Understanding the Beneficial Action of Organic Activators for the Negative Electrode of Lead-acid Batteries

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Abstract

Most of the additives or activators used today for the negative electrode of lead-acid batteries are fine power of solid materials such as barium sulphate, lignin and carbon black. They are generally called as expander. We found that organic compounds soluble in the acid electrolyte are very effective in order to extend the cycle life and improve the discharge capacity. This paper describes the recent improvements and the working mechanism for the soluble organic activators.

Keywords

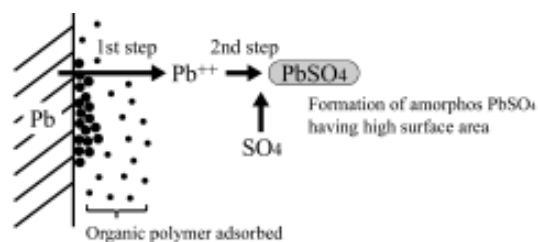*negative electrode, organic activator, organic polymer, charge, discharge, $PbSO_4$*

1. INTRODUCTION

We previously published our findings of the beneficial action of organic polymers with or without fine carbon. [Kozawa et al., 1999; Kozawa et al., 1997; Kozawa et al., 1998] The main beneficial action is recovery from sulfation and high rate capability of the regenerated batteries. Many electroplating system uses organic additive to produce smooth bright deposits for various metals, tin, copper etc. Our organic activator for lead-acid battery would be similar in the working mechanism. Fine lead is produced with our activator. We propose our explanation for the production of fine active lead in the negative electrode.

2. ELECTROCHEMICAL PROCESSES AT THE NEGATIVE ELECTRODE

Figure 1 shows the two steps involved in the discharge of negative electrode. In the first step of the discharge, lead ions (Pb^{++}) are produced on the electrode surface. The lead ions diffuses passing through the adsorbed zone of organic activator layer to the bulk solution. Then the lead ion combines with sulphate ions in the 2nd step to produce PbSO4. Because of the organic polymer layer, the Pb^{++} ions con not diffuse out rapidly to the bulk so-

lution and the Pb^{++} concentration become much higher than the solubility of $PbSO_4$ in the 10 N H_2SO_4 electrolyte (s.g. 1.28), which is the normal lead-acid battery electrolyte. When precipitation of $PbSO_4$ takes place in the concentrated solution, the $PbSO_4$ is amorphous and prous and it has a high surface area. The high surface area $PbSO_4$ is easy to dissolve upon discharge and provide an active (high rate) electrode. If the $PbSO_4$ is crystalline and the surface area is low, it is slow to dissolve and the electrode discharge capability is poor.

1st step: Pb → Pb^{++} + e⁻ (Electrochemical step)
2ns step: Pb^{++} + SO₄⁺⁺ → PbSO₄ (Formation of PbSO₄, chemical step)

Fig. 1 Discharge process of the negative electrode

Both the 1st step and the 2nd step are influenced by the soluble organic polymer activators adsorbed on the electrode or on the $PbSO_4$ surface.

Figure 2 shows the charge process again consisting of two steps. These two steps are influenced by the adsorbed organic polymer molecules. In the presence

of organic polymer molecules, the produced lead is fine particles as reported previously. Finer lead seem to provide much better high performance electrode.
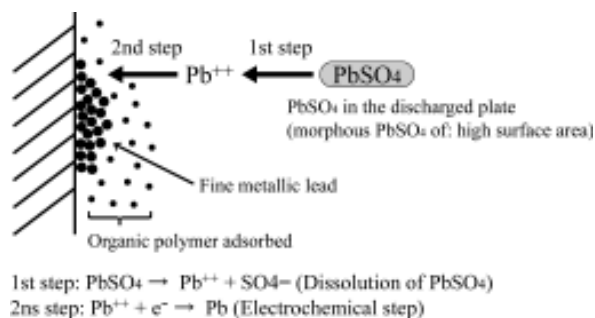

1st step: $PbSO_4 \rightarrow Pb^{++} + SO4=$ (Dissolution of $PbSO_4$)

2ns step: $Pb^{++} + e^- \rightarrow Pb$ (Electrochemical step)

Fig. 2 Charge process of the negative electrode

3. EXPERIMENTAL RESULTS OF PRACTICAL BATTERIS

40 B Type car battery (28 Ah at 5 HR) made by a Japanese company (P-Company) were used for activator tests since this battery is top quality in Japan. Figure 3 are 2
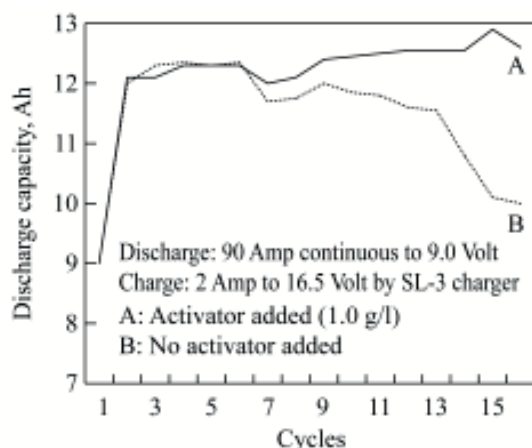

