

# A study of the passivation mechanism of negative plates in lead/acid batteries

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## Abstract

The passivation mechanism of negative plates has been investigated by means of linear sweep voltammetry and scanning electron microscopy. It is found that the reduction peak of  $\text{PbSO}_4$  is split into two peaks on a seriously passivated negative plate. This is attributed to the reduction of  $\text{PbSO}_4$  crystals of different sizes. The reduction rate of the negative plate depends on the diffusion of  $\text{SO}_4^{2-}$  from the depth of micropores to the bulk solution. The narrow and long microporous passageways and the big  $\text{PbSO}_4$  crystals in the active mass result in serious sulfation of the negative plate. The effects of the active mass structure and the additive in the solution are also discussed.

*Keywords:* Lead/acid batteries; Lead sulfate reduction; Negative electrodes; Passivation mechanism

## 1. Introduction

Much work has been done on the structure and electrochemical processes of the negative electrode in lead/acid batteries over the past three decades [1–13]. A dissolution/precipitation mechanism is proposed in the charge/discharge of the negative plate [1–3] and it is found that the passivation of the negative plate is due to a dense and insulated lead sulfate layer formed on the lead surface [4,5]. Although the negative electrode system is simpler than that of the positive electrode system and many papers concerning the negative electrode have been published recently [6–11], its kinetics and mechanism are not yet well understood. The passivation of the negative plate is still one of the main reasons for the shortening of the battery life. Therefore, it is very important to study the structure and the passivation mechanism of the active mass on the negative plate. In this paper, the causes of the negative plate passivation and the mechanism of the cathodic process on the negative plate are investigated.

## 2. Experimental

Working electrodes were the seriously passivated negative plates and the newly-formed negative plates, from each of which a small grid with an area of about  $0.5 \times 0.8 \text{ cm}^2$  was cut. To avoid loss of the active mass, the electrode was fixed with an epoxy resin. The electrochemical experiments were conducted using a conventional, three-electrode system. All

measurements were made at room temperature ( $25 \pm 2 \text{ }^\circ\text{C}$ ) with respect to a  $\text{Hg}/\text{Hg}_2\text{SO}_4$  reference electrode. At different concentrations, the  $\text{H}_2\text{SO}_4$  concentration in the reference compartment was always the same as that in the working-electrode compartment. In the experiments, pure nitrogen passing through active copper at about  $300 \text{ }^\circ\text{C}$  is used to agitate the solution and remove oxygen from it. The instrumentations used are described in Ref. [11].

In the linear potential sweep between  $-1500$  and  $-500$  mV, the negative-going sweep began at  $1 \text{ mV/s}$  from  $-950$  mV, to ensure that the electrode was fully charged before its discharge. The appearance of the interior of the active mass was observed by means of scanning electron microscopy (SEM, S-520) before and after the potentiodynamic cycle. To study the effect of the additive, we also use the  $\text{H}_2\text{SO}_4$  solution containing  $0.0225 \text{ M Al}_2(\text{SO}_4)_3$ .

## 3. Results and discussion

When in a battery many  $\text{PbSO}_4$  crystals accumulate on the positive and negative plates or when a deep-discharge is performed, the concentration of the  $\text{H}_2\text{SO}_4$  solution in the battery decreases slowly. We therefore chose a passivated negative plate of a failure battery as the working electrode and measured its electrochemical behavior in  $5.04$ ,  $2.46$  and  $1.09 \text{ M H}_2\text{SO}_4$ . Fig. 1 shows the initial three typical voltammograms in  $1.09 \text{ M H}_2\text{SO}_4$  between  $-1500$  and  $-500$  mV. It is interesting to find that the high and negative reduction peak

