth in alloys. The mechanism on the effect of bismuth on oxygen evolution reaction on lead–bismuth alloys is related to the adsorption of dissolved bismuth ions onto the lead dioxide.

Acknowledgements

This work was financially supported by national 863 project of China (2003AA302410), NSFC (20373016), EYTP of MOE, Key Project of CISTC, MOST (2005DFA60580), International Cooperation Project of Guangdong Province (2005B50101003).

References

- [1] M. Maja, N. Penazzi, Effect of some elements on hydrogen reduction and hydrogen evolution at lead–acid battery negative plates, *J. Power Sources* 22 (1988) 1.
- [2] L.T. Lam, J.D. Douglas, R. Pillig, et al., Minor elements in lead materials used for lead/acid batteries, *J. Power Sources* 48 (1994) 219.
- [3] M. Johnson, S.R. Ellis, N.A. Hampson, et al., The hydrogen evolution reaction on lead–bismuth alloys, *J. Power Sources* 22 (1988) 11.
- [4] N. Papageorgiou, M. Skyllas-Kazacos, A study of the hydrogen evolution reaction on lead bismuth alloys in sulphuric acid solutions, *Electrochim. Acta* 37 (1992) 269.
- [5] Y.M. Wu, W.S. Li, X.M. Long, et al., Effect of bismuth on hydrogen evolution reaction on lead in sulfuric acid solution, *J. Power Sources* (2004).
- [6] I.H. Yeo, D.C. Johnson, Electrocatalysis of anodic oxygen-transfer reactions, *J. Electrochem. Soc.* 134 (1987) 1973.
- [7] L.A. Larew, J.S. Gordon, Y.L. Hsiao, et al., Electrocatalysis of anode oxygen-transfer reactions, *J. Electrochem. Soc.* 137 (1990) 3071.
- [8] I.H. Yeo, S. Kim, R. Jacobson, et al., Electrocatalysis of anodic oxygen transfer reactions, *J. Electrochem. Soc.* 136 (1989) 1395.
- [9] J. Feng, D.C. Johnson, Electrocatalysis of anodic oxygen-transfer reactions: titanium substance for pure and doped lead dioxide films, *J. Electrochem. Soc.* 138 (1991) 3328.
- [10] H. Chang, D.C. Johnson, Electrocatalysis of anodic oxygen-transfer reactions, *J. Electrochem. Soc.* 137 (1990) 2452.
- [11] A. Damjanovic, B. Jovanovic, Anodic oxide films as barriers to charge transfer in O_2 evolution at Pt in acid solutions, *J. Electrochem. Soc.* 123 (1976) 374.
- [12] D.M. Rice, Effects of bismuth on the electrochemical performance of lead/acid batteries, *J. Power Sources* 28 (1989) 69.
- [13] L.T. Lam, O.V. Lim, V.P. Haigh, et al., Oxide for value-regulated lead–acid batteries, *J. Power Sources* 73 (1998) 36.

- [14] H.Y. Chen, L. Wu, C. Ren, et al., The effect and mechanism of bismuth doped lead oxide on the performance of lead–acid batteries, *J. Power Sources* 95 (2001) 108.
- [15] D. Pavlov, B. Monahov, Mechanism of the elementary electrochemical processes taking place during oxygen evolution on the lead dioxide electrode, *J. Electrochem. Soc.* 143 (1996) 3616.
- [16] D. Pavlov, B. Monahov, Temperature dependence of the oxygen evolution reaction on the Pb/PbO₂ electrode, *J. Electrochem. Soc.* 145 (1998) 70.
- [17] J.R. Macdonald, *Impedance Spectroscopy*, Wiley, New York, 1987.
- [18] K. Juttner, *Electrochim. Acta* 35 (1990) 1501.
- [19] J. Hubrecht, M. Embrechts, W. Bogaerts, *Electrochim. Acta* 38 (1993) 1867.
- [20] C.H. Hsu, F. Mansfeld, *Corrosion* 57 (2001) 747.
- [21] W.S. Li, S.Q. Cai, J.L. Luo, Chronopotentiometric responses and capacitance behaviors of passive film formed on iron in borate buffer solution, *J. Electrochem. Soc.* 151 (2004) B220.
- [22] W.S. Li, N. Cui, J.L. Luo, Pitting initiation and propagation of hypoeutectoid iron-based alloy with inclusions of martensite in chloride-containing nitrite solutions, *Electrochim. Acta* 49 (2004) 1663.