Electrochemical behaviour of SnSO$_4$ in sulfuric acid solution

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Abstract

The effect of SnSO$_4$ on the deep-discharge capacity of lead/acid batteries is investigated when it is added to the sulfuric acid electrolyte. The electrochemical behaviour of Sn^{2+} ions in sulfuric acid is studied by using chemical-analysis and cyclic-voltammetry methods. In the battery system, Sn^{2+} ions will be reduced to tin on the negative plates or will be oxidized to tin(IV) species on the positive plates. Tin metal formed on the negative plates will improve the charge/discharge properties. Tin(IV) species formed on the positive plates may be incorporated as SnO$_2$ in the positive active material (PAM) as well as in the anodic film that is produced at the grid/active-material interface. The effect of SnO$_2$ on the properties of the PAM are explained in terms of the gel–crystal model. The SnO$_2$ is stable during the discharge process. The compound increases the electronic conductivity of the gel zones, thereby, enhances the capacity of the PAM. The SnO$_2$ species may also act as nuclei for the formation of β-PbO$_2$ in the crystal zones. The corrosion of positive grids is inhibited by the presence of SnO$_2$. By virtue of these effects, the addition of SnSO$_4$ is beneficial to the operation of lead/acid batteries.

Keywords Sulfuric acid, Tin sulfate, Lead/acid batteries

1. Introduction

Tin has been widely used as an alloying element in the manufacture of positive grids for lead/acid batteries. Its effect on the properties of the grid and, therefore, of the lead/acid battery itself has been reviewed by several authors [1–4]. With some battery designs, it has been found that a passivation layer (that comprises α-PbO deposited directly under a semi-permeable PbSO$_4$ layer) is formed at the grid/active-material interface. The addition of tin at levels of about 0.2 wt.% or more to antimony-free or low-antimony positive grids will prevent such a detrimental effect [5,6]. It will reduce the level of α-PbO and alleviate the passivation problems. A battery using Pb–Ca–Sn alloys can be recharged after deep-discharge service. Tin in the grids may serve as a source of tin ions; these are formed during the operation process of the lead/acid battery. The tin ions may dissolve into the PAM and also into the sulfuric acid solution. The anodic behaviour of pure tin and a Pb–10wt.%Sn alloy in sulfuric acid solution has been studied recently by Sundholm and co-workers [7,8]. It is concluded that the anodic dissolution of pure tin occurs mainly as tin(II) ions, and that the oxide film

is based mainly on SnO, although higher oxidation states of tin can also be present. The same conclusions hold for the Pb–10wt.%Sn alloy.

In other work, tin(II) compounds (mainly as SnO or SnSO$_4$) have been applied to the PAM by adding the compounds directly to the lead paste [9,10], by soaking the positive plate in sulfuric acid solution containing SnSO$_4$ [11], or by adding SnSO$_4$ to the electrolyte of lead/acid batteries [12,13]. It is generally considered that tin(II) compounds are beneficial to the charge/discharge process of the lead/acid battery, especially that of the positive electrode. The effect of the addition of SnSO$_4$ to sulfuric acid on the capacity level of Planté-type positive electrodes has been discussed [13] in terms of the 'Kugelhaufen' theory. In this case, it is considered that SnSO$_4$ is oxidized to SnO$_2$. With Fauré electrodes, it is claimed that SnSO$_4$ may reduce the non-conductive PbO$_x$ layer, which is formed at the grid/active-material interface, to highly conducting metallic lead [12]. It should be pointed out, however, that a detail evaluation of the potentials involved in the Pb/H$_2$O/H$_2$SO$_4$ system excludes this possibility. Further research on the electrochemical behaviour of SnSO$_4$ and its effect on the Fauré-type electrodes is required.

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In the work reported here, the effect of $SnSO_4$ (added to sulfuric acid solution) on the discharge property of lead/acid batteries using Fauré electrodes is examined. The fate of tin(II) ions is studied using chemical analysis and cyclic voltammetry methods. The mechanism of the effect of $SnSO_4$ on the performance of lead/acid batteries, especially with respect to the positive plates, is discussed in terms of the experimental results that are subsequently obtained.

