BEHAVIOUR OF THE PbO$_2$/PbSO$_4$ ELECTRODE IN SULPHURIC ACID CONTAINING TIN IONS

E. VOSS*, U. HULLMEINE and A. WINSEL

VARTA Batterie AG, Research and Development Center, D-6233 Kelkheim/Ts. (F.R.G.)

Introduction

For many decades, tin and tin compounds have been added to lead/acid cells for a number of reasons and their effects on cell behaviour have been investigated repeatedly. An important example is the application of tin in Pb–Sb and Pb–Ca alloys for grid manufacture. The effect of tin on alloy properties has been discussed in various review papers and no further mention appears to be necessary here [1 - 3]. Nevertheless, it should be pointed out that a tin-containing grid alloy may serve as a source for tin ions in the electrolyte under the highly corrosive conditions prevailing in the lead/acid cell at the PbO$_2$/PbSO$_4$ electrode, and that, particularly at this electrode, tin is said to deploy its beneficial effect. Because of this, tin compounds (such as SnO or SnSO$_4$) have been applied to the positive active material by adding the compounds directly to the paste [4 - 6], by soaking the plates in an acid SnSO$_4$ solution [7], or by simply adding SnSO$_4$ to the electrolyte [8]. In all cases, a higher cell voltage on high-rate discharge, a reduced self-discharge, an improved life, and/or an easy rechargeability after extensive overdischarge are observed in the presence of Sn^{2+} compounds. It is claimed that these additives reduce the anodic grid corrosion and largely prevent the formation of a non-conductive layer at the grid/active-material interface.

In a recent publication, it has been demonstrated that the capacity level of a positive electrode is sensitive to the previous charge and discharge history. This behaviour of a PbO$_2$/PbSO$_4$ electrode has been related to the solid-state properties of PbO$_{2-\delta}$ and to the active material structure that can be regarded as an aggregate of spheres (termed 'Kugelhaufen') [9]. The Kugelhaufen model has been used successfully for a qualitative explanation of the effects of charge, current density, overcharge, and discharge current density on the capacity level of a positive electrode during cycling. It is an objective of practical importance to search for means that will eliminate, or at least mitigate, this capacity sensitivity. As will be considered in detail below, the Kugelhaufen model shows that redox couples

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*Author to whom correspondence should be addressed.

having a potential lower than that of the $PbO_2/PbSO_4$ electrode may help to maintain the capacity at a high level independent of the charge and discharge parameters. In order to test this prediction experimentally, the compound $SnSO_4$ has been selected which, after addition to a lead/acid cell, may form the couples:

Sn/Sn^{2+} $E_0 = -0.136$ V

Sn^{2+}/Sn^{4+} $E_0 =$ 0.151 V

Sn^{2+}/SnO_2 $E_0 = -0.077$ V

Experimental

The experiments were mainly performed on Planté electrodes. Details of dimensions, electrolyte concentration, and temperature, as well as on equipment, have been described elsewhere [9]. In some cases, Fauré-type electrodes were used under forced electrolyte flow through the porous active material. This 'Eloflux' method has also been reported earlier [10].

Tin sulphate ($SnSO_4$) solution in H_2SO_4 of the same concentration as the test electrolyte was added to the positive Planté electrode compartment 60 min before the end of charge. The concentration was 1 g $SnSO_4$ per 100 cm^3 of acid. The addition was repeated when higher $SnSO_4$ concentrations were required in the electrolyte. In the case of the Eloflux experiments, the $SnSO_4$ solution was forced to flow through the positive active material in order to avoid loss of tin at the negative electrode.

