

## The effect of tin on the performance of positive plates in lead/acid batteries

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### Abstract

There are many reports that the use of non- or low-antimonial grids in lead/acid batteries can give rise to the development of a high-impedance 'passivation' layer at the grid/active-material interface. It is generally agreed that the layer has a duplex structure that comprises  $\alpha$ -PbO deposited directly on the grid surface beneath a compact covering of PbSO<sub>4</sub>; basic sulfates and  $\alpha$ -PbO<sub>2</sub> may also be present. The development of this structure hinders recovery from prolonged deep discharge or self-discharge. Similar phenomena can be observed with dry-charged positive plates. Passivation can also occur during cycling and float operations but, in these duties, the formation of a non-conductive layer of PbSO<sub>4</sub> is thought to be the prime cause of the degradation in plate performance. The incorporation of tin in the positive grid (either in the alloy itself or as a surface layer) is found to reduce the level of  $\alpha$ -PbO and greatly alleviate passivation problems relating to charge acceptance. Various mechanisms have been proposed for this tin effect and range from a semiconductor-type doping of  $\alpha$ -PbO to changes in the porosity of the PbSO<sub>4</sub> layer and/or the reactivity of  $\alpha$ -PbO towards oxidation. The benefits of tin in cycling and float duties are less obvious and it is probable that other features of cell design are more important determinants of battery performance. The action of tin when incorporated in the positive active material requires further exploration.

### Introduction

A recent major trend in lead/acid battery technology has been the move to maintenance-free (MF) units for applications such as the starting-lighting-ignition of vehicles ('automotive' batteries), standby power and portable power. These batteries encompass both flooded-electrolyte and gas-recombination systems; the latter include both gelled-electrolyte and absorptive glass-microfibre designs (so-called 'valve-regulated batteries' (VRBs)). To achieve MF characteristics, the grid alloy is conventionally free of antimony. Most manufacturers have opted for lead-calcium-tin ternary alloys, but lead-calcium binaries, and even pure lead, are also being used. An alternative approach is to use a low-antimony alloy (1–2 wt.% Sb). In this case, the antimony content is controlled at a level that is sufficient to exploit the benefit of good cycle life imparted by antimony, but does not evoke the detrimental effects of excessive water loss.

Unfortunately, the move away from conventional high-antimony alloys (6–12 wt.% Sb) has increased the incidence of the following adverse behaviour:

- premature, rapid loss of capacity on cycling and, hence, reduced cycle life
- poor charge acceptance of deeply-discharged batteries
- poor performance of dry-charged positive plates when processed at elevated temperatures

All of these phenomena are associated with the positive plate and have been attributed to two causes, namely; (i) the lack of tin in the positive grid alloy; (ii) the lower content of grid antimony. Giess [1] has separated the behaviour into an 'antimony-free effect' that hinders the discharge of positive plates, and a 'tin-free effect' that creates corresponding problems during recharge.

This paper reviews the literature available on fundamental studies of the effect/role of tin in the positive plate and compares the findings with data obtained from tests on practical batteries. Of particular concern is the topic of 'passivation'. With regard to battery operation, passivation can be usefully described as the process(es) that impede the electrochemical reactions that normally take place at the electrodes. In the case of positive plates in lead/acid cells, the term passivation refers to situations where there is some demonstration of an additional energetic barrier at the grid/active-material interface. This barrier creates either an initial sharp fall in voltage during discharge or a low current during constant-voltage charging (i.e., poor charge acceptance).

Passivation has been mentioned in connection with each of the above three problems that are encountered with MF batteries. Yet, as will be shown, this has not always been justified because other phenomena may have been responsible for the observed behaviour.