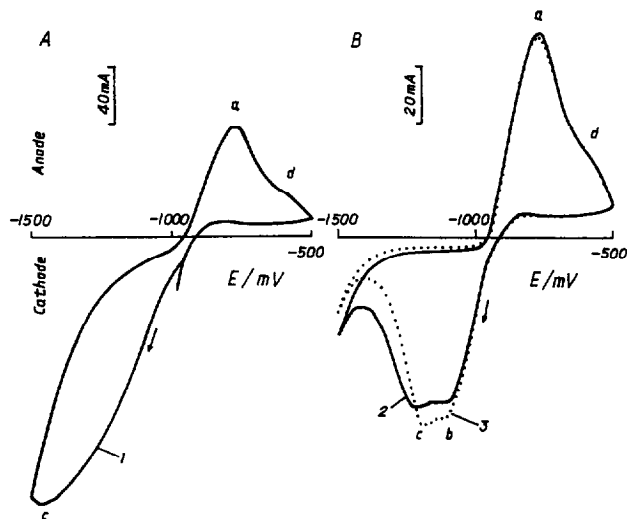


Fig. 1. The initial three typical voltammograms for a small passivated negative plate in 1.09 M  $\text{H}_2\text{SO}_4$ . The negative-going sweep begins at  $-950$  mV; sweep rate: 1 mV/s.

appears in the first cycle (Fig. 1(A)). Its peak potential is  $-1470$  mV and it is more negative than the common peak potential of  $\text{PbSO}_4$ . In the subsequent cycle, Fig. 1(B) shows that two reduction peaks appear simultaneously. The peak potential of peak 'b' always remains unchanged in the cycles, while that of peak 'c' shifts in the positive direction and shifts, more slowly after the third cycle. It is clear that the high and negative reduction peak in Fig. 1(A) corresponds to peak 'c' in Fig. 1(B) and peak 'b' in Fig. 1(A) disappears. Since the behavior of peak 'b' is very similar to that of the  $\text{PbSO}_4$  reduction peak observed on the common cyclic voltammograms [6,11], peak 'b' represents the reduction of  $\text{PbSO}_4$ .

In the positive-going sweep of Fig. 1, a shoulder (peak 'd') is observed at about  $-600$  mV. This may be the formation peak of the basic lead sulfate [11,12]. To study the behavior of peak 'c', Fig. 2 shows the cyclic voltammograms when the switching potential changes from  $-500$  to  $-600$  and  $-760$  mV. It is found that both peaks 'b' and 'c' appear when different switching potentials, even  $-760$  mV which is more negative than the peak potential of peak 'a', are used. If the concentration of  $\text{H}_2\text{SO}_4$  solution increases or if the negative plate is slightly passivated, peak 'c' will become obscure and even be covered by peak 'b'. Thus, a long tail will appear in peak 'b'. It is well known that there is also a long tail in peak 'b' on the negative-going potential sweep curves of a solid lead electrode. Therefore, it is most likely that peak 'c' is also contained in the tail of peak 'b' for a solid lead electrode.

Fig. 2 also shows that peaks 'b' and 'c' become higher when the switching potential decreases (second cycle). This indicates that the higher is the terminal potential of the negative plate in the discharge, the more serious is the passivation of the active mass. In the fourth cycle, peaks 'b' and 'c' become very low. This is because only part of the active mass is discharged.

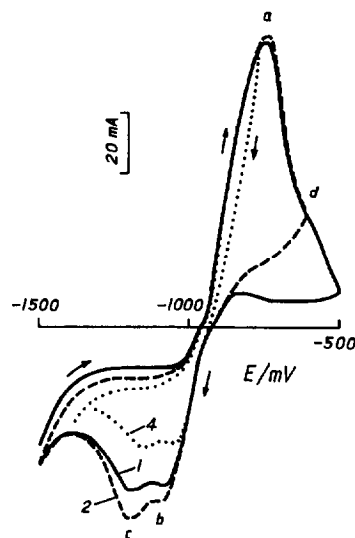


Fig. 2. The 1st, 2nd and 4th cyclic voltammograms on a small passivated negative plate in 1.09 M  $\text{H}_2\text{SO}_4$  when the switching potential changes from  $-500$  to  $-600$  and  $-760$  mV; sweep rate: 1 mV/s.