Results

Behaviour of Planté electrodes

As demonstrated in earlier experiments, the capacity of a Planté electrode is reduced by 25 - 30% within 20 cycles when the charge regime is changed from a high-rate/low-rate/low-overcharge sequence (regime A) to a low-rate/high-overcharge sequence (regime B). More particularly, a high capacity level is obtained on cycling when about 65% of the capacity is recharged at a rate of 3.0 mA cm^{-2} (high rate) and then at a rate of 0.75 mA cm^{-2} (low rate) until a charge factor of 1.25 (25% overcharge, low) is applied (regime A). Under these conditions, a capacity level of 41 A h is maintained over a number of cycles, of which only cycles 200 and 201 are shown in Fig. 1. After cycle 201, a charge regime B is applied, consisting of a constant current at 0.38 mA cm^{-2} (low rate) throughout the charge to give a charge factor of 1.5 (50% overcharge per cycle, high). As a consequence, the capacity immediately drops cycle by cycle and finally arrives at a new lower level of 30 A h. This is the normal behaviour of a Planté electrode and demonstrates its sensitivity to the charge conditions.
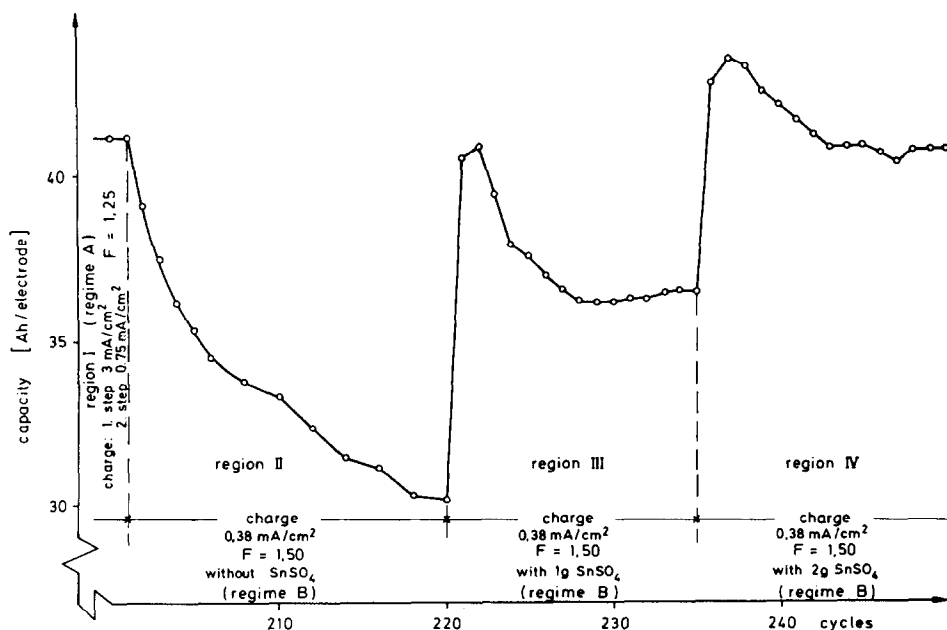
Fig. 1. Effect of SnSO$_4$ on the capacity of a Planté electrode (discharge current: 0.75 mA cm^{-2}).

During the 220th charge, 1 g of SnSO$_4$ is added to the electrolyte, as described in the experimental section. As can be seen from Fig. 1, the capacity increases spontaneously to 40 A h within one cycle (*i.e.*, cycle 221) and then to 41 A h on the next cycle. On further cycling under the conditions of regime B, however, the capacity decreases again and finally reaches a plateau of about 36 A h. This is an improvement of 20% over the capacity level obtained in the absence of SnSO$_4$.

At the 235th charge, another 1 g of SnSO$_4$ is added, and again a spontaneous increase is observed up to a capacity maximum of 43.5 A h. On further cycling, the capacity levels out at 41 A h, which is identical with the initial value obtained under regime A conditions. From these results, it is evident that additions of SnSO$_4$ to the cell are reducing, and finally are even eliminating, the sensitivity of the electrolyte capacity to charge parameter variations.

A second experiment was conducted that was almost identical with that described above except that the discharge current density was increased from 0.75 to 1.5 mA cm^{-2} in order to evaluate the effect of discharge-parameter variation. The results are presented in Fig. 2. Again it can be seen that the effects of SnSO$_4$ additions on the capacity under regime B conditions are spontaneous and resemble those observed during the first experiment. Even after the addition of a total of 3 g of SnSO$_4$, however, the electrode capacity level is still lower than the initial level obtained under regime A conditions. It appears that this can be attributed to the higher discharge current density.
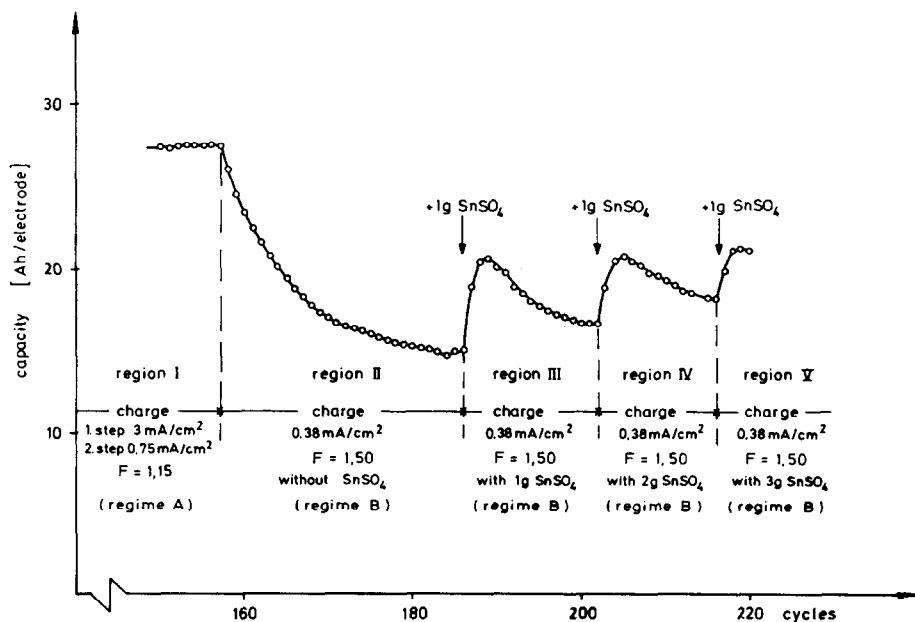
Fig. 2. Effect of SnSO$_4$ addition on the capacity of a Planté electrode and influence of charge regime (discharge current 1.5 mA cm^{-2}).