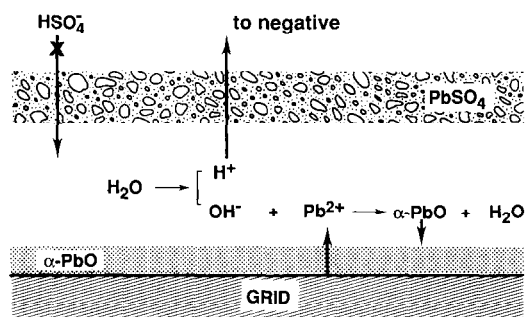
### **Pb/PbO<sub>2</sub> interface**

For reasons of experimental simplicity, many aspects of positive-plate performance have been examined by a consideration of the electrochemical behaviour of the grid metal itself. Numerous studies have focused on the structure and composition of the corrosion layer formed on bare lead electrodes in sulfuric acid solution. Some of this research has included an examination of the effect(s) of tin. From X-ray diffraction (XRD) studies on pure lead, relationships were established between the polarization potential and the phase composition of the corrosion product. These provided a baseline against which the influence of alloying elements could be measured. For example, Pavlov *et al.* [2] showed that PbSO<sub>4</sub> forms at potentials up to -300 mV,  $\alpha$ -PbO develops in substantial quantities together with small amounts of basic lead sulfates between -300 and +900 mV, and both  $\alpha$ - and  $\beta$ -PbO<sub>2</sub> are produced above +900 mV; all potentials are reported with respect to a Hg/Hg<sub>2</sub>SO<sub>4</sub> reference electrode. (Note,  $\alpha$ -PbO has a tetragonal structure and some authors prefer to use the term tet-PbO, or t-PbO.) Consideration of the electrical conductivity of the various lead compounds reveals the importance of these results. While PbSO<sub>4</sub> is non-conducting, both  $\alpha$ - and  $\beta$ -PbO<sub>2</sub> are good conductors. Due to structural defects,  $\alpha$ -PbO generally occurs as a semiconductor. Basic lead sulfates are likely to be non-conducting [3]. The possibility that compounds other than PbO<sub>2</sub> could persist within the positive-plate structure was seen as an obvious cause of passivation. To date, most of the work on bare electrodes has generally pursued this line of investigation.

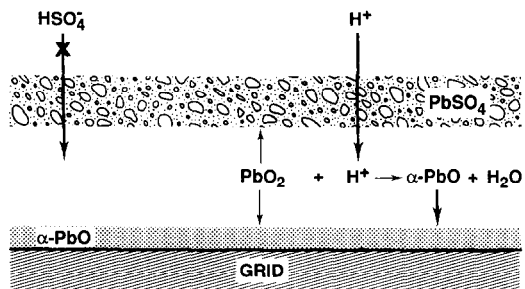
In a continuation of their earlier work, Pavlov and Jordanov [4] postulated that  $\alpha$ -PbO was formed by corrosion of the lead substrate residing beneath a layer of PbSO<sub>4</sub>. A detailed explanation for the stability of  $\alpha$ -PbO in (apparently) acidic media has been advanced by R uettschi [5]. The PbSO<sub>4</sub> layer is considered to act as a semi-

permeable membrane that hinders, or blocks, the migration of  $\text{HSO}_4^-$  and  $\text{SO}_4^{2-}$  ions into the corrosion layer. Deposition of sulfate species trapped beneath the  $\text{PbSO}_4$  film, together with the net flow of  $\text{H}^+$  ions to the negative electrode during electrode (or battery) charging, raise the pH in the interior of the corrosion layer and, hence, allow stabilization of the  $\alpha\text{-PbO}$  (see Fig. 1(a)). Equally,  $\alpha\text{-PbO}$  may be formed during the discharge process by the mechanism shown in Fig. 1(b). In support of this hypothesis, the presence of  $\alpha\text{-PbO}$  has been detected by different workers using a wide range of techniques. Particularly convincing evidence has been obtained from *in situ* techniques such as photo-acoustic spectroscopy [6] and photocurrent spectroscopy [3, 7, 8]. The use of such investigative tools precludes the possibility of  $\alpha\text{-PbO}$  being an experimental artefact (as may happen with *ex situ* analysis) that arises, for example, via a solid-state reaction between lead and  $\text{PbO}_2$  during sample removal from the test cell and subsequent treatment, e.g., washing, drying.

While most demonstrations of  $\alpha\text{-PbO}$  formation on lead anodes have been performed at relatively low potentials ( $< 900$  mV versus  $\text{Hg}/\text{Hg}_2\text{SO}_4$ ), the compound has also been identified under much more severe conditions. At high positive potentials (i.e.,  $\sim 1.4$  V versus  $\text{Hg}/\text{Hg}_2\text{SO}_4$ ), Bullock and Butler [9] have shown that the corrosion layer on pure lead consists of an outer film of  $\alpha\text{-PbO}_2$  and an inner film of  $\alpha\text{-PbO}$ . The overall corrosion rate is probably controlled by oxygen transport through the two films. It is envisaged that a steady-state is reached where the outer edge of the  $\alpha\text{-PbO}$  converts to  $\alpha\text{-PbO}_2$  at the same rate as it is produced at the grid surface.