In order to identify peak 'c', the test specimen was analysed by X-ray diffraction (XRD) and only diffraction lines of Pb and  $\text{PbSO}_4$  were found. To study the structure of  $\text{PbSO}_4$  crystals before and after the charge/discharge, we divided the specimens and observed the appearance of the interior of the active mass by means of SEM. Results are shown in Fig. 3. It is found that the  $\text{PbSO}_4$  crystals formed in the discharge of the non-passivated negative plate are even and very small (see Fig. 3(C)). But, before the sweep of Fig. 1(A), Fig. 3(A) shows that the passivated negative active mass is only composed of very large  $\text{PbSO}_4$  crystals. When the passivated negative active mass undergoes one cycle of Fig. 1(A), a lot of small crystals of  $\text{PbSO}_4$  are formed over these big crystals (see Fig. 3(B)). Therefore, we consider that both peaks 'b' and 'c' are the reduction of  $\text{PbSO}_4$ , but their crystalline structures are different. Peak 'c' is the reduction of the big crystals and peak 'b' is that of the small crystals. The difference of their reduction peak potentials may be due to: (i) the difference of the solubility for the crystals of different sizes, and (ii) different structures of the passivation layer.

When a negative plate is immersed in the  $\text{H}_2\text{SO}_4$  solution, the self-discharge of the active mass and the recrystallization of small  $\text{PbSO}_4$  crystals happen simultaneously. Both processes result in the decrease of the number of small  $\text{PbSO}_4$  crystals and the formation of bigger ones. In Fig. 4, the solid line is a stable cyclic voltammogram (10th cycle). We open the circuit when the sweep potential reaches  $-1500$  mV and immerse the electrode in 1.09 M  $\text{H}_2\text{SO}_4$  for 72 h. Then, the negative-going sweep begins from  $-950$  mV again. The subsequent second cycle is shown in the dashed line of Fig. 4. This indicates that the oxidation and reduction peaks obviously become lower. But in the following eight cycles, they will rise gradually to the same height as the solid line. Therefore, the big  $\text{PbSO}_4$  crystals formed in the self-discharge intensifies the passivation of the electrode and the slightly-



Fig. 3. (A) SEM of the active mass for a passivated negative plate before the sweep of Fig. 1(A). (B) After undergoing one cycle of Fig. 1(A) and (C) for the discharge state of a newly-formed negative plate.

passivated active mass on the negative plate is gradually reactivated in the charge/discharge cycles. In the positive-going sweep, the cathodic current after the self-discharge is higher than that before the self-discharge. It seems that the electrode becomes more hysteric for the cathodic process. It is most likely that many micropores in the active mass are blocked in the recrystallization and self-discharge, which makes the  $\text{PbSO}_4$  crystals in the interior very difficult to be reduced.

Fig. 5 shows a stable cyclic voltammogram on a newly-formed negative plate in 5.04 M  $\text{H}_2\text{SO}_4$ . It is interesting to observe that the peaks 'a' and 'b' become very high and peak 'b' still appears clearly on the positive-going potential sweep

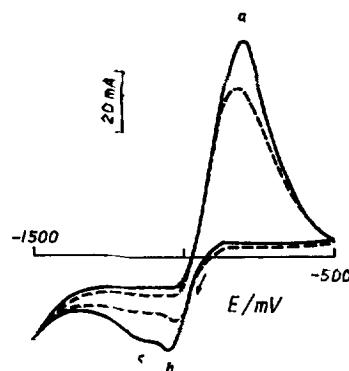


Fig. 4. Typical cyclic voltammograms for a small passivated negative plate in 1.09 M  $\text{H}_2\text{SO}_4$ . (—) a stable cyclic voltammogram; (---) the second cyclic voltammogram after the charged electrode is immersed in the same solution for 72 h; sweep rate: 1 mV/s.

