Journal of Asian Electric Vehicles, Volume 1, Number 2, December 2003

Dissolution of Antimony into the Lead-acid Batteries' Electrolyte for EV Applications

Shoichiro Ikeda [1], Yoichi Mori [2], Masunobu Maeda [3], Shigeyuki Minami [4], and Akiya Kozawa [5]

[1] Graduate School of Engineering, Nagoya Institute of Technology, ikedas@nitech.ac.jp
[2] Graduate School of Engineering, Nagoya Institute of Technology, r15ach01@edsys.center.nitech.ac.jp
[3] Graduate School of Engineering, Nagoya Institute of Technology, maeda@ach.nitech.ac.jp
[4] Department of Electrical Engineering, Osaka City University, minami@elec.eng.osaka-cu.ac.jp
[5] ITE Battery Research Institute, kozawa-akiya@mwb.biglobe.ne.jp

Abstract

EV batteries use Sb-Pb alloy for the grid of the Lead-Acid batteries. EV batteries need a high rate discharge, and some antimony will dissolve into the electrolyte. In this study current-voltage (I-E) curves were studied when some antimony was dissolved. A simple method for chemical analysis of the antimony (1 to 10 ppm) in the battery electrolyte (28% or 5M H_2SO_4) was established. The Sb concentrations of the electrolyte before and after the charge were measured. The relation of the antimony concentration and the I-E curve was established. This relation will allow us to make a good judgment for the negative electrode efficiency.

Keywords

lead-acid battery, antimony, sulfation, lead sulfate, hydrogen over-voltage

1. INTRODUCTION

It is well known that antimony, Sb, is used in the grid alloy of positive electrodes of lead-acid batteries to improve the strength and durability. The Sb content is between 2% and 5% by weight. However, Sb slowly dissolves chemically from the positive electrodes in sulfuric acid and difuses to the negative electrode where Sb is deposited. Sb is one of the metals having a low hydrogen evolution over-voltage. The easy evolution of hydrogen at the deposited Sb sites during charging period causes the shortage of reduction of lead sulfate to lead metal sulfation of lead acid batteries to forming a large grain of lead sulfate by insufficient charging. Therefore, it is important to know the amount of dissolved Sb in the electrolyte of the lead-acid batteries to prevent the sulfation. Rhodamine B is well known as the reagent for the cholorimetric analysis of Sb as shown in the JIS K0102, which is provided as testing methods for industrial wastewater. [*Japanese Industrial Standards*, 1998] However, the procedure for Sb analysis is rather complex to use for field analysis or for consumers who are not familiar with handling chemical reagents. We have developed a convenient determining method of the Sb concentration in the electrolyte solution of lead-acid batteries.

2. MATERIALS AND METHOD

2.1 Materials

Rhodamine B ($C_{28}H_{31}ClN_2O_3$) is purchased from Tokyo Kasei Kogyo Co.,Ltd. (TCI). Diisopropyl ether, cerium (IV) tetra-ammonium sulfate $Ce(NH_4)_4SO_4$ (2-hydrate), hydrochloric acid (HCl), antimony (III) oxide (Sb_2O_3), and sulfuric acid (H_2SO_4) of guaranteed reagent grade are purchased from Kishida Chemicals. The stock solution of Sb was made by dissolving Sb_2O_3 in 5 M (1 M = 1 mol/dm^3) H_2SO_4.

2.2 Analysis

The standard Sb solution was also made from Sb_2O_3. A spectrophotometer of Shimadzu UV-120-02 was used to measure the absorbance of the test solutions.

