

## Function of Indium in the Mixed ITE Activator for Lead-acid Batteries

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The behaviors of  $\text{In}^{3+}$  and activator were studied on Pb anode of lead-acid batteries. The deposition of In with high hydrogen overpotential during the potential scan deviates negatively the hydrogen evolution potential. The current in redox couple of Pb/PbSO<sub>4</sub> is slightly decreased because of PbSO<sub>4</sub> formation on Pb adsorbed with In. This is the important difference between  $\text{In}^{3+}$  and  $\text{Ag}^+$  added to 5M H<sub>2</sub>SO<sub>4</sub>. The activator is less adsorbable on bear Pb, and adsorbed easily on PbSO<sub>4</sub> formed on Pb. The complex ions of  $\text{In}^{3+}$  and activator molecules are adsorbable on Pb, and PbSO<sub>4</sub> is initially formed on the adsorbed layer of complex ion at the potential in redox couple of Pb/PbSO<sub>4</sub>.

**Keywords**

lead-acid battery, anode, electrolyte, indium ion, organic polymer, activator

**1. INTRODUCTION**

Indium (In) is known to be very effective in increasing the hydrogen over-potential for zinc in alkaline solution (KOH) and is now widely used for the anode of alkaline MnO<sub>2</sub>-Zn cells. In lead-acid batteries, indium are commonly used as one of the components of grid alloys. This fact is important to study the effects of indium ion ( $\text{In}^{3+}$ ) dissolved in the electrolyte from grid alloy for lead-acid batteries.

The authors have reported the behaviors of activators for the extension of life of lead-acid batteries. Further studies are now being carried out on the function of activator in the electrochemical measurements and commercial batteries. This paper describes the function of  $\text{In}^{3+}$  in the electrolyte containing the activator by cyclic voltammetry.

**2. EXPERIMENTAL**

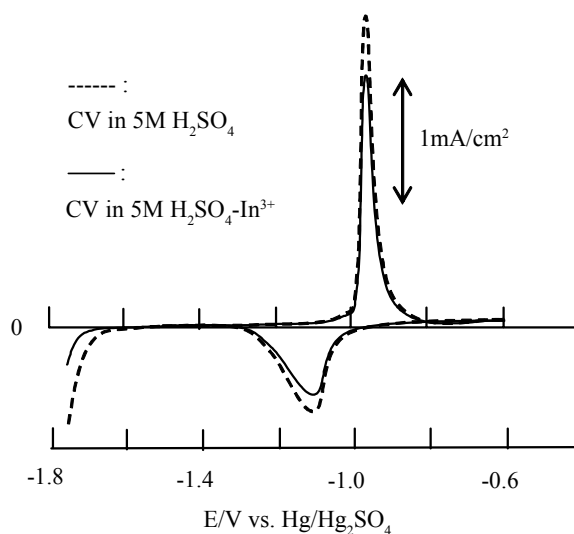
Cyclic voltammograms (CV) were recorded as follows. The test electrode was lead plate (99.99%, 1 x 1cm<sup>2</sup>), which was chemically polished in CH<sub>3</sub>COOH-H<sub>2</sub>O<sub>2</sub> solution at room temperature just before measurements of CV.

Counter electrode was cylindrical lead with large surface area. Reference electrode was Hg/Hg<sub>2</sub>SO<sub>4</sub>/5 M H<sub>2</sub>SO<sub>4</sub>. Electrolyte was 5M H<sub>2</sub>SO<sub>4</sub> with/without additives, which were In<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> as  $\text{In}^{3+}$  and the ITE mixed activator composed of polyvinyl-alcohol. The concentration of In<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and activator was 2mg/100ml H<sub>2</sub>SO<sub>4</sub>,

and 1.0 wt.%, respectively. The test electrode was immersed in the electrolyte, and scanned negatively from the spontaneous potential (-1.05V) to hydrogen evolution region. Then, the potential was positively scanned to -0.6V, and the scan was repeated between these potential region at the scan rate of 10mV/s.