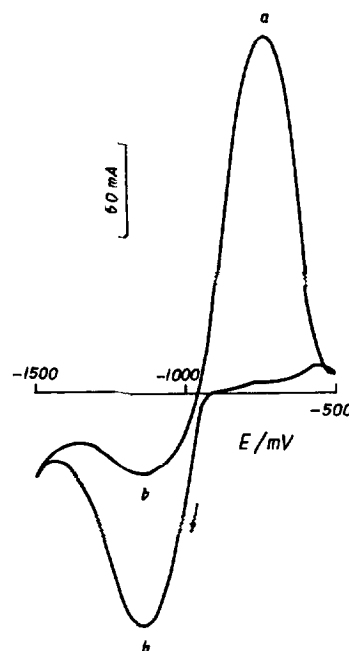


Fig. 5. A stable cyclic voltammogram for a small newly-formed plate in 5.04 M  $\text{H}_2\text{SO}_4$ ; sweep rate: 1 mV/s.

curve. It is the same for different  $\text{H}_2\text{SO}_4$  concentrations. This is because the mass transfer of the reaction ions is controlled by their passing through the micropores in the active mass.

In the negative-going sweep of peak 'b', the falling current is mainly caused by the decrease of the reaction area. At the minimum, only some areas deep in the micropores remain active and hydrogen begins to evolve clearly. At this time, the current of the  $\text{PbSO}_4$  reduction does not depend on the reaction area. According to the mechanism of the dissolution/precipitation, it should depend on the mass transfer of the  $\text{SO}_4^{2-}$  ion from the microporous bottom to the bulk solution. At a small overpotential, there is almost no hydrogen evolution. The concentration of the  $\text{Pb}^{2+}$  ion in the depth of the micropores is lower than that in the bulk solution, while the concentration distributions of the  $\text{SO}_4^{2-}$  and  $\text{H}^+$  ions are opposite. The reduction current of  $\text{PbSO}_4$  is the total of the

migration and diffusion current of the  $\text{SO}_4^{2-}$  ion. The diffusion rate of the  $\text{SO}_4^{2-}$  ion from the microporous bottom to the bulk solution decreases with the positive-going sweep. But at high overpotentials, hydrogen begins to evolve clearly and the concentration of the  $\text{H}^+$  ion in the depth of the micropores drops obviously. To maintain the electroneutrality, the concentration of the  $\text{SO}_4^{2-}$  ion becomes lower than that in bulk solution in this potential range. Therefore, the concentration distribution and the diffusion direction of the  $\text{SO}_4^{2-}$  ion is opposite to those at a small overpotential. We can observe a maximum in the positive-going sweep.

Peak 'b' always appears in the reverse sweep on a porous electrode. But it cannot be observed on a seriously passivated negative plate (see Figs. 1, 2 and 4). Although for the sweep on a solid lead electrode, peak 'b' cannot be observed in the reverse process, it appears again after several hundreds of cycles. This is because the porosity of the anodic film on the solid lead electrode becomes higher and higher with the cycles. Therefore, the micropores in the active mass for a passivated negative plate are narrow and deep and even seriously blocked. As a result, their mass transfer of the ions becomes very difficult. A great part of the active mass in the interior loses their activation.

Because of the recrystallization of small  $\text{PbSO}_4$  crystals and the self-discharge of a negative plate, very big  $\text{PbSO}_4$  crystals are formed in the active mass. The reduction peak of these crystals, peaks 'c', is unsymmetrical and shows a very long tail. The depassivation for a negative plate depends on the reduction of these big crystals of  $\text{PbSO}_4$ . Fig. 6 shows the effects of the additive of the  $\text{Al}^{3+}$  ion on the charge/discharge processes of a passivated negative plate in 1.09 M  $\text{H}_2\text{SO}_4$ . After the 40th cycle, 0.045 M  $\text{Al}^{3+}$  was added to the solution. It is found that with the deep cycles, the discharge capacity decreases in the solution without additive while it increases gradually when the solution contains the additive. The additive can therefore prevent and reduce the passivation of the negative plate.