(a)



(b)

Fig. 1. Schematic of mechanism whereby  $\alpha\text{-PbO}$  can develop during (a) charging or (b) discharging of a lead/acid positive plate.

It should be pointed out, however, that some workers have not detected  $\alpha$ -PbO in lead corrosion layers. Panesar [10], for example, conducted cyclic voltammetric studies on pure lead and found  $\alpha$ - and  $\beta$ -PbO<sub>2</sub>, but neither  $\alpha$ -PbO nor basic lead sulfates. In other work, Takehara *et al.* [11, 12] employed XRD as a searching technique but only PbSO<sub>4</sub> was identified at the Pb/PbO<sub>2</sub> interface. These latter authors established that the PbSO<sub>4</sub> in this region was oriented on the (002) and (020) planes and that the crystals were larger than those produced by the discharge of PbO<sub>2</sub>. Increase in PbO<sub>2</sub> porosity, high temperature (50 °C) and prolonged potentiostatic discharge all caused further growth of the PbSO<sub>4</sub> layer. It was notable that these conditions made removal of the layer (by electrochemical oxidation) more difficult. The behaviour was shown to be a function of the lead substrate by the observation that smaller, non-passivating, PbSO<sub>4</sub> crystals were produced when the experiments were repeated on an inert substrate (*viz.*, a gold electrode).

#### *Effect of tin*

Using XRD, Giess [1] found that the corrosion of pure lead at 1.00 V versus Hg/Hg<sub>2</sub>SO<sub>4</sub> gave rise to a thin (1–2  $\mu$ m) PbSO<sub>4</sub> layer and a massive underlying  $\alpha$ -PbO layer with a preferred (110) orientation. By adding 0.2 to 0.4 wt.% Sn to the lead, the extent of the corrosion was reduced by a factor of 6 to 8 and the formation of  $\alpha$ -PbO was greatly suppressed.

Pavlov *et al.* [13] arrived at similar conclusions and suggested that tin modified the kinetics of the oxidation of  $\alpha$ -PbO in the following proposed reaction scheme for the overall corrosion of the grid metal:



It was proposed that tin is incorporated into the PbO/PbO<sub>x</sub> crystal lattice as Sn<sup>3+</sup>, and accelerates the rate of reaction (2) by increasing the electronic conductivity of  $\alpha$ -PbO and shifting the potential for oxidation of  $\alpha$ -PbO to a more negative value. Clearly, these effects would serve to decrease the amount of  $\alpha$ -PbO produced in the corrosion layer during the anodic oxidation of lead.

From cyclic voltammetric studies, Ijomah [14] concluded that tin in a Pb–30wt.%Sn alloy oxidized to Sn(II) which was then thought to deposit in the corrosion layer as both SnO and SnO<sub>2</sub>. A second alloy, containing 5 wt.% Sn, gave a corrosion current that was approximately twice that obtained from pure lead. In a following paper [15], the characteristics of a wider range of Pb–Sn alloys were examined with the technique of a.c. impedance spectroscopy. The impedance spectra were extremely complicated, however, and yielded little information. Voltammetric evidence was presented for the presence of both PbSO<sub>4</sub> and PbO·PbSO<sub>4</sub> (monobasic lead sulfate) in the corrosion layer.

#### **Pb/PbO<sub>2</sub> interface in battery plates**

The data reviewed to this point have been obtained primarily from reports of the corrosion of bare-metal electrodes. This section examines the results of investigations conducted on electrodes that also contain PbO<sub>2</sub> active material.

