High Rate Discharge for Removing the Antimony Effect of the Lead-acid Batteries for EVs

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Abstract

Antimony is known to be present in the grid alloy of the positive electrode of lead-acid batteries. The antimony dissolves slowly into the electrolyte and moves to the negative electrodes and deposits as a metal. This will change the charge efficiency since water electrolysis takes place. We found that a high rate discharge such as 50-80 A for 40B battery makes the dissolved antimony ions become a part of the $PbSO_4$ and the negative effect of antimony is reduced after a few charge and discharge operations.

Keywords

lead-acid battery, antimony, sulfation, lead sulfate

1. INTRODUCTION

Antimony (Sb) is known to be present in the grid alloy of the positive electrode of lead-acid batteries. Sb dissolves slowly into the electrolyte during charge-discharge cycles and moves to the negative electrodes and deposits as a metal by charge period. Sb is well known as one of the metals having a low hydrogen evolution over-voltage such as the platinum [Kameyama, 1953]. This will change the charge efficiency since water electrolysis easily takes place.

We found that a high rate discharge such as 50-80 A for 40B battery makes the dissolved antimony ions become a part of the $PbSO_4$ and the negative effect is almost completely removed after a few charge and discharge operations.

2. EXPERIMENTAL

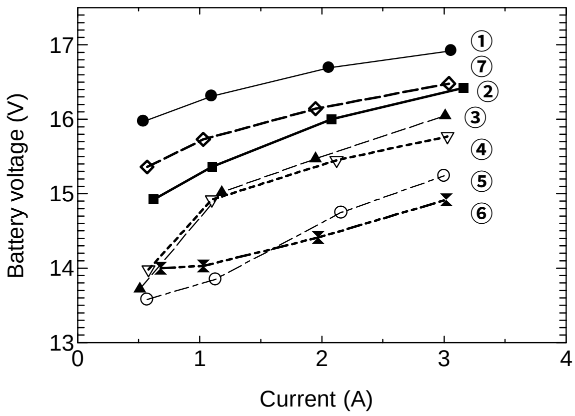
Seven deteriorated lead-acid batteries (NO1-NO7) were collected from gas stations in Nagoya. New battery (NN) of the same type were purchased and used for comparison. Current-voltage (I-E) curves of all the batteries were measured after full-charge and full-discharge until 9.0 V. The content of Sb in the electrolytes of each battery was measured by the method described in another report [Ikeda et al., 2003].

To clarify the effect of Sb to the lead-acid batteries, three experiments were carried out. One is the addition of Sb ions by $SbCl_3$ or Sb_2O_3 to the new battery were carried out and I-E curves were taken after several charge-discharge cycles using a conventional potentio-galvano-stat (Hokuto Denko, HA303). Another is replacement of the electrolytes of a used deteriorated battery with new 5 M H_2SO_4 electrolyte after full-discharge. In the further experiment, the battery was given a very high rate discharge through an parallel set of Ni-Cr resistance wires to dislodge the Sb particles from the lead surface of the negative electrode.

3. RESULTS AND DISSCUSSION

3.1 Sb addition to battery electrolyte

Figure 1 shows the I-E curves of the 40B type battery (28 Ah at 5 h). Curve 1 is that of a new battery as is. Curve 2 is that measured after 55 ppm of Sb is added to the electrolyte of the new battery. Curve 3 is after one hour standing of the battery taken Curve 2. Curve 4 is taken after addtition of additional 102 ppm of Sb (total 157 ppm). Curve 5 is after one hour standing from Curve 4. Standing the battery for a while, the added Sb diffused into the electrode stacks and the effect of Sb on I-



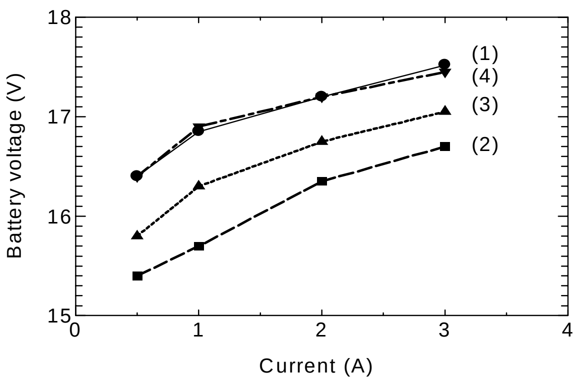
(1) New battery charged as is.
(2) After Sb addition (55.14 ppm).
(3) After one hour standing from Curve 2.
(4) After additional 109 ppm of Sb was added.
(5) After one hour standing from Curve 4.
(6) After charge by SL-3 charger for 12 hr.
(7) After discharge at 15 A and charge by SL-3 charger for 24 hr.

Fig. 1 Effect of Sb addition to the electrolyte and 15 A discharge was examined using 40B type new battery

E curves become significant as shown this figure. Curve 6 is that taken after charge by SL-3 charger for 15 hours. It does not change the profile from that of Curve 5. Curve 7 is after discharge at 15A, and has recovered the performance of I-E as the new one. It is shown that charge operation does not improve the I-E performance, i.e. reducing the Sb effect, but discharge may reduce the bad effect of Sb on lead-acid battery charge, namely may increase the hydrogen evolution over-voltage.

