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Function of Silver in the Mixed ITE Activators for Lead-acid Batteries

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Abstract

The behaviors of Ag^+ and activator were studied on Pb anode for lead-acid batteries. The deposition of Ag and dissolution of Ag^+ take place at lower potential than redox couple of Pb/$PbSO_4$. This process may be considered to activate the reaction in the redox couple of Pb/$PbSO_4$. The activator molecules are less adsorbable on bear Pb, and adsorbed easily on $PbSO_4$ formed on Pb. The complex ions of Ag^+ and activator molecule are adsorbable on bear Pb, and $PbSO_4$ is initially formed on the adsorbed layer of complex ions.

Keywords

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

1. INTRODUCTION

The ITE mixed polymer activator added to electrolyte of lead-acid batteries have been found to extend battery life. The anode (negative electrode) sulfation is the main cause of deterioration in performance of the lead-acid batteries. It has been explained that the activator molecules are adsorbed on anode to produce the beneficial action for battery life.

On the other hand, the active materials are impregnated on grid alloy such as Pb-Ca, Pb-Sb and so on, and the alloy components may be dissolved as metal ions in the electrolyte during charge and discharge cycles. The additional alloy components are added for giving corrosion resistance property.

It is important to study the behaviors of dissolved metal ions from the grid alloy for battery performance. The silver is being used as an alloy component of Pb-Ca grid. This fact is worth paying particular attention, because the participation of Ag^+ in the anode reaction of Pb seems to be important for battery performance in the electrolyte containing activator lmolecules. This paper describes the effects of Ag^+ and activator on anode reaction on Pb by cyclic voltammmetry.

2. EXPERIMENTAL

Cyclic voltammograms (CV) were recorded as follows. The test electrode was lead plate (99.99%, 1 x 1cm^2), which was chemically polished in CH_3COOH-H_2O_2 solution at room temperature just before measurements of CV. Counter electrode was cylindrical lead with large surface area. Reference electrode was Hg/Hg_2SO_4/5 M H_2SO_4.

Electrolyte was 5M H_2SO_4 with/without additives, which were Ag_2SO_4 as Ag^+ and the ITE mixed activator composed of polyvinylalcohol. The concentration of Ag_2SO_4 and activator was 2mg/100ml 5M H_2SO_4, and 1.0wt.%, 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 this potential region at the scan rate of 10mV/s.

3. RESULTS

Figure 1 shows the CV curves of Pb electrode in 5M H_2SO_4 and 5M H_2SO_4-Ag^+ solutions. The redox couple

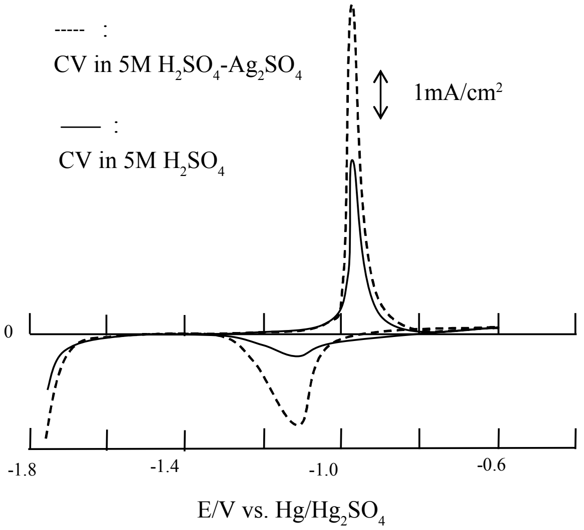

Fig. 1 Cyclic voltammograms of Pb in 5M H_2SO_4 and 5M H_2SO_4-Ag^+

of Pb/$PbSO_4$ appears around -1.1V, and corresponds to the charge and discharge reaction on anode of lead-acid battery. The hydrogen evolution current was observed below -1.6V. When Ag^+ was added to the electrolyte, the reaction of redox couple at -1.1V was activated to increased the current two times. On the other hand, the hydrogen evolution deviates to positive potential. The Ag is formed on Pb at lower potential and decreases hydrogen overpotential.

