

Behavior of Sb on Negative Electrodes of Lead-Acid Batteries

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It is well known that Sb-Pb alloy is employed for the grid of the Lead-Acid batteries. The Sb content is between 2 and 5% by weight. However, Sb slowly dissolves chemically from the positive electrodes in H₂SO₄ and diffuses to the negative electrodes where Sb is deposited. Sb is one of the metals having a low hydrogen evolution reaction (HER) overvoltage. Therefore Sb promotes the competitive HER which causes the accumulation of non-conductive lead sulfate (PbSO₄) crystals, i.e. sulfation, during charging period. A simple method for chemical analysis of the Sb (1 to 10 ppm) in the battery electrolyte (28% or 5M H₂SO₄) was established by modifying the latter complicated conventional rhodamine-B method.

To investigate the behavior of Sb on the surface of Pb negative electrodes, cyclic voltammetry (CV) was carried out between -1.80 and -0.50 V vs. Hg-Hg₂SO₄ (0.5 M H₂SO₄). The Pb electrode was immersed in 5 M H₂SO₄ solution containing 20 ppm Sb³⁺ for 1 or 24 hours. Then the electrode was also tested by CV for 200 cycles. The surface of the Pb electrode was analyzed by XPS about Pb, Sb, O, and S atoms. The depth profile of each element was also measured by sputtering with Ar⁺ ion beam. The relation of the Sb concentration and the I-E curve was also established.

From the CV curves of the negative electrode, the more the cycle number, the larger the effect of Sb, i.e. HER, becomes as shown in Fig. 1.

Tables 1 and 2 show Sb contents in the electrolyte and Pb electrode (dissolved in HCl solution), respectively, before and after immersion for 1 or 24 hr, and additional 200 cycles of CV. The content of Sb is reduced in the last case (Table 1). It is thought that Sb was deposited at the surface of Pb during the negative potential scan, however it was not dissolved during the positive scan where Pb was dissolved, consequently Sb atoms deeply penetrated into the bulk of the Pb electrode (Table 2).

XPS profiles for Pb and Sb elements of the above treated Pb electrode (24 hr & 200 cycles CV) are shown in Fig. 2. With those for S and O, in the case of 24 hr immersion, Pb is present as PbSO₄ at the top surface, then PbO₂, and Pb according to the depth. However Sb was not observed at the top surface but did at the middle depth after consecutive 200-cycles CV. Namely, Sb was incorporated in the electrode bulk as follows. Sb³⁺ was deposited as Sb at the surface of the Pb electrode by electron exchange with Pb due to its nobler redox potential than Pb. Pb metals around the deposited Sb made an exchange reaction with Pb²⁺ ions in the electrolyte. However, Sb did not make the exchange reaction, therefore did not dissolve to the electrolyte. Then, Pb deposited around the Sb atom. Consequently, Sb atoms penetrated to the deep site of the Pb electrode during the CV operation, i.e. charge-discharge cycles in the practical batteries under an appropriate condition. It is one of the reasons that lather high Sb containing Pb alloy can be used as the grid metal.

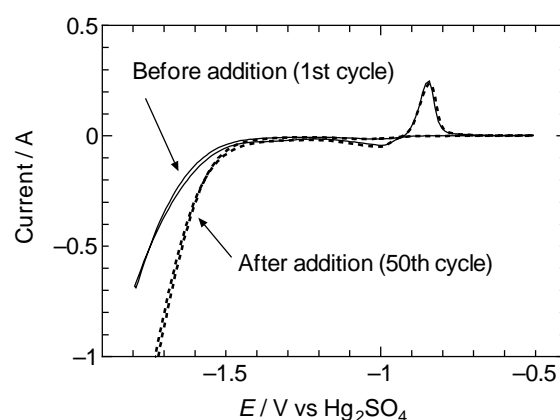


Fig. 1 CV curves of Pb electrode in 5 M H₂SO₄ solution containing 20 ppm Sb³⁺.

Table 1 Concentrations of Sb in H₂SO₄ solutions before and after immersion of Pb electrode.

	Immersion time	Absorbance	Sb/ppm	Rest pot./V
A	Before	2.99	19.4	-1.0
	1 hr	2.99	19.4	-0.4
B	Before	3.35	21.8	-1.0
	24 hr	3.35	21.8	-0.55
C	Before	2.47	15.9	-1.0
	24 hr	2.46	15.9	-0.55
	24 hr & CV (200 cycles)	0.463	2.4	-1.0

Table 2 Concentrations of Sb dissolved by HCl solutions from Pb electrodes immersed in 20 ppm Sb³⁺.

Immersion time	Absorbance	Sb/ppm
Blank (Pb)	0.065	0
1 hr	1.142	6.96
24 hr	0.414	2.07
24 hr & 200 cycles	0.397	1.93

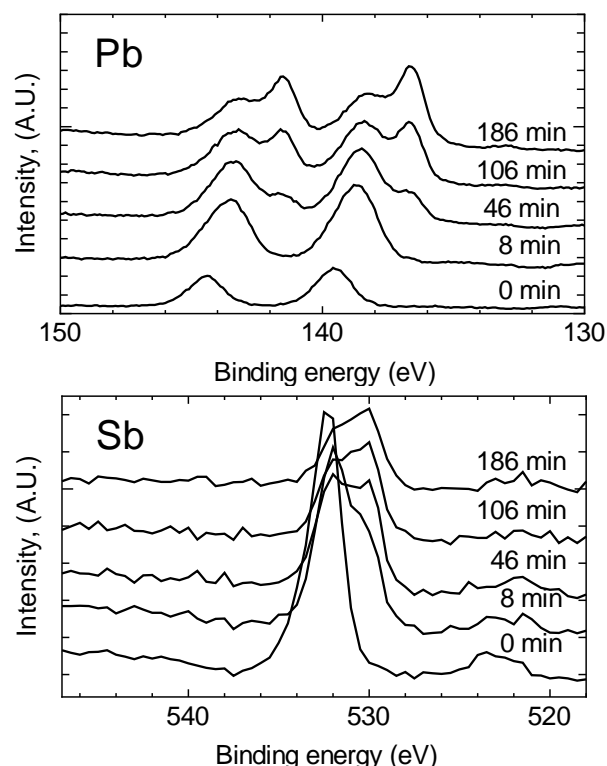


Fig. 2 XPS profiles for Pb and Sb in the Pb electrode immersed in 5 M H₂SO₄ containing 20 ppm Sb³⁺ for 24 hr and subsequent 200 cycles of CV between -1800 and -500 mV vs. Hg-Hg₂SO₄.