### *Thermopassivation and self-discharge*

Thermopassivation is a well-known problem and relates to the failure of dry-charged plates to achieve activation (for details of the activation test see ref. 16). Garche and co-workers [17–19] studied thermopassivation in some detail, together with the behaviour of plates that were allowed to self-discharge. In both situations, significant barriers to subsequent plate discharge were noted. In order to explain such examples of passivation, two reaction schemes were proposed; both involve the deposition of lead monoxide (referred to as 'PbO') at the grid/active-material interface [18]. One reaction occurs in the liquid phase and involves a galvanic coupling of PbO<sub>2</sub> reduction and grid-metal oxidation. This results in the growth of a PbSO<sub>4</sub> semipermeable membrane during the initial stages of self-discharge when the acid concentration is high, and to the formation of underlying PbO and basic lead sulfates when the acid becomes depleted. The passivation will be more severe in acid-starved systems because self-discharge causes a more rapid decrease in acid concentration. The second scheme is a solid-state process in which PbO is produced by the reaction of the grid alloy with adjacent PbO<sub>2</sub>. The initial reaction rate is thought to be limited by oxygen transfer. Studies of the influence of the drying conditions on plate performance suggest that there is a substantial kinetic barrier to the solid-state reaction. The reaction becomes appreciable only at elevated temperatures.

According to both reaction schemes, passivation gives rise to the formation of a range of lead oxides, PbO<sub>x</sub> ( $1 \leq x < 1.5$ ), that exhibit semiconducting properties. Garche and co-workers [18, 19] have underlined the significance of these properties in the context of positive-plate performance by undertaking an analysis of the electrical characteristics of thermopassivated plates. By applying currents (of various magnitudes and both polarities) across the grid/active-material interface of dried plates, it was shown that barriers to the passage of both anodic and cathodic currents developed with the onset of passivation. In the case of 'heavily thermopassivated' plates, the resistance to anodic current flow became very high. This behaviour is analogous to that of a diode and suggests that charging of such plates would be extremely difficult should such electrical characteristics persist during subsequent activation in acid solution. Similar findings were obtained in a later study of plates that had undergone self-discharge [20]. The observed behaviour has been interpreted in terms of a phase-junction model of the interfacial region in which the Pb/PbO<sub>x</sub>/PbO<sub>2</sub> system forms a n-p-n junction.

Several research groups have shown that tin, as a component of the grid alloy, can prevent passivation [1, 12, 18, 20]. As mentioned above, it has been suggested that the tin becomes incorporated in the PbO<sub>x</sub> and thereby increases the conductivity. Garche and co-workers [17, 20] have developed this argument in terms of the phase-junction model. In this case, doping of the intermediate lead oxide with tin could alter not only the magnitude but also the mechanism of conductivity, i.e., from p-type to n-type.

Barton *et al.* [21] observed passivation problems with VRBs that were assembled with pure-lead grids. The cells exhibited a large drop in voltage on high-rate discharge, together with a reduced ability to recover capacity after open-circuit stand for long periods (weeks) in a deeply-discharged state. Performance was improved greatly by the addition of 0.5 wt.% Sn to the positive grid alloy. Cyclic voltammetric, XRD and a.c. impedance spectroscopic studies of bare grid-metal samples revealed the presence of a layer of  $\alpha$ -PbO. The latter was considerably thicker on the tin-free grids and was responsible for the higher ohmic resistance. It was postulated that the  $\alpha$ -PbO layer developed during plate formation when the plate interior became alkaline through

reaction of  $\text{H}_2\text{SO}_4$  with unreacted lead monoxide in the cured-plate material (note, also, VRBs employ an acid-starved design). On subsequent reaction with  $\text{H}_2\text{SO}_4$ , the  $\alpha$ -PbO became protected with a non-porous layer of  $\text{PbSO}_4$ . The presence of tin resulted in a thinner PbO layer that could be easily sulfated and removed during charging of the battery.

Bullock and Laird [22] also concluded that  $\alpha$ -PbO passivating layers were formed in acid-starved systems when units were allowed to self-discharge to below 1.85 V. The batteries under study had antimonial alloy grids. Curiously, when pure-lead grids were used, the  $\alpha$ -PbO layer was much thinner. In a later study, Kita *et al.* [23] provided more detail in this area by investigating the relationships between the occurrence of  $\alpha$ -PbO (identified by its yellow appearance) in the corrosion layer and variables such as temperature, time of storage, acid concentration and initial cell state-of-charge. Although most of the work centred on the behaviour of plates based on a Pb–Ca–Sn alloy, four antimonial alloys (Pb–Sb (0.9 to 2.35 wt.%)) were also examined. With the latter, it was noted that both the extent of grid corrosion and the amount of  $\alpha$ -PbO were greater at lower levels of grid antimony. The authors attributed this finding to differences in the microstructural characteristics of the alloys.

