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The effect and mechanism of bismuth doped lead oxide on the performance of lead-acid batteries

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Abstract

Flooded automotive and motorcycle lead-acid batteries were manufactured from three kinds of lead oxides including electrolyzed pure lead (99.99 wt.% Pb) oxide, electrolyzed pure lead oxide doped with Bi_2O_3 (0.02 wt.% Bi_2O_3) and bismuth-bearing refined lead (0.02 wt.% Bi) oxide. The first cranking and cold cranking curves of the automotive batteries show that there is no obvious difference among the above lead oxides. Bismuth in lead oxide does not affect the water loss of flooded batteries. However, bismuth results in the improvement of capacity and charge-acceptance capability. In discharge, the positive voltage versus cadmium of plates with bismuth decreases more slowly than that of plates without bismuth. In order to investigate the mechanism of the function of bismuth, three other kinds of test electrodes were prepared from electrolyzed pure lead (99.99 wt.% Pb) oxide, electrolyzed pure lead oxide doped 0.02 wt.% Bi_2O_3 and electrolyzed pure lead oxide doped 0.06 wt.% Bi_2O_3. The cyclic voltammetry curve shows that bismuth has no significant influence on the electrochemical behavior of the positive active-material. There is an opposite result concerning the cathodic polarization curves between bismuth doped in the electrode and Bi^{3+} ion doped in the electrolyte. Bismuth doped in the electrode results in a decrease of the hydrogen overpotential. Conversely, Bi^{3+} ion doped in the electrolyte results is an increase. The chemical analysis confirms that a trace of Bi^{3+} ion exists in sulfuric acid solution (e.g. plates soaking, after formation, after cycling). A higher porosity is observed in the positive active-material containing bismuth by SEM technique. SEM morphology shows that needle-like crystals begin to occur after a few cycles. X-ray diffraction phase analysis proves that the amount of α-PbO_2 is increased by doping bismuth in to lead oxide. The existing forms, chemical characteristics and electrochemical reactions of bismuth during manufacture and are of lead-acid batteries are demonstrated clearly. The mechanism of the function of bismuth improving capacity, prolonging cycle-life and reducing water loss has been elucidated in detail.

Keywords: Bismuth; Lead oxide; Lead-acid battery; Capacity; Cycle-life; Water loss

1. Introduction

The influence of Bismuth, is not only discussed in the lead-acid battery industry, but it is also demonstrated as a beneficial element to improve the performance of alkaline batteries. In the alkaline zinc–manganese dioxide battery, bismuth doped MnO_2 was made from electrolyzed MnO_2 powders mixed with a Bi^{3+} ion solution. Bismuth enhanced the deep discharge and shallow discharge characteristics. Between certain voltages, the charge efficiency of MnO_2 was improved by doping with bismuth, and its mechanism of charge and discharge was changed [1]. In the lithium secondary battery, the complex Bi_2O_3 doped MnO_2 increased the capacity of the electrode material and decreased the polarization of the electrode. MnO_2 doped with Bi_2O_3 became more stable than pure MnO_2 during cycling [2]. Others added Bi_2O_3 to the electrolyte to increase the capacity of batteries.

In the lead-acid battery industry, the Bismuth effect is found in both grid alloys and lead oxide. More and more experiments have demonstrated that bismuth-bearing leady oxide improves the performance of lead. The role and mechanism of bismuth on lead oxide has been studied seriously by CSIRO and Pasminco Metals [3–8]. Especially in VRLA batteries, bismuth (i.e. 0.05 wt.% Bi) doped in to lead oxide increased initial capacity and prolonged

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cycle-life. Also, the rates of both oxygen and hydrogen gassing were reduced, and the self-discharge rates were reduced too. Selective discharge of positive or negative plates during float duty was minimized. Dr. Lam and Dr. Rand did much investigation to elucidate the mechanism by which bismuth in the oxide improves the performance of VRLA batteries. Rice and Manders [9] demonstrated that one of main effects with bismuth in lead oxide was the promotion of efficient oxygen recombination in VRLA batteries. In China, researchers tried to test the influence of bismuth doped in lead oxide on the performance of lead-acid batteries. Chen and co-workers [10–12] analyzed the effects of bismuth doped in lead oxide. Luo [13] proved that the presence of bismuth in lead oxide enhanced the utilization efficiency of active-materials in flooded starter batteries. Zhu [14] found that the electrolyte solution containing Bi^{3+} reduced the water loss of the automotive batteries which used a lead-antimony grid alloy (i.e. 3.5 wt.% Sb). In China, several lead-acid battery manufactures have used the refined pure lead containing 0.02 wt.% Bi to produce lead oxide. However, some lead-acid battery manufactures can not accept the fact that bismuth is not harmful to the performance of batteries. They judge bismuth to be an impurity according to traditional theory. At present, studying the theory and the effect mechanism of bismuth in batteries becomes more and more important. A clear theory and mechanism will help these lead-acid battery manufactures to understand the effect of bismuth doped in lead oxide. In this paper, the electrochemical technique and other physical methods are used to investigate the mechanism of bismuth in batteries. The chemical and electrochemical characteristics have been analyzed in detail.

2. Experimental

2.1. Comparison of performance

2.1.1. Lead oxide

Three kinds of ball-mill lead oxide were made from the same factory. These were:

1. lead oxide made from electrolyzed pure lead (primary lead, 99.99 wt.% Pb);
2. lead oxide being doped 0.02 wt.% Bi_2O_3;
3. lead oxide made from refined pure lead (secondary lead 99.99 wt.% Pb, 0.02 wt.% Bi).

With the same technical process for oxide, paste-mixing, paste-curing, formation, washing and drying treatment, the positive and negative plates were produced.

2.1.2. Performance test

The three types of plates prepared from different lead oxide were assembled in automotive batteries (12 V/60 A h). The performance was tested according to the Chinese National Standard (GB5008.1-91).

The grids were low antimony alloys: Pb 1.80 wt.% Sb 0.02 wt.% As 0.02 wt.% Sn 0.02 wt.% Cu 0.02 wt.% Se 0.02 wt.% Bi 0.005 wt.%.

The polyethylene pocket separators were inserted and sulfuric acid solution (1.280 relative density) was introduced.