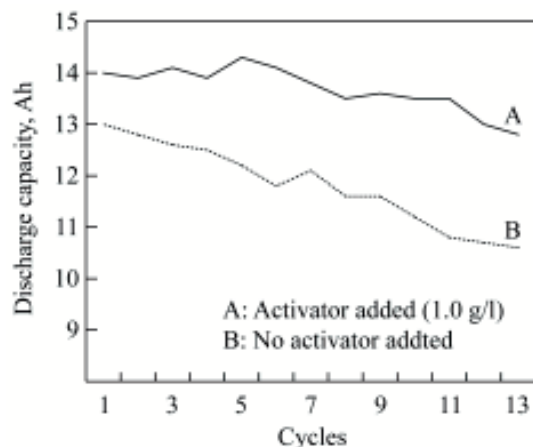**Fig. 3** Car battery (40 Ah, 40 B type, 28 Ah at 5 HR) test with and without activator (organic polymer)

Fig. 4 Car battery cycles (40 B, one year old) tested for activator on the same condition as Figure 3
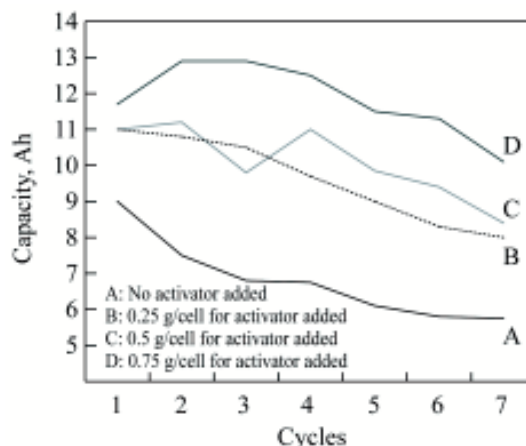

Fig. 5 Effect of organic activator for 40 B type imported battery. See Figure 3 for the charge-discharge conditions.

year (or 40,000 km) guarantee battery and Figure 4 are one yeay (or 20,000 km) guarantee battery. Figure 5 are batteries (40 B) made in Asian countries and imported to Japan. The charge-discharge conditions are described in Figure 3. With our activator (organic polymer compound) the battery capacity gradually increased from 8 to 16 cycles, as seen in curve A of Figure 3. Without activator addition the battery capacity at 90 Ampere discharge decreased as shown in curve B of Figure 3, 4, and 5. Based on these results of Figure 3, 4, and 5 future work conditions are summarized in Table 2.

For one year old batteries (one year guarantee), the discharge capacity decreased slowly as the cycle advanced as shown in Figure 4. These batteries are hybrid type (ca-alloy grid for negative plate and antimony type alloy for positive grid). The Figure 4 is 2002 products and Figure 3 was 2004 products. It seems the effect of

Table 1 Summary of facts for 90 A discharge tests with and without organic activator

(1) With organic activator in the acid electrolyte
    (a) Discharge capacity increase initially
    (b) Discharge capacity decrease slowly
    (c) IR drop is larger (These (a) and (b) lead to cycle lite increase)

(2) Without organic activator in the acid electrolyte
    (a) Discharge capacity decrease faster than those with activator
    (b) IR drop is smaller.

(3) For some batteries, the effect of organic activator does not show for the first 10 to 12 cycles. For some batteries, the activator effect is very large.

Table 2 List of future work area and test conditions

(1) Search for new effective organic compounds
(2) Effect of temperature (activation at 25C, 35C, 45C etc.)
(3) Concentration of activator (0.25, 0.50, 0.75, 1.0 g per cell for 50, 100, 150 Ah battery)
(4) Test current effect, 10A, 20A, 50A, 100A, 150A continuous discharge to 9 Volt and charge for 10-200 cycles
(5) 25%, 50%, 75%, 100% depth discharge test with and without activator at 25C and 45C
(6) Charge conditions (charge current and voltage of end of charge: 15.0, 15.5, 16.0, 16.5 volts etc.)

active material is different for the two battery set even though the battery were made by the same manufacture. One important point is that with the organic polymer activator the discharge capacity increased gradually as seen in curve A of Figure 3. The capacity increase means more active material was produced by the battery reaction within the battery when repeated charge-discharge operations are given.