Figure 2 shows the CV in 5M H_2SO_4-activator solution with that in 5M H_2SO_4. The addition of activator decreases the current in the redox couple of Pb/$PbSO_4$, and splits the anodic current of redox couple into two peaks. This suggests that the two processes take part in the formation of $PbSO_4$ from Pb. There is no effect of activator on hydrogen evolution region.

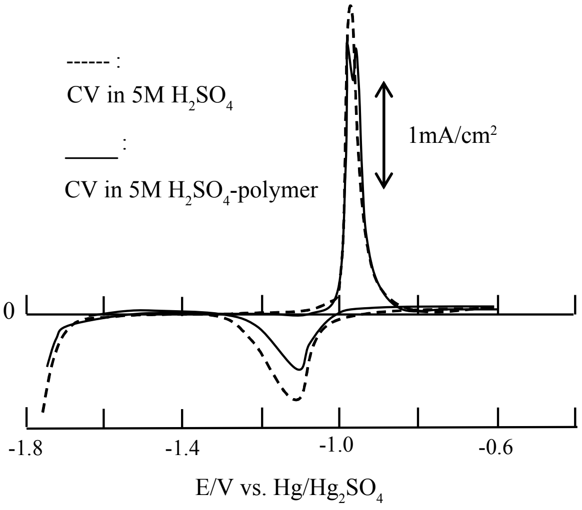

Fig. 2 Cyclic voltammograms of Pb in 5M H_2SO_4 and 5M H_2SO_4-activator

Figure 3 shows the CV in 5M H_2SO_4-Ag^+-activator solution compared with that in 5M H_2SO_4-activator. The first peak current observed in addition of only activator is decreased to give the shoulder in CV. It is considered that some species may be adsorbed on Pb. The hydrogen evolution potential deviates slightly to negative region, because of the presence of Ag^+.

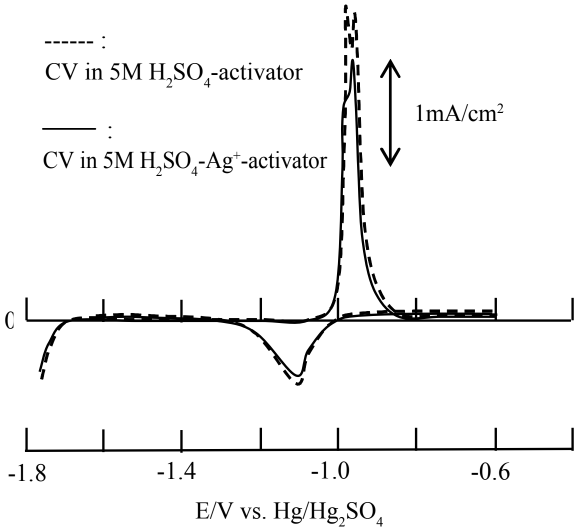

Fig. 3 Cyclic voltammograms of Pb in activator and activator and Ag^+ solution.

4, DISCUSSION

Figure 4 shows the mechanisms, in which the addition of Ag_2SO_4 as Ag^+ increases the current in the redox couple of Pb/PbSO4. When Pb electrode is polarized negatively near hydrogen evolution potential, Ag+ is reduced to deposit Ag metal on Pb. When this electrode is scanned to positive direction, the deposited Ag dissolves as Ag^+ even before $PbSO_4$ formation potential. Such deposition and dissolution during potential scan gives fresh and bear surface of Pb to activate $PbSO_4$ formation. Accordingly, the redox current Pb/$PbSO_4$ is significantly increased in Ag^+ containing solution.