2.2. Electrochemical and physical tests

2.2.1. Electrode preparation

The three kinds of lead oxide being doped with different bismuth contents were marked as followings:

1. a lead oxide made from electrolytic pure lead (primary lead, 99.99 wt.% Pb);
2. lead oxide (1) being doped 0.02 wt.% Bi_2O_3;
3. lead oxide (1) being doped 0.06 wt.% Bi_2O_3.

The outer surface of the active-material of the electrode was a square 10 mm × 10 mm. The electrodes were made through a special apparatus with a Pb 0.10 wt.% Ca 0.70 wt.% Sn 0.02 wt.% Al grid.

2.2.2. Electrochemical test

The cyclic voltammetry curves and cathodic polarization curves were tested by the usual system of three electrodes. The positive active-material prepared from different lead oxides was used as the working electrode (10 mm× 10 mm). The counter electrode was platinum electrode, and the reference electrode was a $Hg/Hg_2SO_4/K_2SO_4$(sat.) 'Calomel' electrode. The electrolyte was sulfuric acid solution (1.280 relative density). All experiments were performed at room temperature using a Potentiostat-Galvanostat EG & G PAR 273.

The electrolytes taken for chemical analysis included the soaking sulfuric acid solution before formation, sulfuric acid solution after formation and sulfuric acid solution after cyclic voltammetry (35 cycles). The pH value and Bi^{3+} ion concentration were tested and analyzed. The pH testing device was used to observe the change caused by the presence of bismuth in the active-materials. The NH $_4$SCN solution (60 wt.% concentration) and $Pb(NO_3)_2$ solution (60 wt.% concentration) were introduced to the experimental solution. If the color of the experimental solution became orange or brown, it proved that there was a trace of Bi^{3+} in the experimental solution. In order to avoid interference by $SO_4{}^{2-}$, a reference solution of H_2SO_4 was compared.

2.2.3. Physical test

The morphology of the positive active-material was examined by Philips XL30FEG scanning electron microscopy (SEM) technique.

The phase composition of the positive active-material was determined by X-ray diffraction (XRD) phase-analysis by D/Max-III A device.

Plates prepared from electrolytic pure lead oxide, electrolytic lead oxide doped Bi_2O_3 and bismuth-bearing soft lead oxide, were produced. Three types of automotive batteries (12 V/60 A h) were assembled with the above plates.

3. Results

3.1. Performance comparison of automotive batteries

The dry-charged performance, discharge ability at low temperature, capacity at the 20 h rate, charge efficiency and water loss of batteries were tested according to the experimental methods of the Chinese National Standard (GB5008.1-91).

After sulfuric acid solution (1.280 relative density) was introduced for 20 min, the batteries were discharged with a current of 240 A for 150 s. The first cranking curves are given in Fig. 1. There is no significant difference in the dry-charged performance between Bi-free plates and Bi-doped plates.

The batteries were kept fully charged at −18°C for 20 h and were discharged with a current 240 A for 60 min. The results of cranking performance at a temperature18°C are shown in Fig. 2. No obvious difference between Bi-free plates and Bi-doped plates is found in Fig. 2.

The batteries, fully charged, were discharged with a current of 3 A to a voltage 10.50 V. The capacity tests (Fig. 3) show that the capacity for Bi-doped plates was slightly higher than that of Bi-free plates. This demonstrates that the presence of bismuth caused the capacity of the plates to be increased. The evolution of charge currents with cycle number are given in Fig. 4.

Compared with Bi-free plates, the charge-acceptance capability of plates prepared from lead oxide with $Bi_2O_3$and bismuth-bearing soft lead oxide is improved. Bismuth in the active mass enhances the charge efficiency of the batteries.

The batteries were charged with a voltage 14.40 V at 40°C for 500 h. There is no obvious difference in the water loss test (Table 1). Bismuth does not promote water loss in flooded automotive batteries.

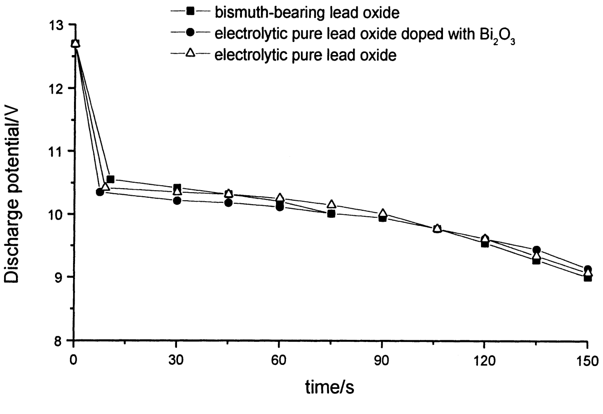

Fig. 1. Discharge curve of first cranking performance.

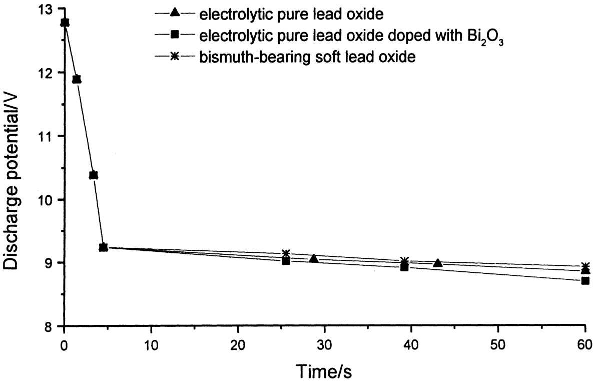

Fig. 2. Discharge curve of cranking performance at low temperature.

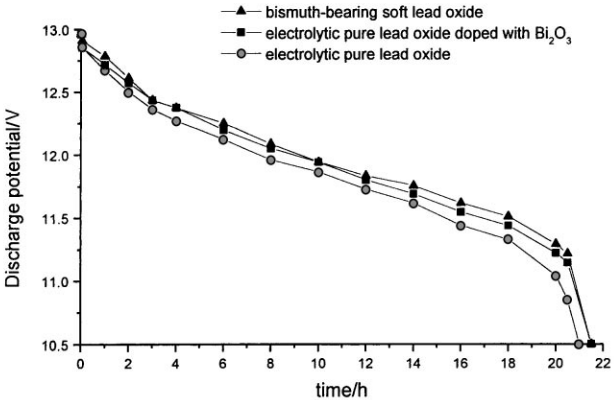

Fig. 3. Discharge curve of capacity performance at $C_{20}/20$ rate.

