

Studies on the corrosion phenomena of Pb alloy negative electrodes for lead-acid battery on charging (3)

K. Kasuya, K. Ui, Y. Idemoto, N. Koura

Department of Pure and Applied Chemistry,
Faculty of Science and Technology,
Tokyo University of Science
2641 Yamazaki, Noda, Chiba 278-8510, Japan

INTRODUCTION

The lead-acid battery used for a main power supply or the backup power supply is usually the valve regulated lead-acid battery (VALAB) of maintenance-free in use. In a charge state, since the current collector of negative electrode is put on reduction atmosphere, it is thought that it is hard to corrode. There are few papers about them^{1,2)}. However, the thin electrolyte film is formed on the current collector which sticks out from the electrolyte since it creeps up on the current collector, and corrosion occurs in the parts (surface exposure part). It is one of the problems that should be solved to lengthen the battery life.

In this study, we used the lead alloy such as Pb-Sn alloy for current collector of the negative electrode, and assumed corrosion of the upper part (strap and pole parts, etc.) of the separator of VALAB. We analyzed corrosion behavior in a surface exposure part in various conditions, and it aimed at finding out the alloy which has a high restraint effect for such the corrosion.

EXPERIMENTAL

A three-electrode cell was used for the experiment which used Pb or Pb alloys (Bi, Se, and Sn) as a working electrode, PbO_2 as a counter electrode, $Pb/PbSO_4$ (in 5.7M H_2SO_4 gel) as a reference electrode, and 1.6M H_2SO_4 solution as an electrolyte. It was carried out in air, N_2 , and O_2 atmosphere. The cell was put into a thermostated bath in order to keep at 333K. Potentiostatic electrolysis (-30mV vs. $Pb/PbSO_4$, it was defined as charge) was performed. As the evaluation method of a surface exposure part, the surface observation by SEM, identification of the product by XRD, the quantitative analysis, and the elemental analysis of the depth direction of the corrosion layer by GD-OES were performed.

In the experiment cell on charging, the Luggin capillary of another $Pb/PbSO_4$ reference electrode was inserted. The tip of it was brought close to a surface exposure part as much as possible, and the electrolyte surface was set to 0cm and measured at every height of 0.5cm.

RESULTS AND DISCUSSION

First, the potential of the surface exposure part on charging was measured in order to investigate the influence of atmosphere on the corrosion of it. The potential of the surface exposure part in oxygen atmosphere showed noble potential about 100-200mV rather than the potential in air atmosphere. It was considered from the fact that the dissolved oxygen concentration controlled the local cathodic reaction.

Next, the corrosion phenomena of the lead alloy (Pb-Se, Pb-Bi, Pb-Sn, Pb-Sn-Bi, Pb-Sn-Se) used for negative electrode was examined. After charging for 168 hours, the corrosion product on the surface exposure part were identified as $PbSO_4$ by XRD analysis. It was known that, in the case of Pb-1.8%Sn-0.03%Se, the grain size of $PbSO_4$ was the smallest. Then, the quantitative analysis of $PbSO_4$ was carried out in order to investigate the

corrosion resistance of each alloy. In the case of Pb-1.8%Sn-0.03%Se, the amount of corrosion product, $PbSO_4$ was also the smallest.

Then, the elemental analysis of the depth direction of the corrosion layer of the surface exposure part was performed by using GD-OES in order to investigate the corrosion-resistant difference in the alloys. As shown in Fig.1, we defined that the vertical line was the interface of the corrosion layer and the substrate. It was known that the corrosion layer of (c) Pb-1.8% Sn-0.03% Se was the thinnest. Moreover, when the distribution of Sn in the corrosion layer was noticed, it was seen in case of (c) Pb-1.8%Sn-0.03%Se that the concentration of Sn in early stages of sputtering is low compared with other alloys. This showed that the Sn concentration near the corrosion layer surface is low. The above things showed that the Se addition to Pb-1.8%Sn affected the distribution of Sn in the corrosion layer, and controlled the formation of $PbSO_4$.

REFERENCES

- 1) D. Pavlov, *et al.*, *J. Electrochem. Soc.*, **142**, 2919 (1995).
- 2) T. Omae, *et al.*, *J. Power Sources*, **65**, 65 (1997).

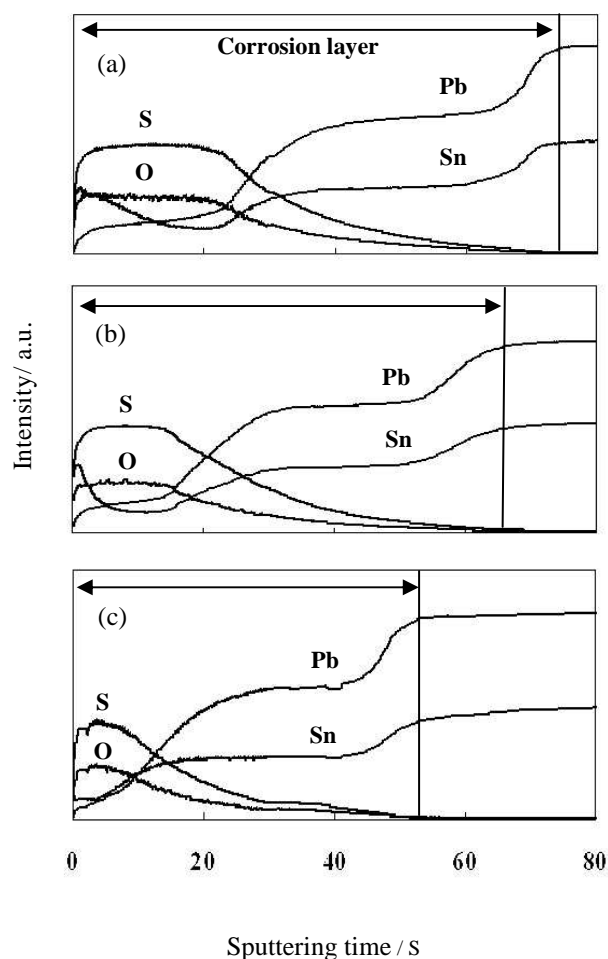


Fig. 1 Elemental analysis of the depth direction by GD-OES in the corrosion layer of a surface exposure part of Pb alloys (after charging).

1.6M H_2SO_4 , 333K, -30mV vs. $Pb/PbSO_4$, 168hours on charging in air, a 1cm part from the surface of electrolyte (a) Pb-1.8%Sn, (b) Pb-1.8%Sn-0.03%Bi, (c) Pb-1.8%Sn-0.03%Se