Takahashi *et al.* [24] observed the appearance of passivation phenomena in VRBs after prolonged discharge. It was found that a high ratio of acid to positive active material (i.e.,  $\text{H}_2\text{SO}_4/\text{PbO}_2 > 0.6$ ) proved an effective remedy. By contrast, this ratio has to be low in VRB designs because of the need for acid-starved conditions to assist gas recombination. The same authors, however, demonstrated that the addition of 3 to 5 wt.% tin in the alloy, or the placement of a tin-rich layer on the grid surface, avoided passivation problems.

#### *Cycling or float conditions*

It is well known that antimony endows positive plates with good cycle life compared with those using non-antimonial alloys such as lead–calcium. Tin has been suggested as a means for raising the cycling performance of the latter alloys.

Chang *et al.* [25, 26] investigated the effects of various design and processing parameters on the cycling performance of positive plates made from lead–calcium–0.3 wt.% tin grids. The studies showed that premature failure was associated with a preferential discharge mechanism whereby the outermost parts of the corrosion layer were discharged before the adjacent active material has reacted. Thus, it was contended that the development of a non-conducting film of  $\text{PbSO}_4$  in the outer corrosion layer prevented complete discharge of the plate material. It was noted also that extensive, concentric cracking occurred in the underlying dense corrosion product. Lead sulfate crystals rapidly grew in the resulting fissures and further weakened the mechanical integrity of the corrosion layer. Given these phenomena, it was concluded that acid ingress is a major determinant of the premature capacity loss of lead–calcium plates and, therefore, it was suggested that cycle life might be improved by decreasing the acid concentration in the vicinity of the grid. In practice, the latter can be achieved by increasing the active-material density and/or plate thickness, or by decreasing the specific gravity or volume of the acid. In this respect, the latter remedy for cycling/float service is opposite to that proposed by Takahashi *et al.* [24], see above, for protecting the grid from passivation under conditions of prolonged discharge or self-discharge where an increase in acid concentration is beneficial.

The effect(s) of acid concentration on the performance of Pb–Ca–Sn plates has been examined in great detail by Nakashima and Hattori [27, 28]. Both the concentration and the volume of sulfuric acid were varied systematically in order to demonstrate

that good cycle life (at  $C_5/5$ , 100% depth-of-discharge) could be obtained under conditions of acid starvation, although the cell capacity was less than that normally available. Active material from these cells, when compared with that from corresponding strong-acid cells (1.28 sp. gr.), was characterized by lower specific surface area and higher average pore size. Cells failed prematurely when cycled in a non-limiting amount of strong acid. A return of 'lost' capacity was obtained by substituting a weaker acid (1.10 sp. gr.). No explanation was given for this behaviour. Examination of cross sections of plates that had failed in strong acid revealed the presence of yellow material (thought to be  $\alpha$ -PbO), and of PbSO<sub>4</sub> in relatively high concentrations. Neither of these features was noted in cross sections of plates that had been cycled exclusively in weak acid.

Jinbo and Watanabe [29] showed that 'sealed' cells with lead-calcium and lead-calcium-tin alloy grids exhibited a capacity loss when on float duty. The degradation in performance could be minimized either by charging in low-gravity acid (1.05 sp.gr.) or by increasing the tin content in the alloy. Constant-current corrosion studies on bare-metal electrodes with tin contents in the range 0.7 to 8.0 wt.% indicated that the presence of tin improved the adhesion between the corrosion layer and the underlying grid metal.

Cyclic voltammetric studies undertaken by Takahashi *et al.* [24] provided circumstantial evidence that  $\alpha$ -PbO<sub>2</sub> was formed in the corrosion layer in amounts that increased with lowering of the acid concentration. The authors also claimed that the presence of tin accelerated the growth of  $\alpha$ -PbO<sub>2</sub>, even under highly acidic conditions. From these results, it was concluded that good cycle life (i.e., reduced grid passivation) is associated with a high level of  $\alpha$ -PbO<sub>2</sub> in the corrosion product. As pointed out by Chang *et al.* [25, 26], it is well known that  $\alpha$ -PbO<sub>2</sub> is more difficult to discharge than  $\beta$ -PbO<sub>2</sub> and this may hinder, or prevent, the formation of a PbSO<sub>4</sub> barrier layer.