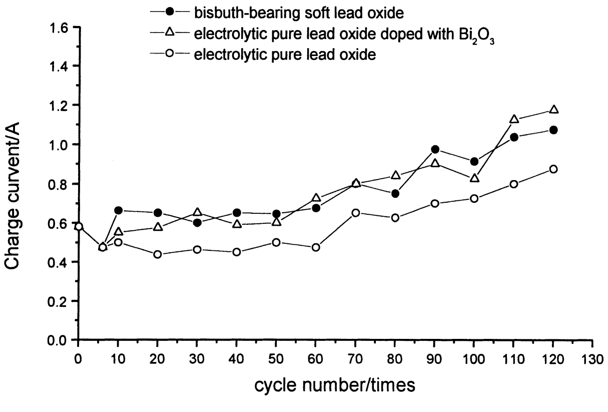

Fig. 4. Evolution of charge currents with cycle number.

Table 1
Water loss of Bi-free and Bi-doped batteries

Oxide type	Weight of water loss per ampere hour (g)
Electrolytic pure lead oxide	2.05
Electrolytic pure lead oxide doped with Bi_2O_3 (Bi_2O_3 0.02 wt.%)	1.89
Bismuth-bearing (Bi 0.02 wt.%) soft lead oxide	2.07

Table 2
Effect of bismuth on discharge performance of lead-acid batteries

Discharge duration (s)	Electrolytic pure lead oxide		Electrolytic pure lead oxide doped Bi_2O_3		Bismuth-bearing soft lead oxide	
	Positive voltage vs. cadmium	Negative voltage vs. cadmium	Positive voltage vs. cadmium	Negative voltage vs. cadmium	Positive voltage vs. cadmium	Negative voltage vs. cadmium
0	2.19	0.08	2.20	0.08	2.19	0.08
17	2.04	0.19	2.08	0.19	2.09	0.18
34	2.04	0.21	2.08	0.21	2.09	0.20
51	2.03	0.22	2.08	0.22	2.09	0.21
68	2.03	0.23	2.08	0.23	2.09	0.22
85	2.03	0.24	2.08	0.24	2.08	0.23
102	2.02	0.24	2.06	0.25	2.08	0.23
120	2.02	0.25	2.06	0.25	2.07	0.24

3.2. Discharge comparison of motorcycle batteries

The motorcycle batteries (12 V/9 A h) were assembled from plates with bismuth or without bismuth. The grid was lead antimony alloy: Pb 3.00 wt.% Sb 0.01 wt.% Sn 0.02 wt.% Cu 0.02 wt.% Bi. The separators were polyethylene pockets and the electrolyte was sulfuric acid solution with a relative density of 1.280. A cadmium electrode was used as a reference electrode ($E^0 = -0.402$ V). Each type of battery was fully charged with the same current. Then the battery was discharged with a current of 45 A.

The average of voltages versus cadmium of six cells is listed in Table 2. The influence of bismuth on the positive voltage versus cadmium is more significant than that of bismuth on the negative voltage versus cadmium.

By comparison of the results for Bi-free oxide and those for Bi-bearing oxide, there is a higher voltage versus cadmium for the positive plates prepared from pure lead oxide doped with Bi_2O_3 and bismuth-bearing soft lead oxide. The positive voltage versus cadmium of plates with bismuth decreased more slowly than that of plates without bismuth. Perhaps the improvement in capacity of cells is determined mainly by bismuth effecting the positive plates.

3.3. Electrochemical results

The cyclic voltammetry (CV) method was applied to observe the change of electrochemical behavior of positive plates with bismuth or without bismuth over a certain voltage range.

In this cyclic voltammetry testing, 35 cycles were performed between +1.00 and +2.20 V at a sweep speed of 10 mV s^{-1}. After 35 cycles, the CV result shown in Fig. 5 was obtained. The presence of bismuth in the positive active-material does not affect the electrochemical behavior of the positive active-material.

No other reductive peaks or oxidative peaks are seen, and the peak potential does not shift significantly.

The cathodic polarization method was used to compare the hydrogen overpotential and the current of hydrogen evolution of negative electrodes with bismuth or without bismuth. Three kinds of negative electrodes after formation were kept at −0.60 V for 10 min, then the curve was performed between −1.0 and −1.60 V at a sweep speed of 20 mV s^{-1}. The results are given in Fig. 6.

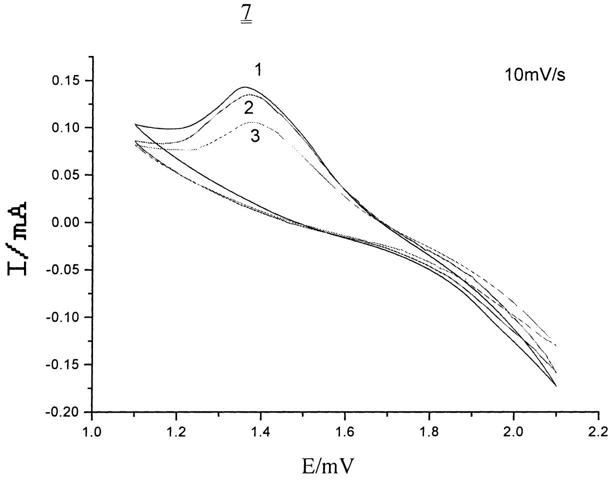

Fig. 5. Cyclic voltammetry curve of Bi-free and Bi-doped positive electrodes; (1) lead oxide made from electrolyzed pure lead (99.99 wt.% Pb) oxide; (2) lead oxide (1) being doped 0.02 wt.% Bi_2O_3; (3) lead oxide (1) being doped 0.06 wt.% Bi_2O_3.

