

Study of passivation at the positive active material/grid interface in lead–acid batteries

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Abstract

A valuable additive — boric acid — to eliminate passivation of the active material/grid interface in positive plates of lead–acid batteries has been selected through comparison of single-cell discharge tests. This overcomes the problem of rapid decline in initial performance when using low-antimony (1.7 wt.%) grid alloys. The performance of the oxide film on positive grids, as well as its composition and amount, is determined through cathodic reduction of the film with a linear sweep voltammetric (LSV) method. The results confirm that passivation of the positive grid and rapid decline in the initial discharge voltage are due to a resistive layer of PbSO_4 , and not PbO_n ($1 \leq n \leq 2$). The PbO_n layer has little effect on passivation. The findings of this study are useful for the production of lead–acid batteries. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

The application of low-antimony grid alloys in lead–acid batteries is well-known. In China, the use of dry-charged batteries with low-antimony grids has become more and more popular in recent years. It has been found, however, that a passive layer can form easily between the positive grid and the positive active material [1]. This results in a major problem in that the initial performance of such dry-charged batteries is very poor, i.e., the voltage decreases sharply with a large discharge current after the batteries are filled with sulfuric acid.

The above decline in performance is particularly severe if dry-charged plates are stored for 20 days. Indeed, the voltage of the batteries decreases so rapidly that the initial performance is unable to meet the required standard. In the worst case, the voltage of a single cell dropped to 1 V and the discharge time lasted for less than 1 s. Note that the Chinese National Standard (GB5008.1–93) requires the time for a single cell to discharge to 1 V to be more than 150 s. Traditional products, which are made with high-antimony alloys, discharge for more than 200 s. In this paper,

a series of studies has been performed to understand and overcome the passivation phenomenon at the positive active material/grid interface.

2. Experimental

2.1. Single-cell discharge

For single-cell discharge studies, the dimensions of the positive plates were $143 \times 126 \times 1.45 \text{ mm}^3$ and those of negative plates were $143 \times 126 \times 1.50 \text{ mm}^3$. The single cell was composed of six positive plates and five negative plates with a capacity of 70 Ah ($C_{20}/20$ rate) and a starting current of 275 A (I_s). A cadmium electrode was used as a reference electrode ($E^\circ = -0.402 \text{ V}$). The separators were made from polyvinyl chloride and the electrolyte was sulfuric acid solution with a relative density of 1.285.

2.2. Determination of oxide film on positive grids

A pure lead electrode (99.99%) was used to study the performance of the oxide film produced by anodic oxidation. Practical positive grid electrodes were made from

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Table 1
Discharge performance of unwashed and washed positive plates

Plate type	Storage time (days)	Cell voltage (V) after given discharge time (s)					Plate voltage at 150 s (V)		Time to 1.0 V (s)
		Discharge, 0 s	Discharge, 60 s	Discharge, 120 s	Discharge, 180 s	Discharge, 240 s	Positive plate	Negative plate	
No washing	0	1.82	1.77	1.72	1.65	1.49	2.02	0.34	264
No washing	15	1.56	1.53	1.46	1.36	1.09	1.75	0.35	248
No washing	30	1.43	1.39	1.31	1.20	–	1.58	0.33	237
No washing	45	1.33	1.22	1.17	1.10	–	1.47	0.33	226
Washing	0	1.82	1.76	1.72	1.66	1.51	2.02	0.33	270
Washing	15	1.77	1.69	1.60	1.44	1.11	1.90	0.34	251
Washing	30	1.55	1.51	1.47	1.39	1.07	1.77	0.35	245
Washing	45	1.36	1.33	1.25	1.15	–	1.54	0.33	235

lead–antimony alloys and were taken from lead–acid battery production lines. These electrodes were used to determine the performance of the oxide film formed under actual battery production conditions. The positive active material was removed carefully from each grid to expose the layer formed at the interface.