**3. RESULTS**

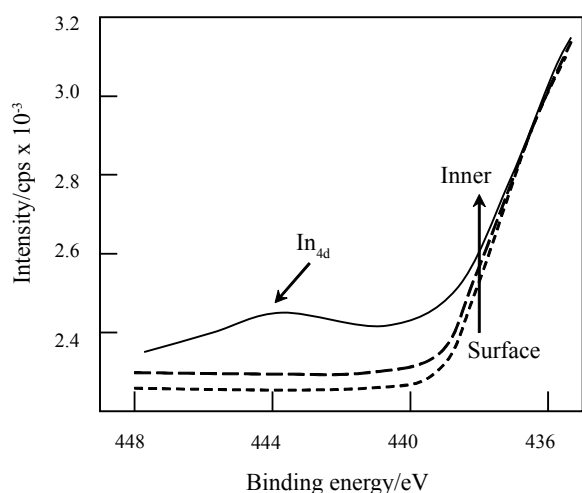
Figure 1 shows the CV of Pb in 5M H<sub>2</sub>SO<sub>4</sub> and 5M H<sub>2</sub>SO<sub>4</sub>- $\text{In}^{3+}$ . The addition of  $\text{In}^{3+}$  decreases slightly in the current of Pb/PbSO<sub>4</sub> redox couple, and the potential of hydrogen evolution deviates to negative region because of the deposition of In with higher hydrogen overpotential on Pb at negative polarization.



**Fig. 1** Cyclic voltammograms of Pb in 5M H<sub>2</sub>SO<sub>4</sub> and 5M H<sub>2</sub>SO<sub>4</sub>- $\text{In}^{3+}$  solutions

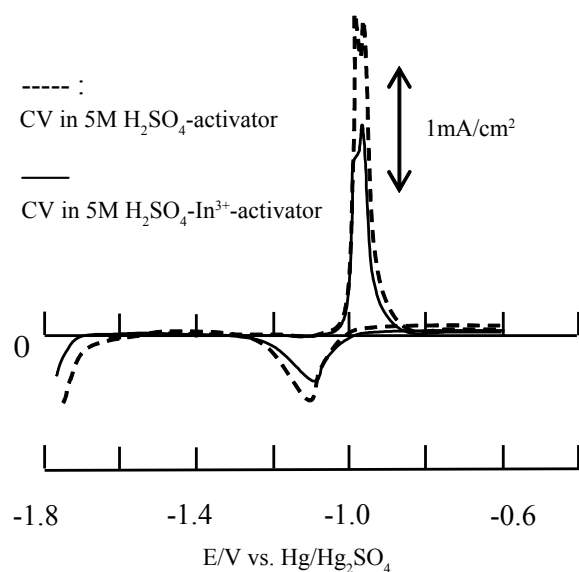
Since the addition of  $\text{Ag}^+$  increased the redox current as reported already, the participation of  $\text{In}^{3+}$  for  $\text{PbSO}_4$  formation on Pb anode is different from that of  $\text{Ag}^+$ . The adsorption of some species may be taken into consideration on the initial formation of  $\text{PbSO}_4$  in the electrolyte containing  $\text{In}^{3+}$ .

After the formation of  $\text{PbSO}_4$  at the potential of redox couple, the electrode was subjected to measure XPS of In. As shown in Figure 2, the depth profiles of XPS indicate the presence of In metal in the inner layer of  $\text{PbSO}_4$  film formed on Pb. Accordingly, it is suggested that  $\text{PbSO}_4$  is formed on Pb surface adsorbed with In.



**Fig.2** XPS profiles of  $\text{PbSO}_4$  film obtained in 5M  $\text{H}_2\text{SO}_4$  containing  $\text{In}^{3+}$

Figure 3 shows the CV in the 5M  $\text{H}_2\text{SO}_4$  containing both  $\text{In}^{3+}$  and activator compared with that in 5M  $\text{H}_2\text{SO}_4$ -activator. The two peak currents of  $\text{PbSO}_4$  formation in