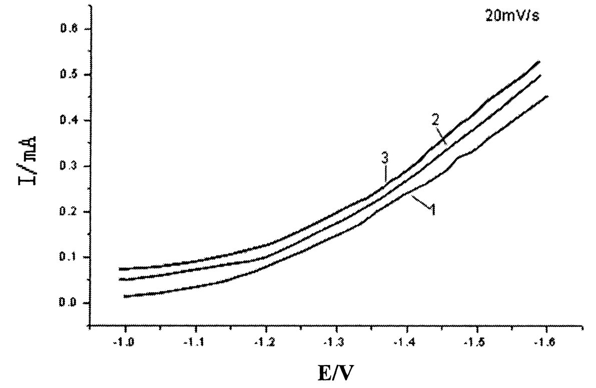

Fig. 6. Catholic polarization curve of Bi-free and Bi-doped negative electrodes; (1) lead oxide made from electrolyzed pure lead (99.99 wt.% Pb) oxide; (2) lead oxide (1) being doped 0.02 wt.% Bi_2O_3; (3) lead oxide (1) being doped 0.06 wt.% Bi_2O_3.

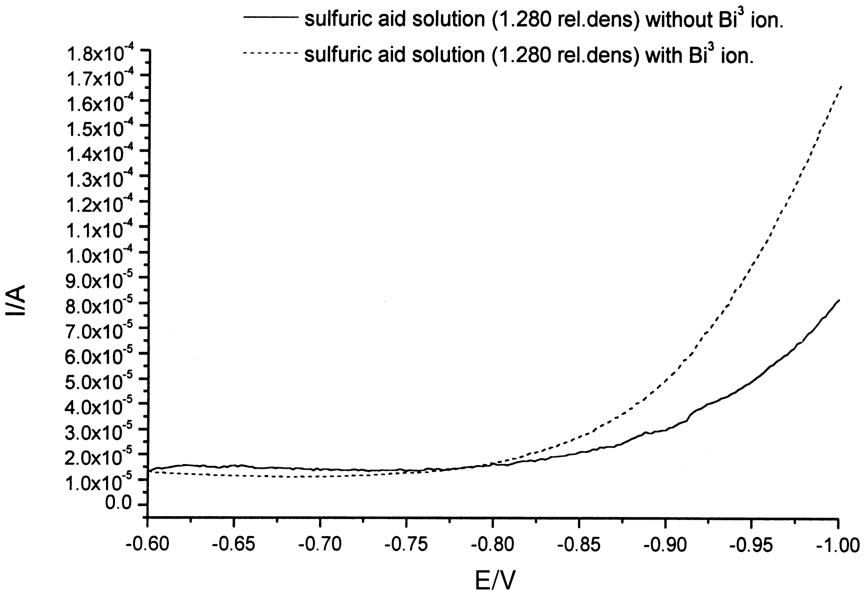

Fig. 7. Catholic polarization curve of a lead electrode in sulfuric acid solution with Bi^{3+}ion and without Bi^{3+}ion.

With the same value of hydrogen evolution current, the hydrogen overpotential decreased as the content of bismuth increased. The negative plates using bismuth doped lead oxide have higher rates of hydrogen evolution than those using no bismuth.

The above result can be explained through the lower hydrogen overpotential of bismuth in sulfuric acid solution. But it is difficult to explain the result for water loss. Some authors [5,9,13,14] demonstrated that batteries using plates with bismuth had less water loss or no change. In order to elucidate this mechanism, the influence of the Bi^{3+}ion in the electrolyte on a lead electrode has been tested by a cathodic polarization technique. The results are shown in Figs. 7 and 8.

Fig. 7 indicates that there is a higher hydrogen overpotential for the lead electrode in the electrolyte containing the Bi^{3+} ion. Fig. 8 shows that the presence of Bi^{3+} ion in the electrolyte also caused the oxygen overpotential to be increased. There is an opposite effect between the electrode with element bismuth and the electrolyte with Bi^{3+} ion.

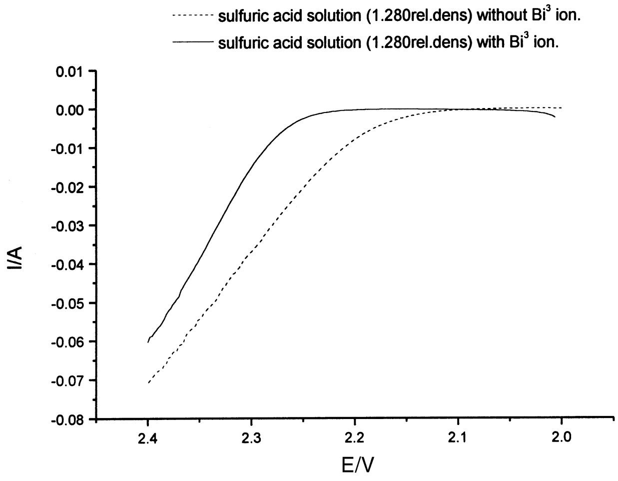

Fig. 8. Oxygen evolution curve of lead electrode in sulfuric acid solution with Bi^{3+}ion and without Bi^{3+}ion.

3.4. Electrolyte analysis

The change of pH value in the electrolyte was tested by the pH testing device. A trace of Bi^{3+} ion in the electrolyte was analyzed by a chemical method. The positive and negative plates were made from electrolytic pure lead oxide and electrolytic pure lead oxide doped with 0.06 wt.% Bi_2O_3. The electrolytes were prepared as follows:

- Sulfuric acid solution (1.050 relative density) with plates soaked for 4 h.
- Sulfuric acid solution (1.280 relative density) after 35 voltammetry cycles of the positive plates.
- Sulfuric acid solution (1.280 relative density) after 35 voltammetry cycles of the negative plates.

The results of the presence of a trace of Bi^{3+} ion are given Table 3. The concentration of Bi^{3+} ion in the sulfuric acid solution is so low that it is difficult to perform with quantitative analysis. The result given is a qualitative chemical analysis. The strength of Bi^{3+} ion trace concentration is concluded as followings: H_2SO_4 solution (1.280 relative density) after 35 cycles for positive plates > H_2SO_4 solution (1.280 relative density) after 35 cycles for negative plates > H_2SO_4 solution (1.080 relative density) after formation > H_2SO_4 solution (1.050 relative density) with plates soaking.

However, no change of pH value caused by the change of Bi^{3+} ion was observed. Due to the small change of Bi^{3+} ion

Table 3

Electrolyte type	Positive plates with bismuth	Negative plates with bismuth
Sulfuric acid solution with plates soaking	+[a]	+
Sulfuric acid solution after formation	+ +	+ +
Sulfuric acid solution after 35 voltammetry cycles	+ + + +	+ + +

[a] The more symbol "+", the higher Bi^{3+} ion trace concentration.

trace concentration, no significant change in pH is expected in a large volume of sulfuric acid.