Electrochemical studies (linear sweep voltammetry, LSV) were performed by means of an EG&G Princeton Applied Research Model 273 potentiostat/galvanostat. The electrochemical cell comprised a working electrode (exposed area 2 cm²) of pure lead or lead–antimony alloy (positive grid), a counterelectrode of platinum foil, and a Hg/Hg₂SO₄/K₂SO₄ (sat.) ‘calomel’ reference electrode. The electrolyte was sulfuric acid solution (1.285 g cm⁻³) with a volume of 250 cm³. All experiments were performed at room temperature.

3. Results

3.1. Discharge of unwashed/washed positive plates

According to the Chinese National Standard, the initial voltage of an automotive battery should be above 9 V

when starting the motor. This means that the voltage of a single cell should not be less than 1.5 V. The results of the discharging of positive and negative plates are listed in Table 1. After storage for 15 days, the voltage of washed plates was higher than that of unwashed plates. After 30 days, unwashed plates are unable to meet the Chinese National Standard. After 45 days, both unwashed and washed plates show no difference in performance — both fail to meet the Chinese National Standard. Therefore, although passivation may be postponed by washing, it cannot be thoroughly suppressed.

According to the voltage at 150 s (Table 1), the values for the negative plates remained steady after being stored for many days. This was not the case for positive plates. Thus, negative plates are not associated with passivation.

3.2. Discharge of washed plates soaked in boric acid

After various tests of additives, it was found that soaking washed positive plates in boric acid solution is an ideal and effective way to restrain the formation of passivation. The procedure was as follows. After being washed to the required pH range, the plates were immersed in solutions with 1 wt.% boric acid for 10 min. The plates were then

Table 2
Discharge performance of positive plates with (A) and without (B) soaking in boric acid

Plate type	Storage time (days)	Initial voltage (V)	Time to 1 V (s)	Plate voltage at 150 s (V)	
				Positive plate	Negative plate
A	0	1.82	287	2.02	0.35
B	0	1.79	270	1.98	0.34
A	20	1.82	282	2.00	0.34
B	20	1.72	270	1.88	0.37
A	40	1.72	253	1.86	0.36
B	40	1.42	235	1.70	0.35
A	60	1.70	242	1.84	0.36
B	60	1.37	230	1.65	0.37

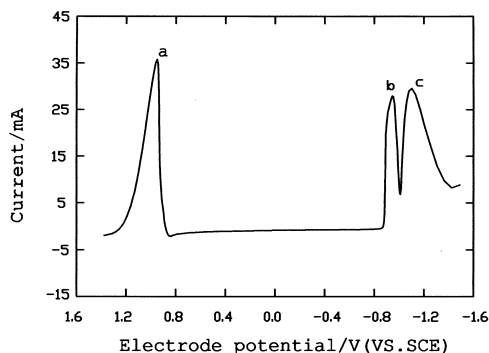


Fig. 1. Voltammetric curve for oxide film on a pure lead electrode.

taken out, dried and stored. Single-cell discharge experiments showed that the starting performance of the treated plates increased (see Table 2). Classifications A and B represent plates after soaking in boric acid solution and with no such treatment, respectively.

The voltage of positive plates soaked in boric acid solution is higher than that of untreated plates. The first discharge performance of the former plates exhibits a marked improvement. In particular, after storage for 40 days, the cell voltage did not decrease appreciably with the starting discharge current.

3.3. Effect of rate of LSV

After being oxidized at 1.3 V for 20 min, the pure lead electrode was reduced at -1.5 V by using LSV. A typical voltammetric curve for the oxide film formed by anodic oxidation is shown in Fig. 1 [2]. The cathodic reduction of the oxide film shows three peaks categorized as follows:

- peak a: reduction of PbO_2 phase;
- peak b: reduction of PbO and PbSO_4 ; and
- peak c: reduction of PbSO_4 phase.