2. Experimental

The test 'battery' consisted of a single three-plate cell that comprised one positive and two negative plates. The grid of the positive plate made from a Pb–Ca alloy with a weight of about 27 g and dimensions: 65 mm (height) × 44 mm (width) × 3.5 mm (thickness). The grids of the negative plates were made from pure lead with a weight of about 18 g per plate and dimensions: 65 mm (height) × 44 mm (width) × 2.0 mm (thickness). The pastes were prepared by mixing lead powder (1000 g) with water (100 cm^3), sulfuric acid (120 cm^3 with 1.30 sp. gr. for positive plate; 155 cm^3 with 1.12 sp. gr. for negative plate) and fibre. The additives of negative plates included $BaSO_4$ (6 g) and humic acid (8 g). Each positive plate contained about 38 g paste and each negative plate contained about 22 g paste. Plates were soaked in sulfuric acid (1.05 sp. gr.) for about 1 min and then dried at 45 °C for 30 h. Plate formation was carried out for 24 h at 300 mA per positive plate in sulfuric acid solutions (1.10 sp. gr.) with (type A) or without (type B) the addition of 1.5 wt.% $SnSO_4$. The corresponding sulfuric acid solution used in the discharge and the recharge experiments had a sp. gr. of 1.28 with (type A) or without (type B) the addition of 1.5 wt.% $SnSO_4$. The discharge experiments were carried out at a constant current of 300 mA and the end voltage for discharge was 1.75 V. This corresponded to a depth-of-discharge (DOD) of 100%. The recharge procedure was as follows: (i) a constant current of 300 mA for 8 h, and (ii) constant voltage of 2.4 V until zero current was obtained.

In cyclic-voltammetry experiments, the working electrode was either a platinum plate with dimensions 1 cm × 1 cm, or a cylinder made from pure lead (99.999 wt.%) set in glass tube with epoxy and with an exposed area of 0.28 cm^2. The counter electrode was a platinum plate (1 cm × 1 cm). A $Hg/HgSO_4$ electrode that contained the same solution as in the cell served as the reference electrode and was introduced via a luggin capillary. Before each experiment, the lead electrode was polished carefully with emery papers until a mirror-like surface was obtained. A 4.5 M (1.28 sp. gr.) solution of sulfuric acid was prepared from concentrated H_2SO_4 and doubly-distilled water. Sulfuric acid solutions with

1.5 wt.% $SnSO_4$ were prepared by dissolving a certain amount of $SnSO_4$ in 4.5 M H_2SO_4. All reagents used in this part of work were of AR grade. Instruments used in the study included a JH-2C potentiostat connected to an XFD-8A signal generator. Cyclic voltammograms were recorded on an LZ3-204 x–y functional recorder. All experiments were carried out at 30 ± 0.1 °C.

3. Results and discussion

3.1. Influence of $SnSO_4$ on discharge capacity

Fig. 1 shows typical discharge curves for the two types of battery when discharged at 300 mA. The discharge voltage of battery A is about 30 mV higher than that of battery B. The capacity of battery A is about 0.78 Ah (21%) higher than that of battery B (3.70 Ah) at cycle 5, and about 22% higher at cycle 25 (Fig. 2). Clearly, $SnSO_4$ can exert a beneficial influence on the discharge and cycle-life properties of lead/acid batteries when it is added to the sulfuric acid solution. According to the experimental results obtained here, this influence is much more significant than that
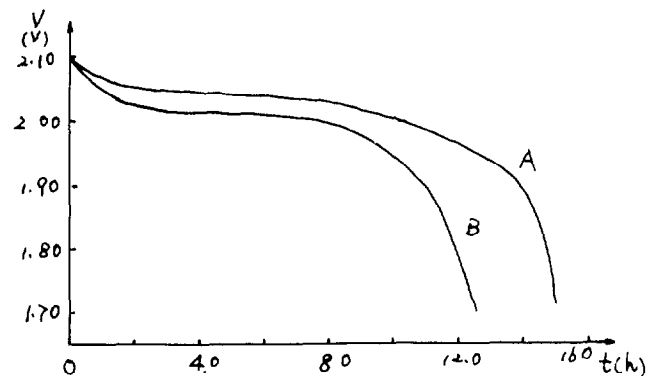