3.5. SEM morphology and XRD results

Electron micrographs show that the morphology of the positive active-material is affected by the bismuth content (Fig. 9).

In Fig. 9 (a), the structure of PbO_2 grain is loose. In Fig. 9(b) and (c), the structure of PbO_2 grain appears stronger. The SEM observations also confirm that there is a higher porosity in the positive active-material with bismuth.

After 35 voltammetry cycles, the morphology of the positive active-material has altered (Fig. 10). After cycling, the positive mass with bismuth element still has a stronger structure than that without bismuth. Needle-like crystals can be found in the material with more bismuth (Fig. 10(c)). This observation corresponds with the electron micrographs observed by Lam et al. [4].

Both α-PbO_2 and β-PbO_2 can be analyzed by means of X-ray diffraction (XRD) phase analysis. XRD results are reported in Table 4. The amount of α-PbO_2 appears to increase with the increasing bismuth content in the positive plates.

4. Discussion

4.1. Chemical characteristics and form in which bismuth exists in the battery plate

It is important to know the form in which bismuth exists within the of lead-acid battery when we begin to discuss the

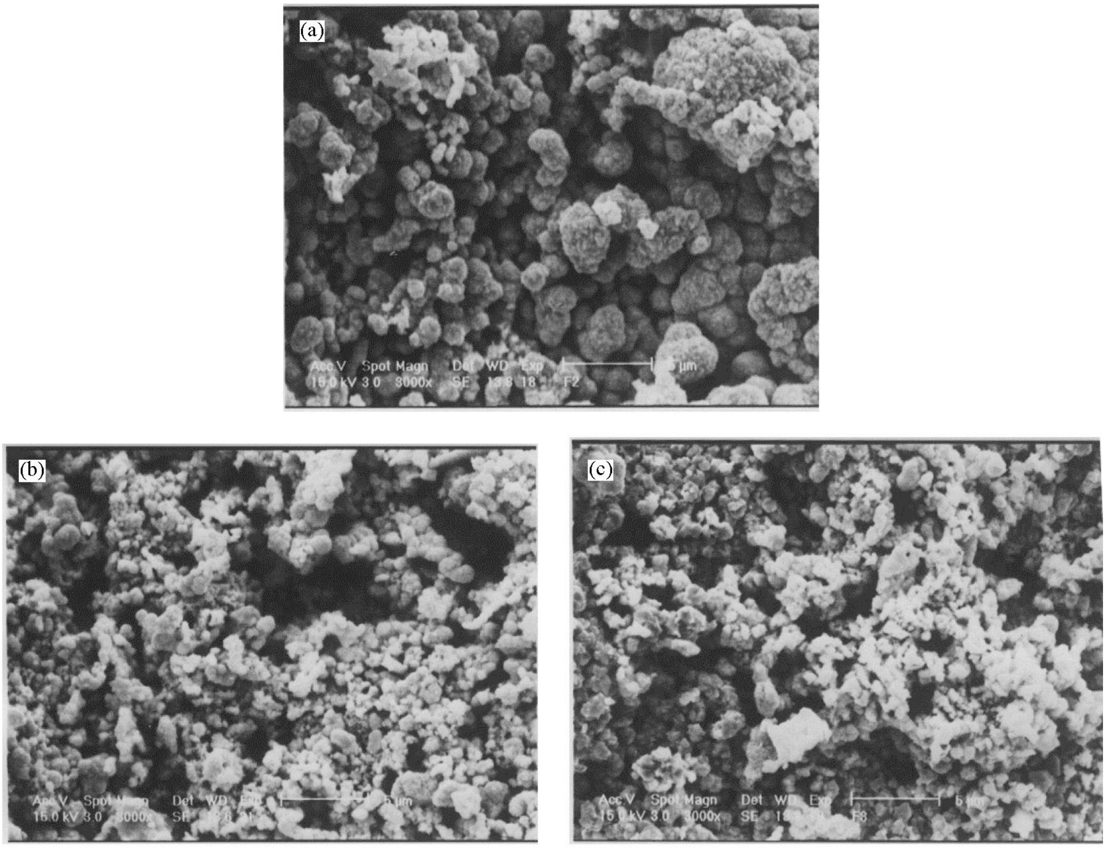

Fig. 9. SEM morphology of positive active-material before cycling: (a) material made with electrolytic pure lead (99.99 wt.% Pb) oxide; (b) material made with electrolytic pure lead oxide doped 0.02 wt.% Bi_2O_3; (c) material made with electrolytic pure lead oxide doped 0.06 wt.% Bi_2O_3.