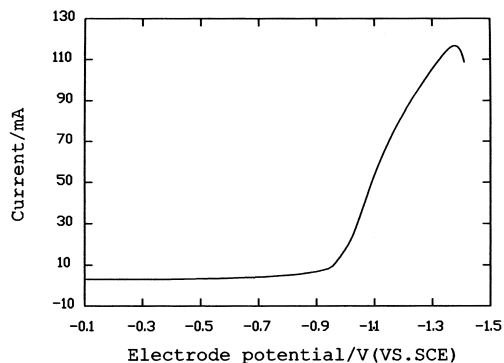


Fig. 2. Rapid voltammetric curve for oxide film on positive grid electrode.

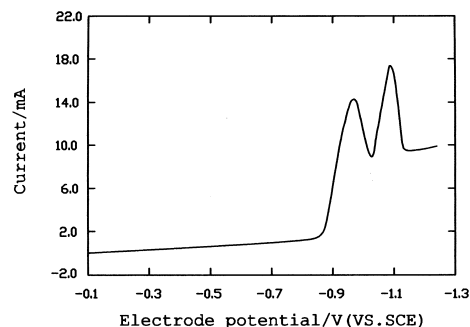


Fig. 3. Slow voltammetric curve for oxide film on positive grid alloys.

The phase composition and the amount of the oxide film can be determined by the number of peaks and the quantity of charge associated with each peak.

The positive grid electrode had a potential of 0.24 V, which is lower than the reductive peak potential of PbO_2 (viz., 1.0 V). This shows that the oxide film on positive grids does not contain a PbO_2 phase. The cathodic reduction curve of the oxide film on a positive grid electrode at 20 mV s^{-1} is given in Fig. 2. There are no obvious characteristic peaks similar to those shown in Fig. 1. Thus, the characteristics of the oxide film cannot be determined from the curve shown in Fig. 2. Cathodic reduction curves for the oxide film on a positive grid were measured at various potential scan rates. It is found that curves similar to Fig. 1 can be obtained when the scan rate is lower than 1 mV s^{-1} . This is because the oxide film on positive grids is too thick to allow each phase to be reduced completely at rapid scan rates. If the scan rate is lower than 1 mV s^{-1} , then the characteristics of the oxide film can be determined via cathodic reduction of the film by using LSV.

3.4. Characteristics of oxide film on positive grids

The cathodic reduction curve for the oxide film formed on a positive lead–antimony alloy grid was obtained at a scan rate of 1 mV s^{-1} (see Fig. 3). The curve shows that the oxide film consists mainly of PbO (including $\text{PbO} + \text{PbSO}_4$) and PbSO_4 phases, but not a PbO_2 phase. This is

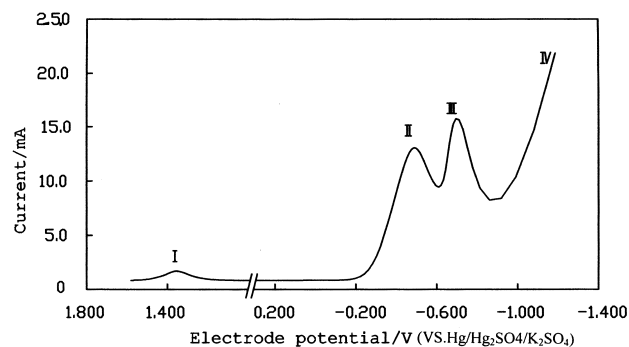


Fig. 4. Voltammetric curve for positive grid alloy.

Table 3
Sequence of PbSO₄:PbO ratio

Storage period (months)	Sequence of ratio			
	Larger	→		Smaller
1	C	A	D	B
2	C	A	D	B
3	A	C	B	D
4	C	A	D	B
5	A	C	B	D
6	A	C	B	D
7	A	C	B	D

an important result. The oxide film on positive grids coated with active materials does not contain PbO₂ through a series of production processes, i.e., paste preparation, formation, washing, drying, storing.

The other positive lead–antimony grid electrodes could be measured by means of the same method. The curves obtained were similar to Fig. 3. Different contents (wt.%) of antimony produced a change in the charge of the cathodic reduction peak, and in the charges of the reduction peaks of the PbO (including PbO + PbSO₄) and PbSO₄ phases.