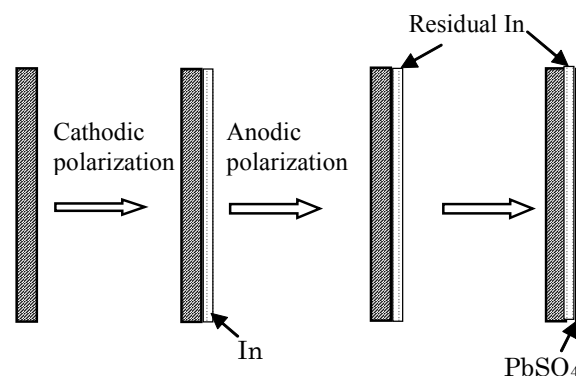
**Fig. 3** Cyclic voltammograms of Pb in activator and activator- $\text{In}^{3+}$  solutions

the solution containing only activator correspond to the reaction on bare Pb and the subsequent growth of  $\text{PbSO}_4$  on  $\text{PbSO}_4$  with adsorbed activator, respectively as shown in the previous paper.

When  $\text{In}^{3+}$  is added to 5M  $\text{H}_2\text{SO}_4$ -activator solution, the first peak current is decreased to give the shoulder in CV. It is considered that some species may be adsorbed on Pb before the initial  $\text{PbSO}_4$  formation as discussed in the next section.

#### 4. DISCUSSION

Figure 4 shows the illustration of mechanisms in the  $\text{PbSO}_4$  formation on Pb. The result of XPS measurements indicates the presence of In species in the inner layer of  $\text{PbSO}_4$  film. Accordingly,  $\text{PbSO}_4$  may be formed on In species, which is adsorbed on Pb. The redox potential of  $\text{In}/\text{In}^{3+}$  is higher than hydrogen evolution potential in acidic solution. The deposition of In is considered to occur before hydrogen evolution in the negative scan. When this electrode is scanned to the positive direction in the measurement of CV, the oxidative dissolution of In as  $\text{In}^{3+}$  takes place. However, some of In remains on Pb before the start of  $\text{PbSO}_4$  formation, which takes place on thin film of In to decrease the peak current compared with that on bare Pb at the potential in redox couple.



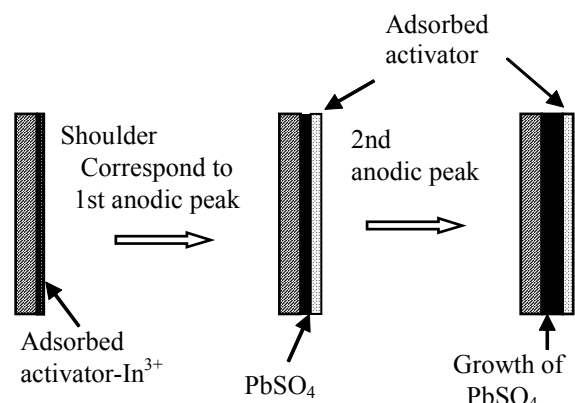
**Fig. 4** Mechanisms of the formation of  $\text{PbSO}_4$  in the redox couple of Pb/ $\text{PbSO}_4$

Figure 5 shows the reaction mechanism in the 5M  $\text{H}_2\text{SO}_4$  containing both In and activator. In this solution the first peak of the redox couple is decreased to give a shoulder. As observed in 5M  $\text{H}_2\text{SO}_4$ - $\text{Ag}^+$ -activator solution, the shoulder indicates the current through the adsorbed layer on Pb. The adsorbed species is the complex ion of activator molecules and  $\text{In}^{3+}$  and more adsorbable than free activator molecules on Pb.

#### 5. CONCLUSION

The results obtained are summarized as follows.

- (1) The addition of  $\text{In}^{3+}$  results in the initial formation



**Fig. 5** Mechanism of the formation of  $\text{PbSO}_4$  in the activator and  $\text{In}^{3+}$  containing solution.

of  $\text{PbSO}_4$  on Pb adsorbed with In, and deviates negatively the hydrogen evolution.

- (2) The activator affects the redox couple of  $\text{Pb}/\text{PbSO}_4$ . This is explained by adsorption of activator on Pb and  $\text{PbSO}_4$ . The activator molecules are less adsorbable on Pb and adsorbed on  $\text{PbSO}_4$ .
- (3) When both of activator and  $\text{In}^{3+}$  are present, the complex ions of  $\text{In}^{3+}$  and activator molecules are adsorbed on Pb. The initial formation of  $\text{PbSO}_4$  proceeds on Pb with the adsorbed complex ions.

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