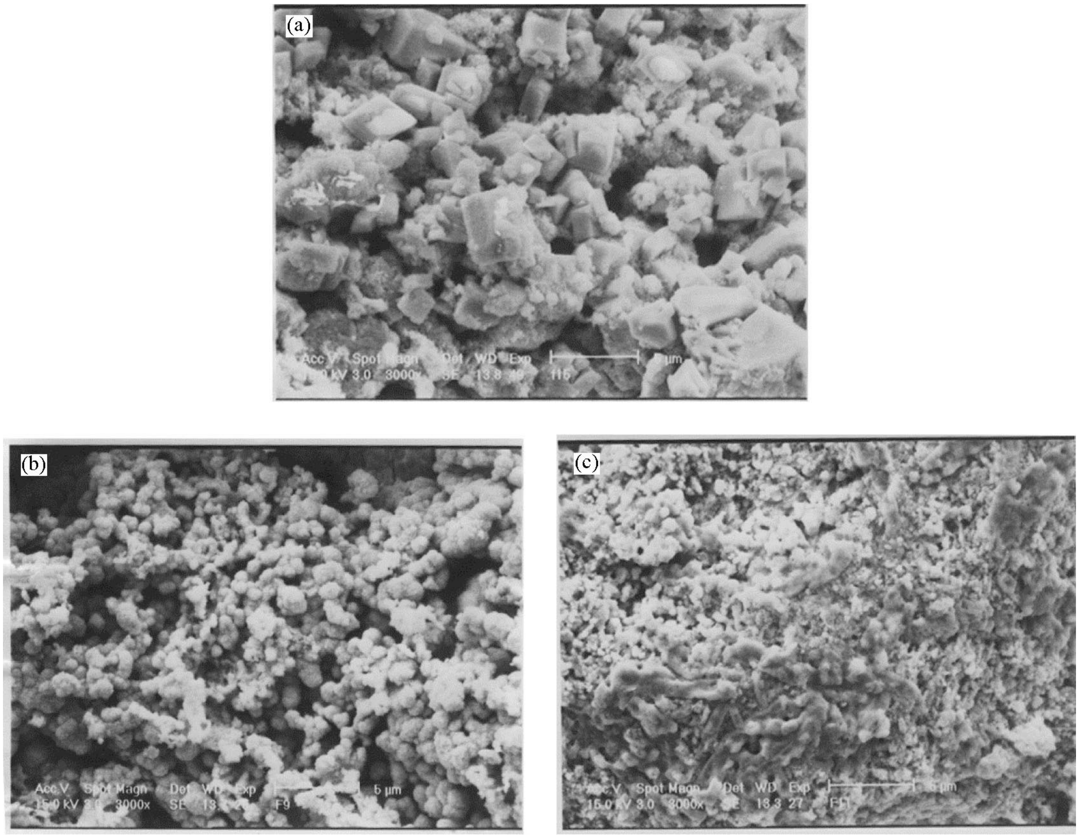

Fig. 10. SEM morphology of positive active-material after cycling: (a) material made with electrolytic pure lead (99.99 wt.% Pb) oxide; (b) material made with electrolytic pure lead oxide doped 0.02 wt.% Bi_2O_3; (c) material made with electrolytic pure lead oxide doped 0.06 wt.% Bi_2O_3.

results and mechanisms. Bi_2O_3 is the only existing stable oxide of bismuth. Bi_2O_5 is not stable and decomposes into Bi_2O_3 and O_2 quickly. Bi_2O_3 is an alkaline oxide compound which dissolves in acid. In the solution, the form of bismuth existing is Bi^{3+} ion or hydrated BiO^+ ion.

In the present experiments, Bi_2O_3 has been doped into lead oxide. If the lead oxide is made with bismuth-bearing soft lead, Bi_2O_3 is the most stable oxide compound in lead oxide. During the manufacture and use of lead-acid batteries, the chemical or electrochemical reactions happen in sulfuric acid solution. Thus, the form of bismuth existing in the Bi_2O_3–SO_3–H_2O system have been investigated.

Although there are several crystal phases such as α-Bi_2O_3, β-Bi_2O_3, γ-Bi_2O_3 and δ-Bi_2O_3, etc. in Bi_2O_3 compound, α-Bi_2O_3 is the only stable phase which is yellow power at room temperature [15]. Because Bi_2O_3 is an alkaline oxide, it reacts with concentrated sulfuric acid solution to form bismuth(III) sulfate. It is not proved yet that the simple $[Bi(H_2O)_n]^{3+}$ ion may exist in the solution. Many complex compounds may be produced by the interaction between $Bi_2O_3$and H_2SO_4. The stable and basic compounds in the Bi_2O_3 –SO_3– H_2O system have been listed in Table 5 [16]. For example, the usual hydrolysis product of bismuth sulfate is not $Bi(OH)_3$, but a compound $Bi(OH)_3 \cdot Bi(OH)SO_4$.

Sulfuric acid solution concentration directly affects the compound form of bismuth. The main products are alkaline compounds (basic salt) when the weight concentration of sulfuric acid solution is <23.4 wt.% (i.e. density 1.16 g ml^{-1} at 25°C) [17].

The above compounds of bismuth are the products of chemical reactions without any voltage effects. The electrochemical characteristics will be discussed in Section 4.2.

Table 4
Quantification of crystalline phases for formed materials (wt.%)

Phase	Positive active-materials made with pure lead (99.99 wt.%) oxide	Positive active-materials made with pure lead oxide doped 0.02 wt.% Bi_2O_3	Positive active-materials made with pure lead oxide doped 0.06 wt.% Bi_2O_3
α-PbO_2	25.52	26.93	30.19
β-PbO_2	63.74	61.68	58.55
Other PbO_2	10.74	11.39	11.26

Table 5
Stable and basic compounds in the Bi_2O_3–SO_3– H_2O system [16]

Chemical formula
$(BiO)OH$
$Bi(OH)_3$
$(BiO)_2SO_4$
$(BiO)_2SO_4 \cdot H_2O$
$(BiO)_2SO_4 \cdot 2H_2O$
$Bi(BiO)(SO_4)_2$
$Bi(OH)SO_4$
$Bi(OH)SO_4 \cdot 1/2\ H_2O$
$Bi(OH)SO_4 \cdot H_2O$
$Bi(OH)SO_4 \cdot 4\ H_2O$
$Bi_2(SO_4)_3$
$Bi_2(SO_4)_3 \cdot 3\ H_2O$
$Bi_2(SO_4)_3 \cdot 7\ H_2O$
$BiH(SO_4)_2$
$BiH(SO_4)_2 \cdot H_2O$
$BiH(SO_4)_2 \cdot 7H_2O$
$BiH(SO_4)_3$
$Bi_3H(SO_4)_5 \cdot 6H_2O$

4.2. Electrochemical reactions of bismuth

When bismuth is present as a constituent of electrodes, its chemistry is influenced by the prevailing voltage. Although the result of the cyclic voltammetry has confirmed that bismuth did not affect the electrochemical behavior of the positive active-materials, this does not mean that there is no electrochemical reaction for bismuth itself. The electrochemical reactions of bismuth are so weak that they can not affect the electrochemical behavior of plates of lead-acid batteries. But these weak electrochemical reactions of bismuth are very important in order to judge the forms of bismuth existing and the influence of bismuth on the electrolyte. It is a regret that the Pourbaix diagram of the Bi–H_2SO_4–H_2O system is not available yet. In this discussion, the Pourbaix diagram of the Bi–H_2O system [18] is used in order to analyze some electrochemical reactions of bismuth in positive plates referenced to pH value.

During the paste-mixing and curing processes, bismuth oxide is in contact with dilute sulfuric acid. According to the discussion (Section 4.1), bismuthyl salt and alkaline bismuth sulfate may be the main existing forms. Certainly, a little Bi_2O_3 and soluble salt of bismuth may also be produced.