3.2 High rate discharge

Figure 2 shows the I-E curves of the 40B type battery (28 Ah at 5 h). Curve 1 is that of a new battery as is. Curve 2 is that measured after 102 ppm of Sb is added to the electrolyte of the new battery. Curve 3 is taken after one discharge and charge cycle of the Sb added new battery. Curve 4 is that taken after additional two cycles of discharge at ca. 55 A to 9.0 V and charge by SL-3. Curve 4 shows almost the same profile as that of the new battery as is. Therefore, it is thought that Sb ions added into the electrolytes is reduced to metallic Sb and deposited to the negative electrode surface during the charge state. Metallic Sb is thought to reduce the hydrogen over-voltage of the electrode. However, the effects of Sb disappeared by several cycles of high rate discharge. It is thought that the deposited Sb may be incorporated into lead sulfate layer by high rate discharge. During high rate continuous tests, it was noticed that the charge voltage returns to higher values and the bad effect of Sb disappears after 3 or 4 high rate charge-discharge cycles.



(1): New battery as is, (2): Sb of 102 ppm is added to the electrolyte, (3): After one discharge and charge cycle, (4): After additional 2 cycles of discharges and charges. Discharge was done at ca. 55 A to 9.0 V.

Fig. 2 Current-voltage curves of 40B type battery (28 Ah at 5 hr)

3.3 Closed circuit voltage tests

A typical engine starting test for the condition of a car or truck battery is to measure the closed circuit voltage (CCV) after 5 s discharge at 150 A. Figure 3 shows the CCV for new 40 Ah and 55 Ah batteries at 75 A, 150 A, and 300 A. The batteries show good performance even at 50% of their rated capacity. Figure 4 shows the results for a similar test on discarded old 55 Ah batteries after full charge. Old batteries can deliver enough high starting current even at 20% of their rated capacity. This means 150 A - 5 s test is not sufficient for judging the battery life. Even at the low capacity, the battery starts the engine if it is fully charged. [Tachibana et al., 2003, Sugawara et al., 2003]

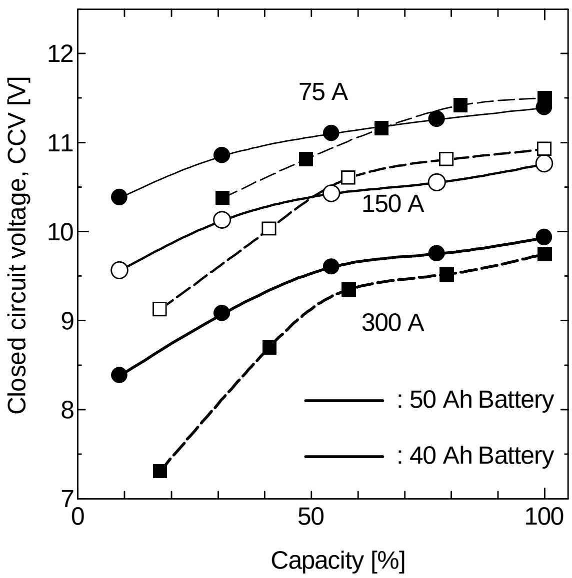


Fig. 3 Closed circuit voltage (CCV) after 5 s discharge at 75 A, 150 A, or 300 A of new 40 Ah and 55 Ah lead-acid batteries

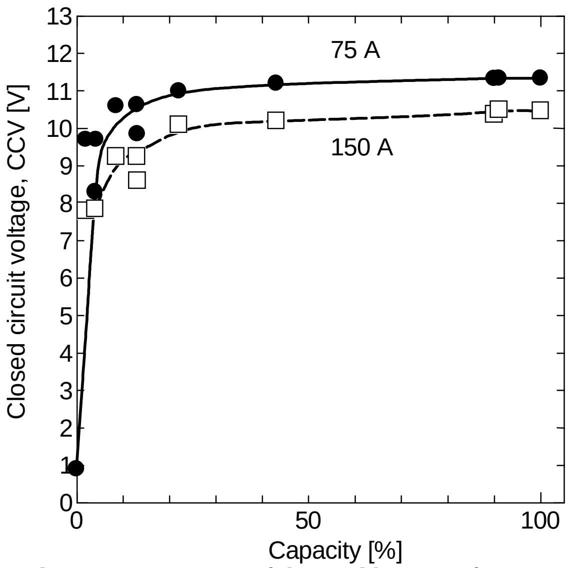


Fig. 4 Closed Circuit Voltage (CCV) curves of the used batteries from a taxy company. CCV are at the end point of 5 s discharge

4. CONCLUSION

During high rate continuous tests, it was noticed that the charge voltage returns to higher values and the bad effect of Sb disappears after 3 or 4 times high rate discharge-charges. Probably Sb may occluded or incorporated into the $PbSO_4$ crystals which are the products on the electrodes during the discharge.

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