On addition of SnSO$_4$ to the electrolyte, an immediate response of the cell voltage is observed. As explained in the experimental section, the SnSO$_4$ solution is added 60 min before the end of charge. At this stage, most of the charge is being converted to hydrogen and oxygen. With SnSO$_4$ addition, it is found that whereas the hydrogen overvoltage at the negative electrode drops by about 30 - 40 mV, the positive electrode potential (oxygen over-voltage) is virtually unaffected and falls by only a few millivolts. At the latter electrode, the potential decrease is annulled within the remaining 60 min of the charge. Consequently, the positive potential does not depend on the presence, or absence, of SnSO$_4$ in the cell during further charge and subsequent discharge. On the next charge under regime A, however, the potential of the positive electrode at the end of the first (high rate) charging step (at which point there is no gassing, i.e., O$_2$ evolution) falls by about 40 mV and stays at the lower value for many cycles. No potential decrease could be observed under regime B charging conditions. Given the 40 mV decrease in potential observed at a high-rate charge current of 3 mA cm^{-2}, a corresponding decrease of 4 mV would be expected at a charge current of 0.38 mA cm^{-2}. Such a small deviation in potential could not be detected to a good degree of accuracy with the equipment used in these experiments.

Behaviour of positive Fauré electrodes

The effect of SnSO$_4$ additions on the capacity of Fauré electrodes was investigated using procedures analogous to those reported above for Planté

electrodes. No beneficial effect on the capacity stability was observed with, or without, electrolyte flow through the porous active material. On the contrary, in some cases it appeared that a capacity decrease occurred on $SnSO_4$ addition. Whether this unexpected result is due to an incorrect dosage of $SnSO_4$ has still to be resolved.

Discussion

The spontaneous effects of small quantities of $SnSO_4$ on the capacity of a Planté electrode is discussed on the basis of the Kugelhaufen model for the electrode [9, 11]. In order to understand the spontaneous capacity increase (cf., Fig. 1) on the addition of 1 g = 1/215 = 0.0047 mole of $SnSO_4$, the PbO_2 volume present in the neck zones of a Kugelhaufen is related to the PbO_2 volume reacting with 0.0047 mole of $SnSO_4$ according to the equations:

$$PbO_2 + SnSO_4 + 4H^+ \longrightarrow PbSO_4 + 2H_2O + Sn^{4+} \tag{1}$$

$$PbO_2 + SnSO_4 \longrightarrow PbSO_4 + SnO_2 \tag{2}$$
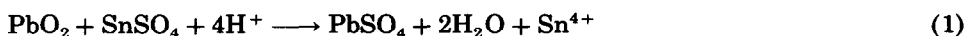
Based on the geometry given in Fig. 3, it is calculated that 0.17% of the total PbO_2 volume is located in the neck zones (for details, see Appendix I). Since the total PbO_2 volume of the Planté test electrode is 24 cm^3 PbO_2, 0.17% amounts to 0.04 cm^3 PbO_2. On the other hand, 0.0047 mol of PbO_2 is equivalent to 0.12 cm^3 of PbO_2. This shows that 1 - 3 g of $SnSO_4$ reacting in one way or another with the PbO_2 present in the neck zones will produce considerable effects, given the fact that the neck-zone resistance (Engewiderstand) determines the resistance of the active material and that the resistance of the latter determines the capacity [12].

Several processes may be considered to be responsible for a reaction in the neck zones. Two of these are as follows.