3.5. Results of LSV

The LSV curve for a positive grid electrode is shown in Fig. 4. Peaks I, II and III correspond to the reduction of PbO₂, PbO (including PbO + PbSO₄) and PbSO₄, respectively. Peak IV represents hydrogen evolution.

Plate samples A, B, C and D were examined after each month of storage. The samples were as follows:

- A: no washing;
- B: washing to pH 3–5;
- C: washing to pH 5–7; and
- D: washing to pH 5–7 and soaking in boric acid.

The sequence of the PbSO₄:PbO ratio is given in Table 3. Unlike the data for both PbO (including PbO + PbSO₄) and PbSO₄, the ratio is regular, i.e., the ratio in A and C is always larger than that in B and D, and is greatest in A and smallest in D. Sample C was washed more completely than B, but its PbSO₄:PbO ratio was larger.

4. Discussion

4.1. Formation conditions of PbSO₄

Many workers claim [3–5] that the passivation layer on the positive plate has a duplex structure, namely: (i) a semi-permeable and resistive layer of PbSO₄; and (ii) a

semi-conducting layer of PbO under the PbSO₄. The latter layer is claimed to be PbO_{*n*} (1 ≤ *n* ≤ 2) [6]. It is also considered, however, to be a mixture of PbO₂ and PbO phases [1]. During storage of the positive plates, the active material and grids may form the positive and negative electrodes of a microcell, if the plates absorb water and contain some sulfuric acid after formation. The reaction of the microcell would be:

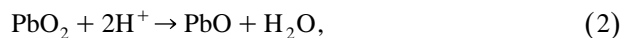


Thus, a resistive layer of PbSO₄ is formed on the positive grid surface. Completely washing out the sulfuric acid inside the plates was difficult, even though there was a prolonged washing process. The pH of the positive plate surface remained at 4–5, even after the plates were washed for 1 h. The pH inside the positive plates would be lower. This may be the reason why the washing method could postpone passivation but could not eliminate it completely. It appears that soaking in boric acid prevents dry-charged plates from absorbing moisture.

4.2. Formation conditions of PbO

The semi-conductor layers at the plate interface are formed by two processes [1]:

(i) liquid-state reaction:



(ii) solid-state reaction, namely PbO, is obtained by reaction of the grid alloy with adjacent PbO₂; the reaction rate is controlled by the rate of oxygen diffusion.

Boric acid may not be sufficiently active to react with PbO. Thus, boric acid has no effect on the process and the formation of PbO takes place. In fact, passivation is eliminated by adding boric acid. Thus, it is concluded that the resistive PbSO₄ layer is responsible for the passivation at the active material/grid interface of positive plates. Although the presence of a PbO semi-conductor layer on low-antimony alloys has been observed by many investigators, it is probably not the main cause of the passivation. This also explains why a PbO or PbO_{*n*} layer has very little effect on the passivation of positive plates. In summary, PbO₂ is a good conductor, PbO is a semi-conductor, and PbSO₄ is a non-conductor.

The discharge performance of unwashed positive plates is the worst, while that of positive plates washed and soaked in boric acid is the best (Table 2). The PbSO₄/PbO ratio in sample A (no washing) is the largest, while the

ratio in sample D (washed and soaked in boric acid) is the smallest. The smaller the PbSO_4/PbO ratio or the PbSO_4 content, the better the discharge performance of the plates.

5. Conclusions

From the above studies, the following conclusions can be drawn:

1. The sharp decrease in voltage of low-antimony batteries is due to passivation between the positive active material and the underlying grid; there is no such effect with negative plates.
2. After washing, positive plates were soaked in 1 wt.% boric acid solution. This is an effective way to eliminate passivation.

3. Formation of a resistive PbSO_4 layer is the main cause of passivation. The PbO_n layer has little effect on passivation, as shown by LSV studies.

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