Fig. 7 shows three cyclic voltammograms in the cycles of Fig. 6. In comparison with the 40th cycle in the solution without additive of the  $\text{Al}^{3+}$  ion, we can see that the reduction current of peak 'c', especially the falling current, becomes

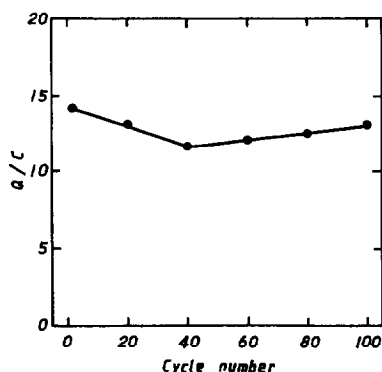


Fig. 6. Discharge capacity of the passivated negative plate vs. cycle number in 1.09 M  $\text{H}_2\text{SO}_4$  with and without the 0.045 M  $\text{Al}^{3+}$  which was added to the solution after the 40th cycle.

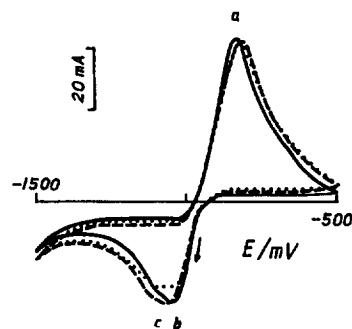


Fig. 7. As for Fig. 6 but for the cyclic voltammograms. Cycle numbers: (—) 40; (---) 42, and (···) 100.

high obviously after the additive is added to the solution. This higher falling current indicates that big  $\text{PbSO}_4$  crystals can be reduced more easily. Thus, the additive can make the active mass depassivated. Fig. 7 also shows that in the discharge, the peak potential of peak 'a' shifts a little in the positive direction in the solution with the additive, while its discharge current in the falling part of peak 'a' and its discharge capacity become obviously great. The higher anodic current also appears in the reverse sweep. Therefore, the negative active mass is not easily to be passivated in the deep-discharge under the action of the  $\text{Al}^{3+}$  ion. Its mechanism is still unclear and needs further study.

#### 4. Conclusions

In the recrystallization and self-discharge, many big  $\text{PbSO}_4$  crystals are formed on a seriously passivated negative plate. The micropores in the active mass become very narrow and long and even their passageways are greatly blocked. The porosity in the active mass decreases obviously. The mass transfer of ions in it becomes very difficult. In charge/discharge cycles, many small  $\text{PbSO}_4$  crystals are formed over the big crystals which are very difficult to be reduced [12]. Two reduction peaks of  $\text{PbSO}_4$  appear clearly on the negative-going potential sweep curve. They represent the reduction of  $\text{PbSO}_4$  crystals of different sizes. The more negative reduction peak is the reduction of the big  $\text{PbSO}_4$  crystals. When the concentration of  $\text{H}_2\text{SO}_4$  solution increases, this peak becomes obscure. This is because the electrode surface is covered by many small  $\text{PbSO}_4$  crystals. The reduction rate of the negative active mass is controlled by the diffusion process of the  $\text{SO}_4^{2-}$  ion from the depth of the micropores to the bulk solution. When the active mass on the negative plate is passivated seriously, the passageway in the micropores becomes so small that the shifting of the peak potential of the  $\text{PbSO}_4$  reduction in the negative direction exceeds 200 mV. In the solution containing  $\text{Al}^{3+}$  ions, the big  $\text{PbSO}_4$  crystals can be reduced more easily and it is more difficult for  $\text{PbSO}_4$  crystals formed in the discharge to passivate the electrode. Therefore, the additive can be used to prevent and eliminate the passivation of the negative plate.

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