Fig. 1. Discharge curves for test batteries (A) with or (B) without 1.5 wt.% $SnSO_4$ in sulfuric acid. Discharge current = 300 mA
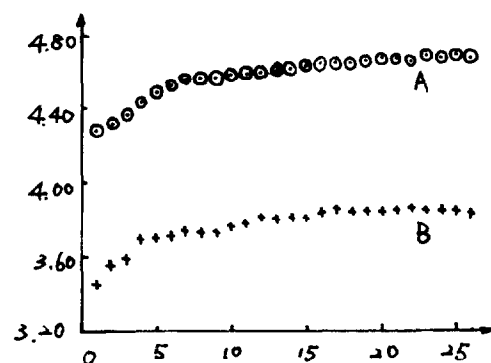

Fig 2. Capacity changes during the first 25 cycles of test batteries (A) with or (B) without 1.5 wt.% $SnSO_4$ in sulfuric acid. Discharge current = 300 mA; DOD = 100%

observed for the corresponding addition of H_3PO_4, K_2SO_4, or citric acid.

3.2. Chemical analysis of sulfuric acid solution

Ammonium molybdophosphate can be used to identify qualitatively the existence of Sn^{2+} ions. When it is added to a solution that contains Sn^{2+} ions, the solution will exhibit a black-blue colour. When ammonium molybdophosphate is added to sulfuric acid solution after the charge process, no colour change is observed. After the discharge process, however, a change in colour to blue-black is always observed. Needle-like crystals with a metal lustre appear on the surface of the negative plates and the latter turn to grey gradually after the plate-formation process has begun. The crystals disappear completely during the discharge process. A quantity of the crystals were removed from the negative plates, washed with distilled water, and then dissolved in 4.5 M sulfuric acid. A colour change to black-blue was observed after some ammonium molybdophosphate was added to the solution. These phenomena persisted during the following recharge/discharge processes.

Since Sn and $SnSO_4$ dissolve in sulfuric acid as Sn^{2+} ions, the above phenomena show obviously that these ions are reduced to tin metal during the charge process, and then the tin is reoxidized to Sn^{2+} ions during the following discharge process. This transformation process, to some extent, is reversible [14]. The possibility of the transformation process of the Sn^{2+}/Sn couple can also be illustrated from the corresponding value of the standard potential, which is more positive for the Sn^{2+}/Sn couple than that for the $PbSO_4/Pb$ couple. Thus Sn^{2+} ions will be reduced before $PbSO_4$, but the resultant tin metal will be reoxidized after lead.

During the recharge/discharge process of negative plates, tin metal existing in $PbSO_4$ will increase the electronic conductivity of the active material. Hence, more $PbSO_4$ will take part in the charge process to produce more lead active material, and more lead will take part in discharge process to give a higher capacity. The recharge/discharge properties (e.g., discharge capacity and cycle life) of negative plates will be improved by the presence of $SnSO_4$ in sulfuric acid. Since the overpotential for hydrogen evolution is higher on tin than on pure lead, it can also be expected that the charge efficiency of negative plates will be improved by the presence of $SnSO_4$.

Although tin dissolves from pure tin and Pb–10 wt.%Sn electrodes mainly as tin(II) ions, and tin(IV) ions appear only if potential is ≥ 3 V [7,8], the standard potential of Sn^{4+}/Sn^{2+} couple is only 0.151 V (versus SHE) [15]. Since this is much more negative than that of $PbO_2/PbSO_4$ couple (given the influence of pH), Sn^{2+} may be oxidized to Sn^{4+} before $PbSO_4$ is oxidized to PbO_2. The existence of Sn^{4+} ions in sulfuric acid

solution after the charge process is demonstrated by the fact that a colour change to black-blue can also be observed when ammonium molybdophosphate is added to sulfuric acid solutions in which a piece of zinc metal is dissolved. That is, Sn^{4+} ions will be reduced to Sn^{2+} by zinc. The formation of Sn^{4+} ions is caused by the oxidation of Sn^{2+} on the positive plate during the recharge process. As discussed below, the reduction of Sn^{4+} ions to Sn^{2+} may be irreversible [14] and, therefore, an accumulation of Sn^{4+} as SnO_2 may occur in the positive plate.