During the formation and cycling processes, the standard positive potential is 1.685 V and the pH value of the sulfuric acid solution (1.050−1.280 relative density) is low. Of course, the positive potential and the pH value will change during charging and discharging. From Fig. 11, the possible existing forms of bismuth include: Bi^{3+}, $BiOH^{2+}$,BiO^{+}, Bi_4O_7, Bi_2O_4, Bi_2O_5, etc. The electrochemical reactions among these compounds can be expressed by [19]:

$$Bi_2O_5 + 2H^+ + 2e^- = Bi_2O_4 + H_2O \qquad (1)$$

$$2Bi_2O_4 + 2H^+ + 2e^- = Bi_4O_7 + H_2O \qquad (2)$$

$$Bi_4O_7 + 2H^+ + 2e^- = 2Bi_2O_3 + H_2O \qquad (3)$$

$$Bi_2O_4 + 8H^+ + 2e^- = 2Bi^{3+} + 4H_2O \qquad (4)$$

$$Bi_2O_5 + 10H^+ + 4e^- = 2Bi^{3+} + 5H_2O \qquad (5)$$

$$Bi_4O_7 + 14H^+ + 2e^- = 4Bi^{3+} + 7H_2O \qquad (6)$$

$$Bi_4O_7 + 6H^+ + 2e^- = 4BiO^+ + 3H_2O \qquad (7)$$

$$Bi_4O_7 + 10H^+ + 2e^- = 4BiOH^{2+} + 3H_2O \qquad (8)$$

In view of the foregoing, it is unlikely that Bi_2O_3 will keep this simple oxide form in the paste and active-materials. During the paste-mixing and curing processes, oxy-bismuth salt and alkaline bismuth sulfate are the main existing forms. During formation and cycling, bismuth oxide compounds may react and the high valence state oxide compound may be formed. The bismuth may not be continued to the paste and active-materials of plates. Some of bismuth may transfer to the sulfuric acid solution. This has been indicated by the results of chemical analysis in Section 3.4. Its effects will be discussed below.

4.3. Mechanism of bismuth improving capacity

In Section 3.4, the results of chemical analysis confirm that a trace of Bi^{3+} ion exists in the sulfuric acid solution from plate-soaking, sulfuric acid solution after formation, and sulfuric acid solution after cycling.

In Section 3.5, the SEM morphology of the positive active-materials shows that there are more pores in plates with bismuth present than in plates without bismuth. The higher ratio of porosity in the positive active-materials may be caused by chemical or physical transfer of bismuth compounds.

- Chemical transfer process:

$$Bi_2O_3 + 3H_2SO_4 = Bi_2(SO_4)_3 + 3H_2O \qquad (9)$$

$$(BiO)_2SO_4 + 2H_2SO_4 = Bi_2(SO_4)_3 + 2H_2O \qquad (10)$$

$$2Bi(OH)SO_4 + H_2SO_4 = Bi_2(SO_4)_3 + 2H_2O \qquad (11)$$

$$2Bi(OH)_3 + 3H_2SO_4 = Bi_2(SO_4)_3 + 6H_2O \qquad (12)$$

- Physical transfer process:

$$Bi^{3+}(s) \rightarrow Bi^{3+}(l) \qquad (13)$$

Alkaline oxide compound, oxy-bismuth salt, alkaline bismuth sulfate, bismuth hydroxide, etc. can react with sulfuric acid solution, so that the Bi^{3+} ion leaves the active-material and enters the electrolyte. The soluble bismuth compound (salt of bismuth) can transfer physically from the active-materials into the electrolyte. These transfers of bismuth can produce micro pores in the active-material. The above two mechanisms lead to a higher porosity in the positive active-material. This has also been demonstrated by SEM in other experiments [10], and there

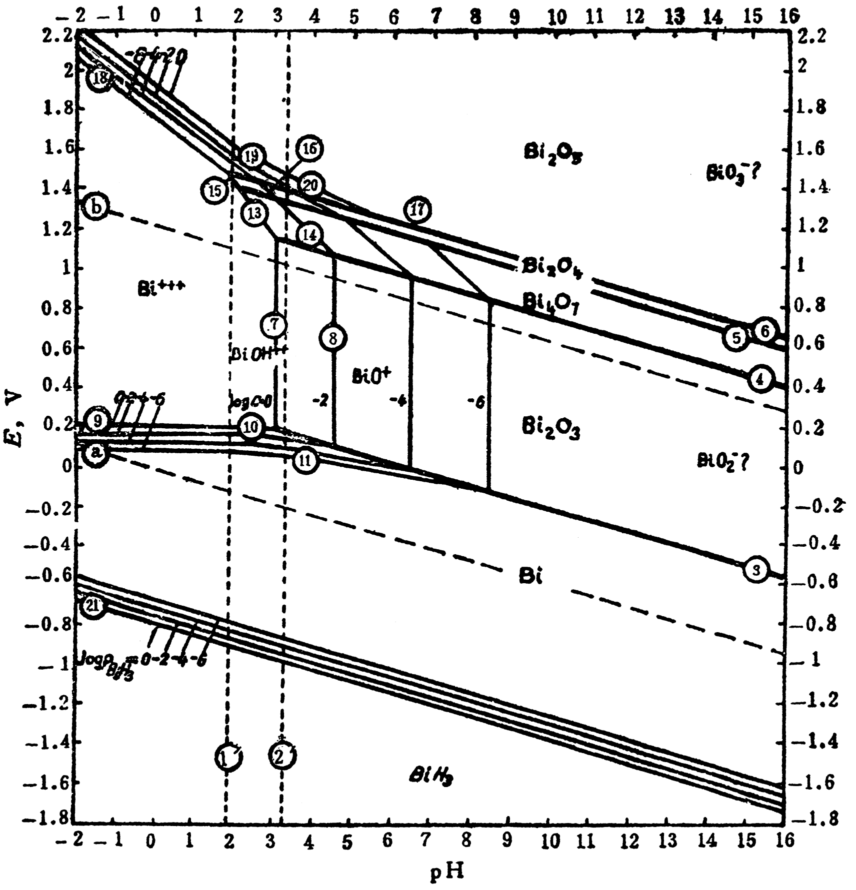

Fig. 11. Pourbaix diagram of the Bi–H_2O system [18].

were more pores in the positive active-material with bismuth than in the negative active-material with bismuth. In Section 3.2, it was pointed out that bismuth has a more effective influence on positive plates than on negative plates. The capacity improvement is determined mainly by bismuth 'pore-creating' in the positive active-materials. This 'pore-creating' effect of bismuth can be applied to explain Dr. Lam's result that bismuth-bearing oxide yielded higher initial capacity and then a significantly faster rise in capacity to the full value with subsequent cycling [3]. After formation, there are more pores in the plates with bismuth than in the plates without bismuth. Especially, transfer reactions (9)–(13) happen violently during the initial cycles, and the number of pores increases rapidly to a full value. After the initial cycles, it is difficult for transfer reactions (9)–(13) to happen, Therefore, the use of bismuth-bearing oxide provides higher initial capacity and attains full capacity more quickly [3].

