Electrochemical Behavior of Anodizing Films on Lead and Its Alloys in a Sulfuric Acid Solution

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The behavior of lead dioxides, which are formed on lead and its alloys by electrochemical oxidation in a sulfuric acid electrolyte is clarified. Lead dioxides, electrochemically formed on pure lead and lead-calcium alloys, were found to have a higher reactivity during the electrochemical reduction which produces lead sulfate than those formed on lead-antimony alloys. This behavior was shown to result from a higher content of β - PbO_2 , which is more reducible than α - PbO_2 , in the oxidation layer of lead-calcium alloys than in lead-antimony ones. The capacity loss phenomena of the positive plates comprising pure lead or lead-calcium alloys in lead acid batteries were due to the formation of an electrically resistive lead sulfate layer on the grids during discharge.

1 Introduction

In recent years, lead-calcium alloys have been widely used as the grid material of lead-acid batteries. This is because lead-calcium alloys have smaller self discharge rates than lead-antimony alloys. However, the positive Pb-Ca plates of batteries have a major disadvantage of a comparatively short cycle life during deep cycles. Considerable research effort has been devoted to explaining the beneficial effect of antimony on the cycle life of the positive plate. Burbank¹⁾ reported that antimony inhibits the softening of active materials on the positive plate and stabilizes the plate structure because the concentration of α - PbO_2 in the active materials is maintained at a minimum by antimony.

However, it has now become apparent that the capacity loss of Pb-Ca positive plates is caused by the increase in electric resistance at the grid/active material interface²⁻⁵⁾. Evidence corroborating this was found by Tudor, *et al.*³⁾. They found that PbSO_4 is locally present in the active material near the surface of a Pb-

Ca grid.

However, the formation mechanism of a resistive layer, PbSO_4 , on the surface of Pb-Ca grid has not yet been clarified. This paper clarifies the difference in electrochemical behavior between pure lead, Pb-Ca alloys and Pb-Sb alloys, especially for the formation and reduction of PbO_2 . The relations between the electrochemical behavior of these alloys and the cycle life of positive plates are also discussed.

2 Experimental

Electrochemical measurements were carried out using a potentiostat (Nichia-Keiki, NL 101), a function generator (made in this laboratory), and an X-Y recorder (Hitachi, 056). A disk electrode, 15 mm in diameter, was immersed in the main part of an H-type pyrex cell containing a 4.5 M H_2SO_4 solution. The counter electrode in a side compartment was a platinum net. A reference electrode of $\text{Hg}/\text{Hg}_2\text{SO}_4/4.5$ M H_2SO_4 was placed near the test electrode surface via a Luggin electrode probe.

The test electrodes used were pure lead, binary alloys of Pb-Ca and Pb-Sb, and commercial alloys of Pb-Sb-As-Sn and Pb-Ca-Sn. Pure lead and binary alloys were prepared from high purity metals (Pb: Mitsuwa Chemicals; 99.9999%, Sb: Osaka Asahi Metals; 99.9999%,

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Ca : Soekawa Chemicals; 99.99%) by melting them in a silica glass tube under a vacuum at 800°C. After heating for 2 hours, the alloys were cooled slowly. After molding these metals into an epoxy resin, each electrode surface was mechanically polished with fine alumina powder. They were then chemically etched in a mixed solution of glacial acetic acid and a 30% solution of hydrogen peroxide (1:2 by volume). Prior to electrochemical measurement, specimen surfaces were subjected to cathodic polarization treatment in the measuring cell under -2.0 V for 10 min.