One mL of the test solution of practical lead-acid batteries or 5 M H_2SO_4 solution containing the known concentration of Sb is sampled into a separating funnel. Concentrated HCl of 5 mL and 5 mL of distilled water are added to the funnel, then the funnel is shaking well for a while. The color of the solution becomes pale green. 0.5 mL of 1 M $Ce(NH_4)_4SO_4$ solution was added and mixed well to oxidize Sb3+ in the solution and then the solution was rest for 5 min (The color became yellow.). Diisopropyl ether of 5 mL was added to the funnel. Then shaking well with releasing the evolved gas frequently for 2 min. After resting to separate the solution to two phases, the water layer was released. The ether phase was added with 5 mL of 0.5 M H_2SO_4 solution containing 0.02 % of rhodamine B and then shaken to develop the color with releasing gasses. The absorbance of the ether solution was measured at 553 nm.

2.3 Charge and discharge operation

Seven deteriorated (used) lead-acid batteries were collected from gas stations. One new battery of the same type was purchased and used for comparison. The current-voltage curves of all the batteries were measured after full-charge using an SL-3 charger without a special voltage regulation system (DAIJI Industry Co.,Ltd., Osaka) and full-discharge until 9.0 V using Ni-Cr resistance wires (EV Meltech, Co.,Ltd., Kyoto) [Mori et al., 2003]. The Sb content of their electrolytes was measured after full-charge and full-discharge.

3. RESULTS AND DISSCUSSION

3.1 Sb content

The analysis method for Sb according to JIS K0102 [*Japanese Industrial Standards*, 1998] uses a mixture of nitric acid and sulfuric acid to dissolve Sb in the sample. In the analysis for the electrolyte of lead-acid batteries Sb has been already dissolved so this procedure may be eliminated. However, if eliminate the addition of HCl to the test solution, the coloring did not occur after addition of rhodamine B solution. The shortage of water also caused insufficient separation between the ether and water layers. The addition of rhodamine B solution required discarding of water layer, otherwise the coloring of the ether layer did not occur.

Figure 1 shows the calibration curve for the proposed method. Therefore, it is found that the content of Sb in the sulfuric acid solutions may easily be measured at least from 1 to 10 ppm.

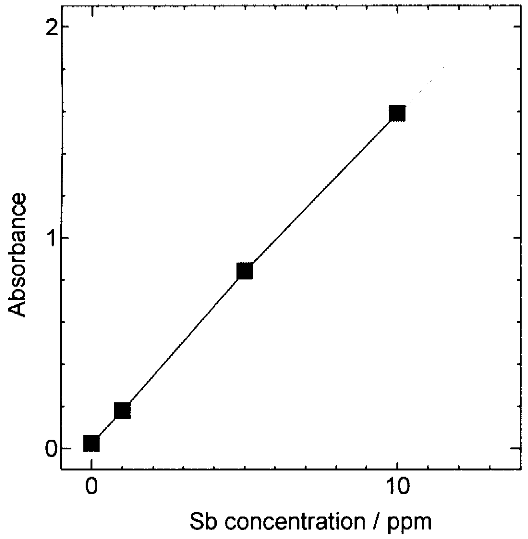


Fig. 1 Calibration curve for determination of Sb content in electrolytes measured at 553 nm by the proposed method

Table 1 shows the Sb concentration [ppm] in the battery electrolytes of used and new batteries. After charging by SL-3 charger for 1 day, the contents of Sb in electrolytes were between 0.1 and 1.3 ppm in old batteries, while that of new one was 0 ppm or under detection limit.

Table 1 Antimony concentration [ppm] in the battery electrolyte of used and new batteries

State	NO1	NO2	NO3	NO4	NO5	NO6	NO7	NN1
I	0.1	0.2	0.5	1.3	0.8	1.3	0.1	0
II	1.1	0.5	0.8	4.0	7.3	8.1	1.0	1.2
III	0.1	0.0	0.1	0.6	1.9	1.0	-	0.4
IV	-	-	0.6	15.3	6.0	-	-	-