3.3. Cyclic voltammetric experiments

Fig. 3 shows cyclic voltammograms obtained with a platinum-plate electrode (1 cm × 1 cm) in 4.5 M sulfuric acid solution containing 1.5 wt.% $SnSO_4$. The curves between -0.7 and $+1.3$ V are enlarged by 50 times. The anodic peak appearing at -0.90 V can be ascribed to the oxidation of tin to Sn^{2+}; the corresponding reduction peak appears at -1.0 V. Another anodic peak appears at $+0.10$ V. According to the standard potential [14], this peak may be caused by the oxidation of Sn^{2+} to Sn^{4+} species. The peak current is much lower than that of the anodic peak of the Sn^{4+}/Sn^{2+} couple and the charge consumed is smaller than a half of that consumed in the later peak. Thus, only part of the Sn^{2+} ions are oxidized to Sn^{4+}. This current peak decreases in size and moves to more negative potentials from cycle 1 to cycle 3 (Fig. 3). The corresponding cathodic peak is observed at about -0.40 V. The peak current and the charge consumed are even smaller than those of the corresponding anodic
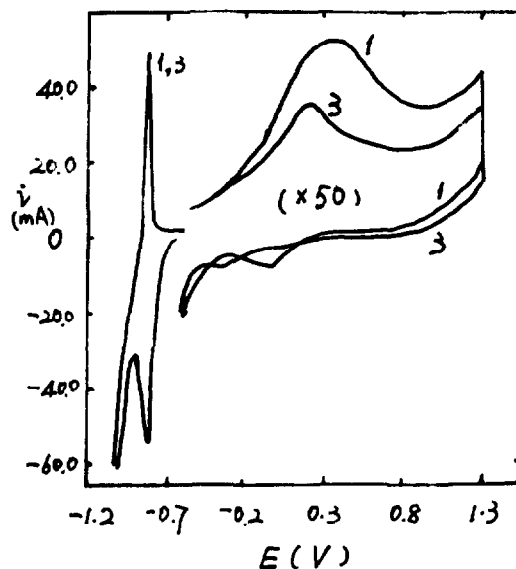
Fig. 3. Cyclic voltammograms for 4.5 M H_2SO_4 containing 1.5 wt.% $SnSO_4$. Numbers of curves give the cycle number. Scan region: -1.3 to $+1.3$ V; scan rate: 30 mV s^{-1}.

peak. This cathodic peak does not change significantly with the cycle number. Therefore, only part of the Sn^{4+} species formed at the more positive potential is reduced at this potential. The reduction of Sn^{4+} may also occur in tandem with the hydrogen-gas evolution of more negative potentials [14].

Cyclic voltammograms for a lead electrode in the same solution as above are given in Fig. 4. Corresponding data for lead in 4.5 M sulfuric acid is included for comparison. The former curves between -0.7 and $+1.3$ V are enlarged by a factor of 10. The oxidation process of the lead electrode, as well as the oxygen- and hydrogen-gas evolution processes, are inhibited by the presence of $SnSO_4$. The current peaks corresponding to the oxidation and reduction of the Sn^{2+}/Sn couple are masked by those corresponding to the $PbSO_4/Pb$ or the $PbO\cdot PbSO_4/Pb$ couples. An additional anodic peak attributed to the oxidation of Sn^{2+} is also observed at $+0.10$ V. The peak current is still very small, and the peak potential does not shift with cycle number. The corresponding cathodic peak has not been observed. Thus, it is difficult for tin(IV) species to be reduced to tin(II). These species will not be reduced to a lower valence at a potential that is more negative than the reduction potential of PbO_2.