(i) Sn^{2+} generates Pb^{2+} species at the spheres according to eqn. (1). These Pb^{2+} species migrate primarily to the neck zone which is anodically polarized in the sphere–neck zone couple forming additional $PbO_{2-\delta}$ in the neck zone, thus decreasing the resistance of the active material. Sn^{4+}
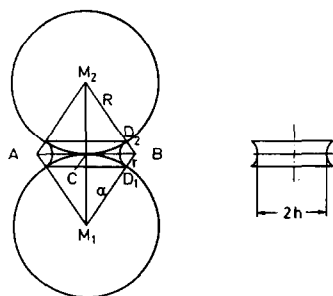

Fig. 3. Geometrical relationships in a Kugelhaufen (aggregate of spheres).

species formed by this reaction remain in the electrolyte and eventually may be reduced at the negative electrode to Sn^{2+} or even to Sn.

(ii) $SnSO_4$ may be oxidized to SnO_2 by $PbO_{2-\delta}$ of the neck zones according to eqn. (2). SnO_2 may be incorporated into the $PbO_{2-\delta}$ of the neck zones, forming an SnO_2-doped $PbO_{2-\delta}$ or a $PbSnO_{4-\delta}$ with a high δ-value and, consequently, a decreased potential that stabilizes the Kugel-haufen structure during discharge due to a better protection of the neck zones against premature corrosion. It appears, however, that $PbO_2 \cdot SnO_2$ compounds are unknown. Therefore, a discussion of SnO_2-doped PbO_2 is not pursued at this time.

In an earlier publication [8], it is claimed that $SnSO_4$ may reduce the non-conductive PbO_x layer, which is formed at the lead grid/active material interface of a Fauré electrode, to highly conducting metallic lead. As a consequence, $SnSO_4$ additions maintain the rechargeability of the cell even after deep discharges. At first sight, this explanation may also be applied to a Planté electrode. A more detailed evaluation of the various potentials involved at a $PbO_2/PbSO_4$ electrode, even in the deep-discharged state, clearly shows, however, that the reduction of PbO_x by Sn^{2+} can only proceed to Pb^{2+} species, i.e., to non-conductive PbO, $PbSO_4$, etc. Since the structure of the lead/active material interfaces of both elec-trode types are almost identical, it would be expected that $SnSO_4$ additions should react in a similar way independently of the electrode design. To date, it has not been possible to demonstrate experimentally the $SnSO_4$ effect on Fauré electrodes, and further research on this type of electrode is required.

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Appendix I

Calculation of the active material volume ratio $V_h:V_K$ ($V_h = PbO_2$ volume in the neck zones, $V_K = PbO_2$ volume in the spheres)

The basis for the calculation of $V_h:V_K$ is the geometric relationships shown in Fig. 3. The volume of PbO_2 in the neck zone is given by

$$V_h = 2\pi r h^2 \cdot \cos \alpha \tag{1}$$

(r = radius of meniscus, h = radius of neck zone, α = angle at M_1).
Since:

$$\cos \alpha = \frac{R}{R+r} \tag{2}$$

and

$$r = \frac{h^2}{2(R-h)} \tag{3}$$

it follows:

$$V_h = 2\pi h^2 \frac{h^2}{2(R-h)} \cdot \frac{R}{R + h^2/2(R-h)} \tag{4}$$

Calculation yields:

$$V_h = \pi h^4 \frac{R}{R(R-h) + h^2/2} \tag{5}$$

and since $h^2/2 \approx 0$

$$V_h = \frac{\pi h^4}{R-h} \tag{6}$$

The volume of the PbO_2 sphere is:

$$V_K = \frac{4}{3}\pi R^3 \tag{7}$$

Accepting an octahedral coordination of spheres, each sphere having 6 nearest neighbours, i.e., 6/2 neck zones, yields the ratio

$$\Phi = \frac{6/2 V_h}{V_K} = \frac{18h^4}{8R^4(1-h/R)} \tag{8}$$

In previous publications [9, 11] it has been shown that $R/h \approx 6$. Therefore, it appears reasonable for a first approximation to set $(1-h/R) \approx 1$.
Then, eqn. (8) simplifies to:

$$\Phi = \frac{9}{4}\left(\frac{h}{R}\right)^4 \tag{9}$$

With $h/R \approx 1/6$:

$$\Phi = 1.7 \times 10^{-3} \tag{10}$$

In other words, 0.17% of the total PbO_2 volume is located in the neck zones. In the case of an hexagonal close-packed structure, *i.e.*, each sphere having 12/2 neck zones:

$$\Phi = 3.4 \times 10^{-3} \tag{11}$$