3 Results and Discussion

3.1 Cathodic sweeps after anodic treatment

The Pb or alloy electrodes were oxidized potentiostatically in a sulfuric acid solution to form a PbO_2 layer on the electrode surface. After this treatment, cathodic sweep voltammetry was carried out. Typical traces of cathodic sweeps following anodic oxidation treatment at 1.5 V for 30 min are shown in Fig. 1. The

Fig. 1 Cathodic sweep voltammograms for lead and its alloys after anodic treatment at 1.5 V for 1800 s
Sweep rate: $1 \text{ mV} \cdot \text{s}^{-1}$

Fig. 2 Cathodic sweep voltammograms for commercial alloys

Measuring conditions are same as for Fig. 2

a) : Pb-0.1%Ca-0.5%Sn, b) : Pb-3.5%Sb-0.2%As-0.02%Sn

traces exhibit cathodic peak "C" which corresponds to the reduction of PbO_2 to produce PbSO_4 , followed by an anodic peak. Although, several interpretations were reported for this peak⁷⁻¹⁰, the assignment of this anodic peak is still ambiguous.

It is noteworthy that the height of peak "C" in the Pb-Sb alloy is much lower than the one in pure Pb or Pb-Ca alloy. These differences become still more remarkable with commercial alloys, as shown in Fig. 2. Cathodic peak "C" in a commercial Pb-Sb alloy almost disappears, while the peak in a commercial Pb-Ca alloy is nearly as high as the binary Pb-Ca alloy.

There are two possible reasons to explain why the peak "C" of Sb type alloys is lower than that of the Sb free ones. One is that the amount of PbO_2 formed on Sb alloys is less than that on Sb free alloys or pure lead. The other is that the PbO_2 formed on Sb alloys is less reducible than that formed on Sb free alloys or pure lead.

To clarify these points, the influence of anodic treatment time on the cathodic sweep voltammogram was examined. The cathodic sweep for pure Pb following anodic treatment at 1.5 V for 1 min, as shown in Fig. 3(a), already exhibits

Fig. 3 Effect of anodic treatment time at 1.5 V, on cathodic sweep voltammograms
Sweep rate: $1 \text{ mV} \cdot \text{s}^{-1}$
a): Pure Pb, b): Pb-4.0% Sb

a small cathodic peak "C" overlapping a broad anodic peak. The height of peak "C" increases with treatment time. On the other hand, no cathodic peak in Pb-Sb alloy is observed even after 12 min treatment (Fig. 3(b)). A small peak "C" appeared after 70 min treatment.

This is due either to the difference in the amount of PbO_2 formation or the difference in the properties of the formed PbO_2 in the two cases. To clarify this, the coloration of the electrode surfaces of these alloys during the anodic treatment was compared. We assumed that the color of the electrode surfaces is indicative of the amount of PbO_2 formed on the surfaces. Then the deeper coloration in Pb-Sb electrode after 12 min treatment than in pure Pb electrode after 1 min treatment suggests that more PbO_2 was formed on Pb-Sb electrode than on pure Pb electrode. However, peak "C" for the former electrode was much smaller than that of latter one. Therefore, it can be concluded that the PbO_2 formed on Sb contained alloy is less active against electrochemical reduction than that formed on pure Pb or Pb-Ca alloy.

3.2 Cyclic voltammetry

The difference in electrochemical reactivity

Fig. 4 Cyclic voltammograms for pure lead
Sweep range: $0 \sim 1.6 \text{ V}$
Sweep rate: $5 \text{ mV} \cdot \text{s}^{-1}$
—: Anodic sweeps, ...: Cathodic sweeps
Numeric: Number of cycles

of PbO_2 can be attributed to the distinction in electrochemical properties between α - and β - PbO_2 . Chang, *et al.*⁹⁾ and Visscher¹¹⁾ showed that there are two anodic peaks related to the formation of two types of PbO_2 in the cyclic voltammetry of lead electrodes.

Cyclic voltammograms for pure Pb in the potential range of $0 \sim 1.6 \text{ V}$ are shown in Fig. 4. Two anodic peaks "A" and "B" are observed at 1.1 and 1.45 V respectively on anodic sweeps. The peak current of "A" increases during cyclic treatment until about the 6th cycle. However, it decreases gradually in subsequent cycles. On the other hand, the peak current of "B" increases continuously under the same experimental conditions up to the 12th cycle. In the cathodic sweeps (dotted lines in Fig. 4), complicated cathodic and anodic peaks, similar in shape to the single cathodic sweep in Fig. 2, are observed in the first cycle. This anodic peak in the cathodic sweeps disappears in subsequent cycles, whereas the cathodic peak increases during the cyclic process.