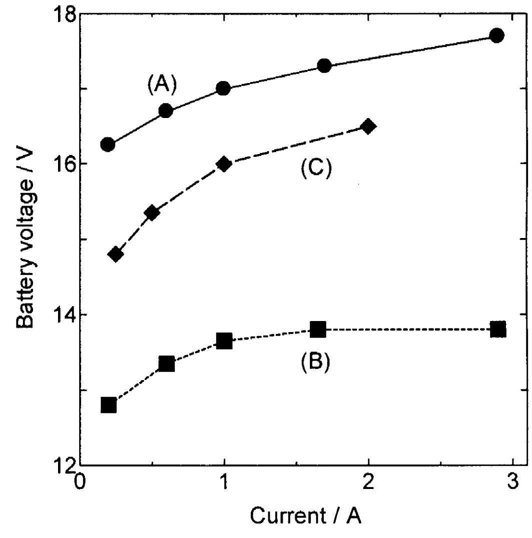
NO1: Nagoya Old (Used) Battery, NN1: Nagoya New (Fresh) Battery. State I: After charge by SL-3 charger, II: After 55 A discharge until 9.0 V, III: After complete charge for 3 days, IV: After 55 A discharge until 9.0 V

After full discharge until 9.0 V at ca. 55 A through the resister (State II), the Sb content of each battery increased and was ranging from 0.5 to 8.1 ppm, while that of new one is 1.2 ppm. After complete charge for 3 days, the contents of Sb in the electrolytes decreased again to almost the same values of those in State I, although that of new one was 0.4 instead of the initial value of 0.

Consequently, Sb dissolved into electrolyte from the positive electrode's grids during discharging period and probably deposited to the negative electrodes in charging period. These changes in Sb concentration in the electrolyte are repeated during discharge-charge cycles.

3.2 Charge and discharge operation

Figure 2 shows current-voltage (I-E) curves of 40B type new and old batteries. A new one (Curve A) showed a high voltage characteristic, because hydrogen evolution reaction hardly occur. However, the old deteriorated one (Curve B) showed low voltages in the range of 12.8 to 13.8 V accompanied to low hydrogen over-voltage due to deposited Sb sites on the negative electrodes even on 3 A charge. Therefore most electricity supplied by the charger was consumed not for reduction of lead sulfate but for hydrogen evolution, resulting in sulfation.



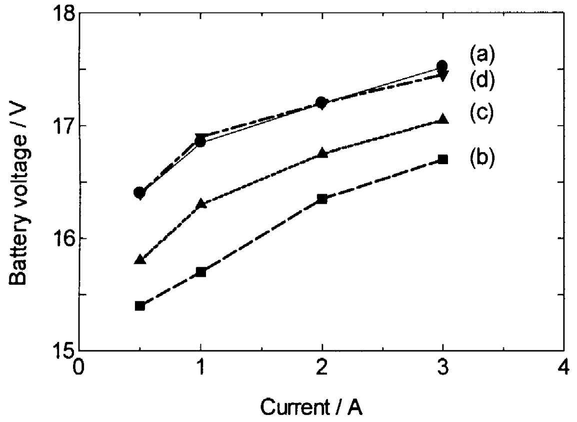
A: New battery, B: Old (used & discarded) battery, C: The electrolyte of the old battery used for curve B was changed to new electrolyte after discharge

Fig. 2 40B type battery's current-voltage curves

Curve C is the I-E curve of the old battery of which electrolytes were replaced with fresh 5 M H_2SO_4 solution after taken Curve B. The current-voltage curve raised upward and became similar to that for new one (Curve A). Namely, it is possible to decrease a considerable amount of Sb was removed from the cell, because Sb was dissolved into the electrolyte during discharge.