In tests conducted by Carter *et al.* [30], cells constructed with lead-calcium-tin alloy grids typically lost 20% of the initial capacity after 50 cycles of deep discharge. Examination with scanning electron microscopy (SEM) revealed poor contact between the grid and the active material, while energy dispersive spectrometry identified a high concentration of sulfur at that interface. The thickness of the sulfur-rich layer (claimed to be PbSO<sub>4</sub>) increased with charge/discharge cycling and thus correlated with the observed decline in capacity.

Further evidence that the development of PbSO<sub>4</sub> in the corrosion zone causes capacity loss in cycled plates (Pb-Ca-0.75wt.%Sn grids) was obtained by Tsubota *et al.* [31] from EPMA studies. It was also found that flooded designs were more susceptible to this problem than acid-limited designs. This was demonstrated by flooding a healthy VRB design, observing a progressive loss of ~30% of the initial capacity, and then achieving a return to full performance by draining off the excess electrolyte.

Nelson and Wisdom [32, 33] showed that the addition of tin to pure-lead grids in VRBs assisted: (i) recharge after deep discharge; (ii) charge acceptance; (iii) capacity loss during early cycle life. The poor capacity performance in the absence of tin could be removed by heating the batteries at 50 to 60 °C for 15 to 34 days, or by cell reversal. It was thought that both these processes converted  $\alpha$ -PbO to PbSO<sub>4</sub>. Generally, tin was found to have only a temporary effect and deterioration in performance occurred later in cycle life. Under float conditions, cross sections of plates with pure-lead grids exhibited substantial layers of corrosion product after about 18 days. By comparison, much thinner and discontinuous layers were formed on plates with a lead-tin alloy. Lead-tin alloys exhibited increased corrosive attack along the grain boundaries at various sites on the grid surface. It was proposed that these areas provide avenues for the current to flow through the corrosion zone.

Valeriotte *et al.* [34] studied the effect of tin in expanded grids made from lead-calcium alloys and arrived at different conclusions. They found that tin gave only a slight improvement in capacity retention during the initial stages of cycle life. Early capacity loss was witnessed only if the acid concentration was high (1.32 versus 1.25 sp.gr.) or the recharge was low (105 versus 115%). While material identified as  $\alpha$ -PbO was detected in many of the corrosion layers examined, it was not possible to establish a relationship with the decrease in plate performance.

As noted at the beginning of this review, Giess [1] was one of the first to suggest that a clear distinction should be made between the effects of antimony and tin on the performance of positive plates. This contention was based on the findings from a study of the charge acceptance of positive electrodes with different grid alloys. Single-spine tubular electrodes were subjected to discharge at the  $C_5/5$  rate and then charged at constant current. When the spine was composed of either pure lead or a tin-free Pb-1.5wt.%Sb alloy, the positive electrode potential (versus Hg/Hg<sub>2</sub>SO<sub>4</sub>) rose to extremely high values during charging at the  $C_5/5$  rate. The potential peaked at values of  $\geq 1.70$  V before returning to lower levels near the end of charging. By comparison, electrodes with current collectors made from a Pb-0.6wt.%Sn alloy showed no such voltage excursions; the positive-plate potential increased smoothly to a plateau at 1.4 V. Thus, it was argued that a significant ohmic impedance could develop within the positive electrode during discharge at moderate rates and that the incorporation of small amounts of tin in the spine/grid alloy overcame the problem. This study provided one of the clearest demonstrations of passivation in lead/acid battery electrodes. Substantial amounts of  $\alpha$ -PbO were shown to form on bare-metal specimens. There was, however, no discussion of any connection between the observed passivation and the capacity/cycle life profile of battery plates.