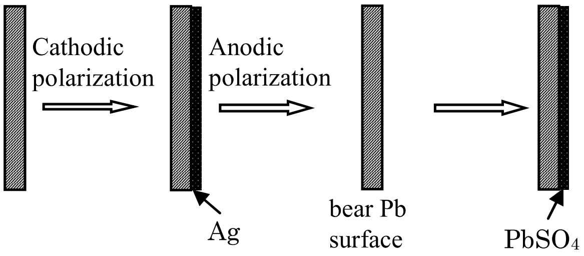

Fig. 4 Mechanisms of the formation of $PbSO_4$ in the redox couple of Pb/$PbSO_4$

Figure 5 shows the illustration to explain the effect of activator on the oxidation of Pb to $PbSO_4$. It is considered that the adsorption of activator takes an important role on this reaction. Activator has negative charge on oxygen atoms of the molecules, and hence is easily adsorbed on positive center of the electrode. If the Pb electrode is polarized near hydrogen evolution region, activator molecules are less adsorbable. Therefore, there is no deviation of hydrogen evolution potential compared with that in 5M H_2SO_4.

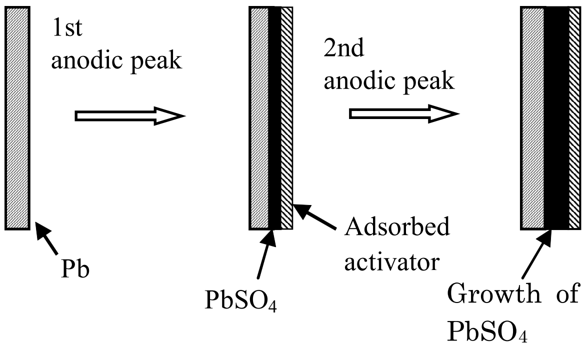

Fig. 5 Mechanism of the formation of $PbSO_4$ in the activator containing solution

In the positive scan of Pb electrode from hydrogen evolution region, the oxidation of Pb to $PbSO_4$ starts on bear Pb surface. The electrode is covered with $PbSO_4$ by anodic current. The electrode covered with $PbSO_4$ is positively charged, and then the activator molecules are adsorbed on the film of $PbSO_4$. It is considered that this process gives the first peak current. The growth of $PbSO_4$ proceeds on the electrode with adsorbed activator to give the second peak current.

Figure 6 shows the reaction mechanism in the presence of both Ag^+ and activator molecules. In this case, the first peak current is decreased to give the shoulder in CV curve. This result indicates the some species are adsorbed on Pb electrode before the initial formation of $PbSO_4$.

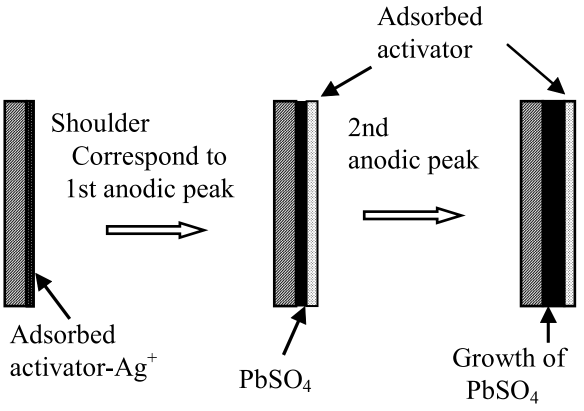

Fig. 6 Mechanism of the formation of $PbSO_4$ in the activator and Ag^+ containing solution

The complex ions of Ag^+ and activator molecules must be considered for the explanation of CV curve. Activator itself is less adsorbable species on Pb polarized negatively. The activator molecules with negative charge center react with Ag^+ to give complex ions. This is more adsorbable on Pb than free activator molecules. Accordingly, the first peak current is decreased to give the shoulder by the $PbSO_4$ formation on the polymer adsorbed layer. Then, the formation and growth of $PbSO_4$ proceed on the electrode adsorbed by activator to give the second peak current in CV.

5. CONCLUSION

The results obtained are summarized as follows.

(1) The addition of Ag^+ activates the reaction of $Pb/PbSO_4$ redox couple, and deviates the hydrogen evolution to positive region.

(2) The activator affects the reaction in redox couple of $Pb/PbSO_4$. This is explained by adsorption of activator on Pb and $PbSO_4$. The activator molecules are less adsorbable on Pb and adsorbed on $PbSO_4$.

(3) When both of activator and Ag^+ are present, the complex ion of Ag^+ and activator molecules is adsorbed on Pb. The initial formation of $PbSO_4$ proceeds on Pb adsorbed by the complex ion.

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