3.3 Sb addition

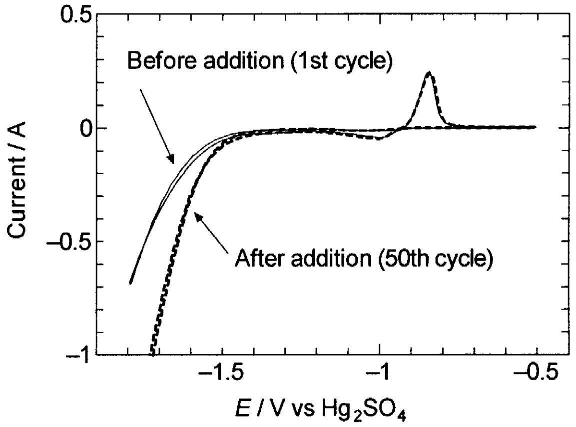
Figure 3 shows the effects of Sb addition to the electrolyte of a new battery. When 102 ppm of Sb was added, the current-voltage curve of charging significantly dropped as indicated by Curve (b). After one discharge-charge cycle, the Current-voltage curve recovered somewhat, Curve (c). After 3 additional cycles of discharge and charge, the current-voltage curve returned to the original level as shown by Curve (d). Namely, the baneful influence of Sb was removed by normal battery operation of discharge and charge. Consequently, the high rate discharge and charge operation would remove the Sb from the electrolyte of the deteriorated batteries. The effects of high rate operation will be presented another paper [Minami et al., 2003]. The current-voltage curve on fully charged battery is a good indication of the degree of battery deterioration.



(a) New battery as is; (b) Sb of 102 ppm is added to the electrolyte of (a); (c9 After one discharge and charge cycle; (d) After additional two cycles of discharge and charge. Discharge was done at ca. 55 A to 9.0 V, and charge was done at 3 A for 1 day.

Fig. 3 Current-voltage curves of 40B type battery (28 Ah at 5h)

Figure 4 shows a typical cyclic voltammogram of a Pb electrode in 5 M H_2SO_4 solution before and after addition of Sb (25 ppm). Soon, the rest potential sifted to about -0.45 V vs Hg_2SO_4 after addition of Sb, while that for the pure Pb was about -1.0 V. This fact indicates that metallic Sb, which has a low hydrogen over-voltage, would deposited on the Pb electrode surface. The hydrogen evolution reaction became more significant after addition of Sb as shown in Figure 4. However, the anodic peak indicating Pb to Pb SO_4 was not affected by such the addition amount of Sb. So, one of the reasons of deterioration of lead-acid batteries is thought to be due to the sulfation of lead electrode by deposition of Sb from the electrolyte.



Scan rate: 50 mV/s

Fig. 4 Cyclic voltammogram of Pb electrode in 5 M before and after addition of Sb (25 ppm)

4. CONCLUSION

(1) Antimony (Sb) dissolves from positive electrode's grids of lead-acid batteries independent of the age of batteries by discharge.
(2) Sb concentration in the electrolyte solutions of lead-acid battery is easily determined from 0 to 10 ppm or more by a simply modified method for the analysis of industrial materials; i.e. JIS K0102.
(3) Sb deposited to the negative electrodes from the electrolyte and Sb content in the electrolyte decreased again during the charging state.
(4) High Sb content in the electrolytes causes lower current-voltage curves due to easy evolution of hydrogen at deposited Sb sites during the charge.
(5) Replacement of electrolyte solutions in a deteriorated lead-acid battery with a fresh 5 M H_2SO_4 solution after discharge recovers the battery performance.
(6) Baneful influence of Sb was removed by normal battery operation of discharge and charge.
(7) The current-voltage curve on fully charged battery is a good indication of the degree of battery deterioration.

References

Japanese Industrial Standards, K0102, 242-246, 1998.

Minami, S., S. Ikeda, I. Katsuyama, and A. Kozawa, *Journal of Asian Electric Vehicles*, Vol. 1, No. 2, 2003.

Mori, Y., S. Ikeda, M. Maeda, I. Katsuyama, H. Yagi, and A. Kozawa, *Kagaku Kogyo*, Vol. No. 5, 399-401, 2003 (in Japanese).

(Received October 30, 2003; accepted December 1, 2003)