However, X-ray diffraction experiment shows that increasing the bismuth content results in an increase in the proportion of α-PbO_2.·α-PbO_2 has a smaller surface area and gives less capacity than β-PbO_2. Consequently, β-PbO_2 promotes a greater capacity. From Table 4, the increase of α-PbO_2 and reduction of β-PbO_2 are limited. Perhaps the effect of 'pore-creating' which promotes capacity is more significant than the phase change which reduces capacity.

The 'pore-creating' mechanism can be also used to explain why the percentage utilization of active-material is increased by bismuth [13,14].

4.4. Mechanism of bismuth prolonging cycle-life

According to the SEM results and the X-ray diffraction phase analysis in Section 3.5, the following two factors may be the main reason why the cycle-life of batteries is prolonged by bismuth. First, the amount of the α-PbO_2 phase is increased in the positive plates containing bismuth. Secondly, the needle-like crystals and the 'bridges' of agglomerates in the positive active-material increase with bismuth contents after cycling. In the pores of the active-material, chemical reactions (9)–(12) and electrochemical reactions (1)–(8) may take place. Due to the diffusion of H^+ ion from the electrolyte, there is a decrease of H^+ ion concentration and an increase of pH value in the microprobes. The amount of α-PbO_2 increases with increasing pH value in the microprobes.

It is well known that the structure of α-PbO_2 is stronger and this provides a longer battery cycle-life. α-PbO_2 strengthens the skeleton of the positive active-material and prevents premature capacity loss (PCL) [20]. Though the content of α-PbO_2 decreases during cycling, it still remains in the skeleton of the positive active-material to form a 'backbone' that maintains the integrity of the positive active-material structure [21,22].

As to the change of structure in the positive active-material after cycling, bismuth encourages the growth of fine needle-like crystals to spread out and to form 'bridges' between the agglomerates. This result of needle-like crystals forming 'bridges' supposed by Lam et al. [4] can be used to explain how the presence of bismuth strengthens the positive plates. In addition, the theory of bismuth replacing Pb^{4+} ions in the PbO_2 lattice and the formation of a complex oxide containing Pb^{4+}, Bi^{5+} and O^{2-} ions [3,4] suggests that only part of the bismuth transfers into the electrolyte by means of electrochemical reactions. Bismuth in the solid phase helps to prevent the positive active-material being lost from the grids.

For comparison, 'bridges' formed by needle-like crystals in the positive active-material with bismuth may be the most important factor that prolongs the cycle-life of lead-acid batteries. The increase of the α-PbO_2 content and the formation of new solid matter may be a second important factor for prolonging cycle-life.

4.5. *Mechanism of bismuth reducing water loss*

According to the Tafel formula, the value of '*a*' for lead is 1.56, the value of '*a*' for antimony is 1.00, and the value of '*a*' for bismuth is 0.84. So bismuth should lead to a greater water loss. The catholic polarization curves of negative active-material containing bismuth, and with no bismuth (Fig. 6), confirm that solid bismuth results in a decrease of hydrogen overpotential. This should enhance the water loss of batteries. The same result was obtained with Bi-free grid alloys and Bi-bearing grid alloys [10]. However, Table 1 shows that the water loss is not increased by bismuth doped in lead oxide. Lam et al. [5] and Rice and Manders [9] also found that the VRLA batteries made from Pasminco VRLA Refined oxide (i.e. Bi-bearing oxide) had a less water loss and a lower rate of self-discharge. Zhu [14] introduced the sulfuric acid solution with Bi^{3+} ion into the starter batteries (12 V/105 A h) which were made with Pb–Sb 3.5 wt.% grid alloys. The water loss was reduced by the presence of the Bi^{3+} ion the in electrolyte. The presence of Bi^{3+} ion in solution may be the key factor for affecting water loss. Fig. 7 shows an opposite experiment result to Fig. 6. The difference may depend on whether the bismuth is present in the solid phase on in solution (as Bi^{3+}). In Section 4.3, it was suggested that, chemical reactions (9)–(12) and physical transfer (13) cause Bi^{3+} ion to exist in the electrolyte. Table 3 also indicates that there is Bi^{3+} ion in the electrolyte. The effect of Bi^{3+} ion in the electrolyte a leads to reduced water loss in the battery.

In addition, the above discussion can be used to explain the reason why bismuth enhances the charge-acceptance capability. Bi^{3+} ion in the electrolyte results in an increase of hydrogen overpotential and oxygen overpotential. It reduces the electricity consumed for hydrogen evolution and oxygen evolution. Then there is more electricity available for charging the active-material. Thus, the charge-acceptance capability is promoted by the effect of bismuth.

5. Conclusion

The performance of automotive and motorcycle batteries prepared from bismuth-bearing lead oxide and bismuth-free lead oxide has been tested and compared. The results prove that bismuth in lead oxide is a beneficial element for lead-acid batteries. The electrochemistry technique, chemical analysis and physical methods are used to study the effect and mechanism of bismuth doped in lead oxide on the performance of lead-acid batteries. The forms in which the bismuths oasis are the chemical characteristics and the electrochemical reactions of bismuth during manufacturing and using process of lead-acid batteries have been demonstrated clearly and appear to be suitable for explaining the phenomenon of bismuth in lead-acid batteries. A new concept 'pore-creating' of bismuth presented in this paper can elucidate the mechanism of improving capacity and percent utilization. The growth of needle-like crystals and the change of phase composition caused by bismuth play an important role in prolonging cycle-life. Moreover, this paper has addressed the effects of Bi^{3+} ion on water loss and charge-acceptance.

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