The cathodic peak current of "C" is further influenced by positive reversal potential in cyclic voltammetry. The relation between positive

Fig. 5 Effect of positive reversal potential on cyclic voltammogram for pure Pb
Sweep rate: $5 \text{ mV} \cdot \text{s}^{-1}$
Sweeps were reversed at a); 1.6 V, b); 1.5 V, c); 1.4 V, d); 1.3 V, e); 1.2 V

reversal potential and the peak current of "C" for pure Pb is shown in Fig. 5. The experimental sequence was as follows. After eight potential sweeps between 0 to 1.6 V, the positive reversal potential was successively reduced from 1.6 to 1.2 V in 0.1 V intervals. The peak "C" current decreased in this way, but the variation was fairly small when the reversal potential was higher than anodic peak "B". However, when the reversal potential was below peak "B" (1.3 V), the peak "C" current suddenly decreased to almost zero. Consequently, the cathodic reaction occurring at peak "C" can be attributed to the reduction of PbO_2 which formed at peak "B". Thus, the reduction rate of the PbO_2 formed at peak "A" must be very small. Since $\beta\text{-PbO}_2$ is known to be more reactive in electrochemical reduction than $\alpha\text{-PbO}_2$ ^{7,12}, peaks "A" and "B" correspond to the formation of α - and $\beta\text{-PbO}_2$ respectively.

The traces of anodic sweeps during cyclic voltammetry in the potential range of 0 and 1.6 V for Pb-Ca and Pb-Sb alloys are shown in Fig. 6 (traces of cathodic sweeps are omitted

Fig. 6 Cyclic voltammograms for binary alloys
Trace of cathodic sweeps are omitted
Sweep rate: $5 \text{ mV} \cdot \text{s}^{-1}$
a): Pb-0.09% Ca, b): Pb-4.0% Sb

Fig. 7 Change in peak current "A" during sweep cycles for various alloys
○: Pure Pb, △: Pb-0.06% Ca
▲: Pb-0.09% Ca, □: Pb-1.3% Sb
■: Pb-2.5% Sb, ◆: Pb-4.0% Sb

from the figure). The peak "B" currents, *i.e.* formation of $\beta\text{-PbO}_2$, increase for both alloys with cycles, whereas peak "A", *i.e.* formation of $\alpha\text{-PbO}_2$, exhibits a different behavior for these alloys. To gain more systematic information, the variations in peak "A" current during cycles for various alloy compositions are shown in Fig. 7. The peak currents for the Pb-Sb

alloys increase with cycles. The increasing rate becomes larger when the Sb content increases. On the other hand, the peak current for Pb-Ca alloys and pure Pb reach a maximum value at about the 6th cycle and then gradually decrease with further cycles. Thus the pattern of peak current variation was almost independent of the Ca content in alloys.

It seems likely that α -PbO₂ formation is enhanced by Sb presence in Pb alloys. This effect of Sb can also be verified by X-ray diffraction. The diffraction patterns of PbO₂ formed on pure Pb and Pb-Sb alloy by anodic oxidation are shown in Fig. 8. The peak intensity ratios of α -PbO₂ (111) to β -PbO₂ (101) formed on pure Pb and Pb-Sb alloy are 1.4 and 2.6 respectively. This indicates α -PbO₂ is easily formed on an Sb alloy. One reason for this Sb effect may be the formation of a complex Pb and Sb oxide eg. PbSb₂O₆, which has acted as a nucleus for α -PbO₂ crystal growth⁹. However, no evidence of PbSb₂O₆ presence was detected by X-ray diffractometry.