When Sn^{2+} ions are oxidized on the positive plate of a lead/acid battery, they may be incorporated as SnO_2 in PAM and/or in the lead anodic film. It has been suggested that the particles and agglomerates of PAM consist of gel zones and crystal zones [16]. The gel zones are composed of hydrated polymer chains that exhibit both proton and electron conductivity. These zones are partially dehydrated to form α- or β-PbO_2 crystal zones, which are electron-conductive. The polymer chains act as electronic bridges between the crystal

zones. The electrochemical activity of the PAM is determined by the concurrent existence of gel and crystal zones. The SnO_2 may probably take part in the gel zones and facilitate the electron transport through this zone from one crystal region to another. This allows more agglomerates to take part in the discharge process and hence the capacity increases. The quantity of SnO_2 will grow with cycling and its effect will expand over a greater number of agglomerates. Furthermore SnO_2 and β-PbO_2 have a similar rutile structure and similar cation size. Since SnO_2 is stable and will not be reduced during discharge of the positive plates, it may, when incorporated in the crystal zones of the PAM, act as nuclei for the formation of β-PbO_2 during the recharge process and, therefore, will decrease the required charge potential. This has also been demonstrated in Fig. 4.

When lead electrode is cycled in sulfuric acid solution without $SnSO_4$ and the potential is higher than 1.0 V, the positive-going curve is lower than the negative-going curve. This indicates a nucleation process for β-PbO_2. This phenomenon is not observed when a lead electrode is cycled in a solution that contains $SnSO_4$, where SnO_2 formed by the oxidation of Sn^{2+} provides nuclei for the formation of β-PbO_2. When SnO_2 is incorporated into the oxide film between the grid and the active material, the conductivity of the oxide film is modified and further growth of the film is hindered. Indeed, SnO_2 has been used as a corrosion protection coating for lead/acid battery grids [17] and exhibits good stability under the oxidative conditions encountered in positive plates.

4. Conclusions

The capacity of lead/acid batteries under deep-discharge conditions is improved by the presence of $SnSO_4$ in sulfuric acid. The Sn^{2+} ions will be reduced to tin metal on the negative plates during the recharge process. The tin metal formed is reoxidized to Sn^{2+} ions during the following discharge process. The discharge capacity and the charge efficiency of negative plates will be enhanced. The Sn^{2+} ions may also be oxidized to Sn^{4+} species on the positive plates. These Sn^{4+} species may exist as SnO_2 both in the PAM and in the lead anodic film. The presence of SnO_2 species in the PAM will modify the electronic conductivity of the gel zones and act as nuclei for the formation of β-PbO_2 in the crystal zones. The discharge capacity and charge efficiency of positive plates are enhanced by the presence of SnO_2 in the PAM. The corrosion of the positive grid will be inhibited when SnO_2 is incorporated into the lead anodic film. Clearly, the addition of $SnSO_4$ to sulfuric acid is beneficial to the operation of the lead/acid battery.

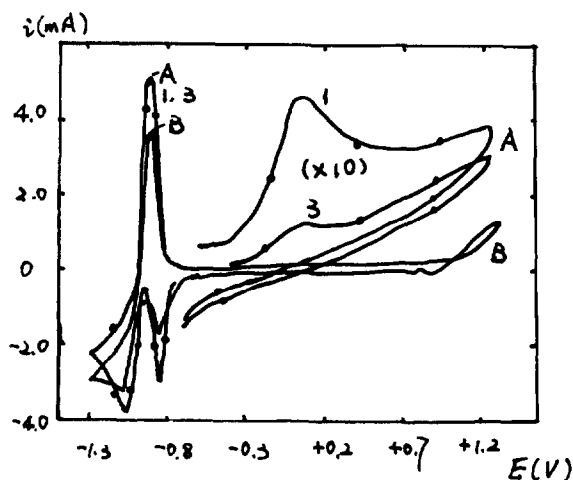Fig 4. Cyclic voltammograms for lead electrode in 4.5 M H_2SO_4 containing (A) 1.5 wt.% $SnSO_4$, and (B) no $SnSO_4$. Numbers on curves give the cycle number. Scan region: -1.3 to $+1.3$ V; scan rate 30 mV s^{-1}

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