### Effect of tin in positive active material

Although much of the literature relates the effect of tin to modification of the corrosion products at the grid/active-material interface, tin may also exert an influence upon the characteristics of active material. For example, Voss *et al.* [35] discovered that the capacity loss of Planté cells could be reversed by adding small amounts of SnSO<sub>4</sub> to the electrolyte; the extent of the recovery was dependent upon the applied charging regime. This effect was discussed in terms of the 'Kugelhaufen' theory in which the resistance of interparticle contact in the active material is considered to be the primary determinant of positive-plate condition [36-38]. The improvement in capacity due to tin was explained by an increase in the connectivity, and hence the conductivity, of the active material. Any influence of tin on the corrosion layer was ruled out because Sn<sup>2+</sup> species cannot reduce PbO<sub>x</sub> to Pb but only to Pb<sup>2+</sup> species, e.g., to PbO, PbSO<sub>4</sub>, and hence passivation will persist, or may even be increased. It was noted that cells with pasted plates gave no recovery of capacity when treated similarly with SnSO<sub>4</sub>.

The fate of Sn<sup>2+</sup> in the electrolyte is not known but, undoubtedly, it will be oxidized to a Sn<sup>4+</sup> species at positive-plate potentials. Sn<sup>4+</sup> is soluble at pH=0 [39] but could precipitate as SnO<sub>2</sub> in the positive active material. Indeed, SnO<sub>2</sub> has been used as a corrosion protection coating for lead/acid battery grids [40, 41] and exhibits good stability under the oxidative conditions normally encountered in positive plates [42]. In a recent development, a novel tin-dioxide-coated, glass-fibre additive has been



incorporated into the positive active material with a view to increasing both the mass utilization and the cycle life [43–46].

Both  $\text{SnO}_2$  and  $\beta\text{-PbO}_2$  have a rutile structure. The cation sizes are similar, namely,  $\text{Pb}^{4+} = 0.84 \text{ \AA}$ ,  $\text{Sn}^{4+} = 0.74 \text{ \AA}$ , and, therefore, yield similar unit-cell dimensions [47, 48]. As a result, the two compounds can form a mixed oxide of general formula  $\text{Pb}_x\text{Sn}_{1-x}\text{O}_2$  with  $0 < x < 1$  [47, 48]. Nevertheless, significant intergrowth of the two forms is probably limited at ambient temperature [49].  $\text{Pb}_x\text{Sn}_{1-x}\text{O}_2$  can be doped with elements, such as antimony, to improve its conductivity [48–51] and this suggests that tin may influence the bulk properties of  $\text{PbO}_2$ , particularly if antimony is also present. This possibility has not been explored in detail in the open literature. It should be pointed out, however, that Voss *et al.* [35] have reviewed the chemical literature and have found no evidence for the existence of  $\text{PbO}_2 \cdot \text{SnO}_2$  compounds.

## Discussion

The experimental data obtained from corrosion tests on bare-metal electrodes are in general agreement that the corrosion product has a duplex structure consisting of  $\text{PbSO}_4$  and an underlying layer of  $\alpha\text{-PbO}$ . At low-to-moderate positive potentials, the  $\alpha\text{-PbO}$  is protected by the perm-selective film of  $\text{PbSO}_4$ . Basic lead sulfates have also been found, but their electrochemical behaviour is poorly characterized, and hence it is difficult to gauge their impact on electrode performance. At much higher potentials, a covering layer of  $\alpha\text{-PbO}_2$  stabilizes the  $\alpha\text{-PbO}$  deposit. It should be noted that the nature of the corrosion product is most likely a consequence of the composition, structure and preparation of the electrode (or battery plate), and/or the conditions of the test regime. Therefore, it is possible that  $\alpha\text{-PbO}$  may not always develop in the corrosion layer.

It appears that the action of tin is to modify the features of the corrosion film such that the  $\text{PbO}$  layer becomes thinner and non-passivating. This may be due to a corresponding change in either the porosity of the  $\text{PbSO}_4$  (or  $\alpha\text{-PbO}_2$ ) or the reactivity of  $\alpha\text{-PbO}$  towards oxidation.

Several authors have postulated the development of a  $\text{PbO}_x$  phase in the corrosion layer. While reports have appeared on the physical and electrical properties of materials that nominally fall within the limits of the  $\text{PbO}_x$  composition [48, 52], it is difficult to understand the exact nature of this substance. In early work, Peter [53] found that electrodeposited  $\text{PbO}_2$  undergoes incomplete reduction and suggested that a  $\text{PbO}_x$  phase is formed with  $x$  close to 1.5. A later, more detailed, study [54] by the same author of the reduction of  $\alpha\text{-PbO}_2$  revealed that the product was in fact a two-phase mixture of  $\alpha\text{-PbO}$  and  $\text{PbO}_2$ .