4. CHEMICAL AND ELECTROCHEMICAL PROCESSES INFLUENCED BY THE CONCENTRATION AND ORGANIC ADDITIVES

It is well known that various metal plating process uses organic additives in order to produce bright plating (to make a shinny surface). Without organic additives, tin sulphate solution can not produce smooth deposit (satin finish), but when a certain organic compound is added to the $SnSO_4 + H_2SO_4$ solution, good smooth deposit is produced. Organic polymers are often used in order to avoid needle like deposit. Figure 6 shows summary of the metal deposit process. In the chemical precipitation process (Figure 7), the size of the deposit depends on
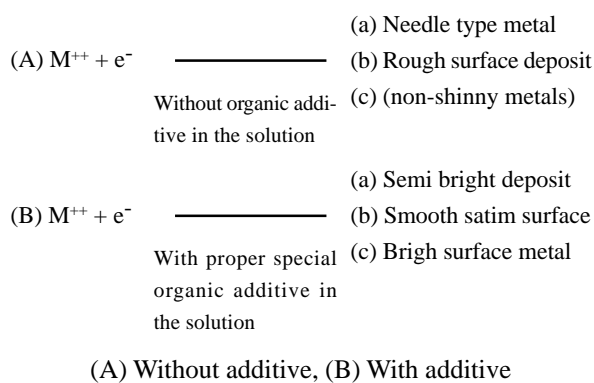
(A) $M^{++} + e^-$ ———— (a) Needle type metal
(b) Rough surface deposit
Without organic additive in the solution
(c) (non-shinny metals)

(B) $M^{++} + e^-$ ———— (a) Semi bright deposit
(b) Smooth satim surface
With proper special organic additive in the solution
(c) Brigh surface metal

(A) Without additive, (B) With additive

Fig. 6 Metal deposition on metal plating from aqueous solution with and without organic additive
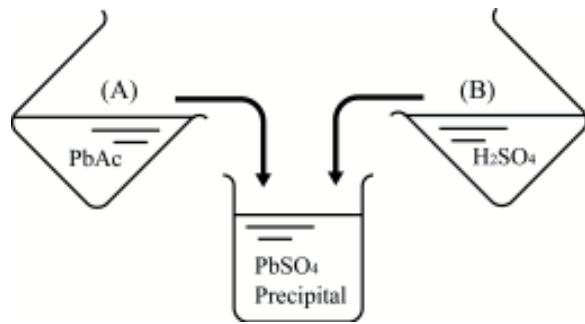
Precipitation products depend on the concentration of (A) and (B) and presence or absence of organic additive and speed of mixing.
Precipitate vary from colloidal solution to crystalline material.

Fig. 7 Chemical precipitation process

the concentration of the two components. Figure 7 shows precipitation of $PbSO_4$ from PbAc solution and sulfuric acid. If the two mixing solution is very dilute and the two solutions were mixed very slowly, the produced $PbSO_4$ is crystalline large size precipitate. If the concentrated solutions were mixed rapidly the precipitate are very fine. Sometimes a colloidal solution is produced.

5. EFFECT OF CHARGE-DISCHARGE CURRENT DENSITY

Figure 8 shows effect of the charge or discharge current for the particle size of the $PbSO_4$ or Pb particles in the battery electrode pictorial schematics. These results indicate charge and discharge current density influence the electrode materials for the electrode. In order to examine the effect of organic activator, we need a series
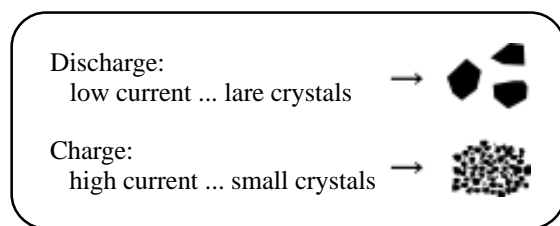

Fig. 8 Pictorical presentation of deposit size ($PbSO_4$ or Pb)

of current densities for the tests.

6. DISCUSSION AND SUMMARY

Our trial of soluble organic activator for lead-acid battery is a new approach compare to the traditional addition of solid powder expander.
Soluble organic polymers are found to be very effective activators as shown in Figure 3, 4, and 5. The effectiveness continued more than one year, sometimes their ben-

eficial effect continues more than 3 years. The best example is 200 trucks tested for 8 years without battery change [Kozawa et al., 2002].

The scientific reasons of the activator are increase in the hydrogen over voltage [Sugawara et al., 2003] similar to the effect of the additions for metal plating solutions.

Since the discharge and the charge process involves a chemical precipitation steps, the particle size of $PbSO_4$ and Pb (lead) are greatly influenced by the discharge and charge current dencity applied.

Adsorption of organic activator (usually polymer) molecules on the lead or $PbSO_4$ surface has influence the electrode reaction. It should hinder the current flow and IR drop may be increased. These details should be studied further. Table 2 shows summary of future research areas.

In the history of lead-acid battery, manufactures tried to produce best lead powder (PbO_x) for the battery production. These oxides are converted to Pb or PbO_2 by formation. The size and shape are greatly influenced by the precipitation condition upon charge and discharge and by presence of soluble organic material (activator). Therefore, we have to re-examine the battery system based on soluble organic activator materials.

We believe lead-acid battery life can be extended 5 to 10 years if properly used with soluble organic activators and proper current density is used for reactivation. This means we can reduce the waste battery substantially to 1/5 to 1/10 of the current situation. This will contribute greatly to our environment. Lead-acid batteries are inexpensive and very useful for trucks, busses, and cars, and therefore this battery system will remain long time even the system use toxic materials (Pb and H_2SO_4).

Current production is $25 billion (U.S. dollars) but it will be 10 times in 20 years from now since China, India etc.will use trucks, bussed and cars more.

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