It can be concluded from these results that Sb in a Pb alloy leads to an increase in α -PbO₂ in the oxidation layer. The decrease in the reducibility of the oxidation layer on a Pb alloy by Sb presence, shown in Fig. 1, can therefore be attributed to the increase in α -PbO₂ in the oxidation layer. To make these relationships clearer, the dependence of the α -PbO₂ amount in oxidation layers and of their reducibility on Ca and Sb content in Pb alloy are shown in Fig. 9. Curve A is the plot of anodic peaks "A" at the 12th cycle in cyclic voltammograms (cf. Fig. 4), indicating the α -PbO₂ amount in the oxidation layer. Curve C is the plot of cathodic peaks "C" in cathodic sweep voltammograms (cf. Fig. 1), indicating oxidation layer reducibility. Thus reducibility of the oxidation layer decreases with the increase of α -PbO₂ in the oxidation layer as can be seen in Fig. 9.

The results for oxidation layer reducibility on commercial alloys of Pb-Sb-As-Sn and Pb-Ca-Sn are also shown in Fig. 9. Extremely small reducibility is exhibited by the oxidation layer on the commercial Sb alloys. On the other hand, the reducibility for the commercial Ca alloys is nearly the same as for Pb-Ca binary alloys. The decrease in reducibility for the

Fig. 8 X-ray diffraction pattern of oxide films on (a) Pb and (b) Pb-4.0% Sb
Anodic treatment: 1.3 V, 17000 s
(1) α -PbO₂ (111), (2) Pb (111)
(3) β -PbO₂ (101)

Fig. 9 Change in peak currents with Ca and Sb contents

A(▲): Peak "A" at the 12th cycle of cyclic voltammetry
B(●, ○): Peak "C" of cathodic sweep voltammetry after anodic treatment
▲, ●: Binary alloys
○: Commercial alloys

former alloys is probably caused by the enhancement of α -PbO₂ formation by As, but not by Sn. This is because Sn in the latter alloy had no effect on reducibility.

We then attempted to interpret the capacity loss phenomena of the positive plates comprising

pure Pb or Pb-Ca alloys in lead acid batteries as follows. Formation of PbO_2 layers on the grid surface of the positive plates proceeds during the initial forming and succeeding recharging steps of the battery. When pure Pb or Pb-Ca alloys is used as a grid material, the β - PbO_2 content in the oxidation layer will become greater than when using Pb-Sb alloys. Therefore, the reduction of PbO_2 to PbSO_4 in discharging on the former grids (β - PbO_2) can occur more easily than on the latter ones (α - PbO_2). Consequently, more PbSO_4 is formed on the Pb or Pb-Ca alloy grid surface than on the Pb-Sb alloy grid. This retards the discharge process because PbSO_4 has poor electrical conductivity.

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会員のページ

第5回 IS,I (フローレンス市) に出席して

International Symposium on Solute-Solute-Solvent Interactions (通称 IS,I) というひどく長い名前の国際会議が第5回を迎えて、今年の6月2日から5日間、イタリアのフローレンスで開かれた。読んで字のごとく、溶液中の分子間相互作用のすべてが会議の対象となるので、含まれる領域は無機、分析、有機、物理化学、生物化学など、きわめて広範囲である。次回が1982年に日本(大阪、箕面市)で開かれることもあって、日本からの参加者も多く、田中(信)(東北大理)、田中(元)(名大理)、田伏(京大工)、上平(繊維高研)氏など10

名以上の顔ぶれが揃った。50ヶ国近い国から600名を超える参加があり、花の都フローレンスの国際会議場で、口頭、ポスターの2本建てにより約300報の論文が発表された。

次回主催の代表として田中信行教授がバンケットであいさつをされたが、ポーランドのツェビアトフスカ教授のご指名で、私も話をさせられた。フローレンス風の数々の料理にお腹を一杯にし、色とりどりのワインに頬を火照らせて、フローレンス市郊外の丘の上のバックケット会場をいつまでも去らず、人々は次回の箕面市での再会を約したものである。

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