The above fundamental research on bare electrodes appears to correlate well with the thermopassivation and self-discharge passivation that is observed in actual batteries. With battery plates, few workers have shown that the corrosion layer comprises a duplex structure. On the other hand, it has been found that tin greatly alleviates passivation problems. Of particular interest is the proposal by Garche and co-workers [18–20] that the interfacial layer exhibits semiconductive properties. This finding provides very strong evidence for the presence of a ‘ $\text{PbO}$  type’ phase as a semiconductor junction is unlikely to be formed by the  $\text{Pb/PbSO}_4/\text{PbO}_2$  system. Thus, it has been proposed that tin exerts its effect via a doping mechanism of  $\alpha\text{-PbO}$ . Such action would explain the demonstration by Takahashi *et al.* [24] that a tin-rich surface layer offers the same benefits as a high-tin alloy. One aspect of the role of tin that is still

unclear is its influence on passivation phenomena throughout the life of the battery. According to Garche and co-workers [18], thermopassivation is only manifested prior to the first discharge and does not cause problems in subsequent duty. There is apparently no information available on any relationship between the incidence of passivation under self-discharge and service life.

Whereas the tin effect seems reasonably well understood in the phenomena of thermopassivation and recovery from self-discharge, the situation is quite confused for cycling and float duties. The confusion mainly arises from the widespread, and often inappropriate, usage of the term 'passivation'. Few reports have demonstrated the presence of barrier(s) to electrode reactions under cycling conditions in a fashion similar to that witnessed in thermopassivation and self-discharge. Nevertheless, the studies of Giess [1], and to a certain extent those of Barton *et al.* [21], indicate that similar processes are operative under cycling duties. This is understandable since only minor differences are expected between the corrosion layer of a plate that is allowed to undergo self-discharge and one that is deliberately discharged at a moderate rate.

Most workers studying battery performance during cycling service have focused on the phenomenon of capacity loss and descriptions of passivation and passivating layers have generally not been supported by demonstration of the expected current/voltage characteristics. At the heart of this particular issue is the widely held, though unproven, belief that deposits of  $\text{PbSO}_4$  and/or  $\alpha\text{-PbO}$  in the corrosion layer are responsible for premature, rapid capacity loss in non- and low-antimonial positive plates. For example, Nakashima and Hattori [27, 28] have observed a corrosion layer with a duplex structure of  $\text{PbSO}_4$  and  $\alpha\text{-PbO}$ . To date, there has been no evaluation of the electrical properties of such a structure. Perhaps the most important finding from cycling studies is that tin appears to have little effect on cycle life under deep-discharge conditions. This observation has been made by both Nelson and Wisdom [32] and Valeriote *et al.* [34].

The final point that should be mentioned is the relationship of tin and antimony in the processes discussed here. The studies of thermopassivation and self-discharge have involved pure lead and an extensive range of antimonial alloys. The results have shown that passivation phenomena affect positive plates with grid antimony contents of 0 to 5 wt.%. This is good evidence for concluding that tin functions independently of antimony in minimizing passivation and that the latter element exerts no obvious effect on passivation. Under cycling conditions, the converse is almost true. Antimony has been shown, in numerous studies, to be the principal agent in preventing capacity loss, while the benefits, if any, of tin are debatable. Thus, good cycle life from non-antimonial grids appears to be determined more by the general cell design than by the presence of tin. In this respect, the importance of factors such as grid/active-material adhesion, active-material density and loading, acid concentration, acid/active-material ratio and overcharge has been demonstrated. Nevertheless, no consensus of opinion has been reached as to the required magnitude of each of these parameters to give a maximum-benefit product. The effect of tin in these circumstances may be solely to increase the corrosion of the grid and thus provide a more porous structure that modifies the properties of the material in the corrosion layer. Any such advantage may, however, be cancelled out by the intensified attack of the grid.

Virtually all of the investigations reviewed here indicate that passivation problems originate at the grid/active-material interface and argue that tin provides a panacea by modifying the structure/properties of the corrosion layer. Comparatively little work has been reported on the effect of tin on the bulk active material ( $\text{PbO}_2$ ) and perhaps this is an area worthy of future investigation.

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