

Discussions on the Lead/Acid Battery No. 3

Premature capacity loss in lead/acid batteries: a discussion of the antimony-free effect and related phenomena

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Abstract

Instances of severe capacity loss in apparently healthy lead/acid batteries have been reported over a period of many years, and are still common today. In most cases, these phenomena are linked to the use of antimony-free positive grids and are invoked by repetitive deep-discharge duties. This situation represents probably the greatest barrier to the expansion of markets for lead/acid batteries. To date, research has focused on several possible explanations for capacity loss, notably, degradation of the positive active mass (e.g., relaxable insufficient mass utilization) and the development of electrical barriers around the grid. Although much of the evidence gathered is circumstantial, it does point to the key issues that must be addressed in future work.

Definition of the effect

Not long after the first practical demonstrations of the utility of lead/acid batteries, the mechanical limitations of the base materials became plainly apparent. In particular, the production of plates according to the pasted grid technique, patented in 1881, exposed the weakness of pure lead as a grid material. The same year saw the first use of a lead–antimony alloy for the construction of grids and, to date, antimonial lead alloys are still the standard materials for the manufacture of lead/acid battery grids. This is not to say that antimonial lead is the ideal choice. Certainly, antimony confers a number of beneficial features on the lead/acid battery [1]. Improved castability and strength, compared to pure lead, are the most important mechanical effects, while the widely documented, but as yet poorly understood, enhancement of deep-discharge cycle life highlights the major benefit in terms of electrical performance. Opposed to these features are (i) the overpotential for hydrogen evolution is less at antimonial electrodes than at lead electrodes; (ii) stibine, SbH_3 , is a poisonous gas that may be liberated during charging [2].

In fact, the problem of stibine generation provided the major incentive for research into alternative grid materials. By far the most important of

these are the alloys derived from the Pb–Ca–(Sn) system which are noted for their excellent mechanical and electrochemical properties. The addition of tin, at levels generally in the region of 0.5 to 1.0 wt %, improves both the castability and the mechanical properties of the fully aged material. This effect is due to changes in the distribution and precipitation kinetics of the various intermetallic species present [3] so that significant control can be exerted over parameters such as grain size. Some authors are of the opinion that the ternary alloys of calcium and tin with lead are acceptable alternatives to antimonial lead, under all conditions. The balance of evidence, though, indicates that in certain circumstances the performance of lead/acid batteries based on *any* antimony-free system is hampered by a factor, or factors, commonly termed 'the antimony-free effect' (AFE). Such batteries, when compared to antimonial equivalents, exhibit distinctly inferior performance under various forms of charge/discharge cycling service, this feature provides the principal identification of the effect.

Typically, lead/acid cells displaying the AFE exhibit a rapid loss of discharge capacity early in the projected life of the cell (based on consideration of the quantity of active material present). This phenomenon has been observed for cells with positive plates based on grids of pure lead, lead–calcium alloys, lead–calcium–tin alloys, and lead–antimony alloys with antimony contents $< \sim 2$ wt %. The last of these is obviously not consistent with the term antimony-free and, in any case, 'antimony-free effect' tends to deny the existence of a 'calcium effect' or, as has been proposed, a 'tin-free effect'. In order to avoid the confusion associated with using several descriptors, the following discussion will, whenever possible, refer to the 'effect' as 'premature capacity-loss (PCL)'.

Observations/explanations of the effect

Phenomena in the active material

Burbank carried out the earliest detailed studies of PCL [4, 5]. First, a preliminary survey of the structural characteristics of positive plate material, before and after charge/discharge service, was undertaken [4]. Samples were collected from a variety of commercial plates and examined by microscopic techniques. It was found that plates in which the positive material took on, and maintained, a prismatic crystalline form during cycling retained their capacity. This applied to examples of both antimony- and calcium-based plates although it should be noted that sample plates were sourced from several manufacturers. Therefore, factors such as material loading and plate thickness may have been significant.

The second study [5] embodied a more controlled approach. Cells that were identical in every way, except for the variation in grid composition (typical examples of Pb–Ca and Pb–Sb alloys), were subjected to combined float/shallow discharge service that reflects the duty of submarine batteries.

in the US Navy. In this way, a much clearer relationship between structural features and grid composition emerged. The 'submarine' or '23 1' cycle involves discharge at $C_{10}/10$ for 1 h, followed by constant-current/constant-voltage charging ($V_{\max} = 2.35$ V/cell) for 23 h. Antimony-based plates developed a structure that comprised a network of small polyhedral crystals. In the case of lead-calcium, crystal size was similar, but crystal shape was anhedral and little, or no, agglomeration or interlocking was apparent. The latter point formed the basis for the explanation of the lower strength of positive material observed for plates with lead-calcium grids. In addition, significant differences were recorded for the relative amounts of α -PbO₂ and β -PbO₂ in the plate material of Pb-Ca and Pb-Sb cells. Before commencement of the duty cycle, the material of the antimonial cells contained an appreciable amount of α -PbO₂ while little was present in that of the calcium cells. At the end of the charge/discharge programme, the abundance of the alpha form had decreased in both plate types but remained considerable in the antimonial variant. Thus, two parameters of the positive plate material — crystal shape/size and PbO₂ polymorphism — had emerged as important determinants of the incidence of PCL.

In the next investigation of PCL from the Naval Research Laboratory, Burbank and Ritchie [6, 7] replaced positive plates based on lead-calcium with pure lead analogues and compared the performance with antimonial plates. Positive plate material was prepared from three different leady oxides yet there was little variation in the structural characteristics of the resultant active mass (PbO₂). Comparison was also made between the structure of the active mass for the two types of grid (pure and antimonial (7 wt % Sb) lead) immediately after formation. Again, no significant difference in morphology was noted.

The performance of cells incorporating the above plates was evaluated. The duty cycle consisted of discharges at $C_{20}/20$ interspersed with discharges at higher rates (up to 50 times $C_{20}/20$) along with periods of overcharge and low-temperature operation. The difference in behaviour between cells with pure lead positive grids and their antimonial analogues was considerable. The former displayed losses of capacity of around 80% prior to the tenth charge/discharge cycle. Under the same conditions, the capacities of the antimonial cells were essentially constant for the duration of the test schedule (~20 cycles). Electron microscopy was used to characterize active material taken both before and after failure. The main differences related to the size of PbO₂ crystals. Those comprising the positive material on pure lead grids grew in size markedly and became anhedral in shape within a few charge/discharge cycles, while samples from the antimonial plates maintained a smaller size and took on a polyhedral character. The authors concluded that premature failure of the pure lead cells was related directly to the loss of structural strength associated with the enhanced crystal growth rate. It was postulated that the preservation of small crystal size, and concomitant material strength, was due to some enhancement of PbO₂ nucleation, caused by adsorbed antimony species.

No changes were noted in the relative proportions of α -PbO₂ and β -PbO₂ in the two types of cell. This finding contrasted sharply with earlier work from the authors' laboratory [5], although it must be remembered that the latter was a comparison of lead-antimony grids with lead-calcium analogues, not with pure lead. While both types of antimony-free plates suffered PCL, the apparent causes of failure were not the same. Observations regarding crystal size and morphology were similar in both cases, but those pertaining to phase composition were completely different.

The role of antimony

Antimony and PbO₂ polymorphism

The possible relationship between antimonial species in the positive material and the distribution of PbO₂ between its two polymorphs is regarded by many as an important issue in the explanation of PCL. For instance, early work on PCL at Yuasa Battery Co. contended [8] that α -PbO₂ was the major product of corrosion in the positive plates of non-antimonial cells, while β -PbO₂ predominated in antimonial cells. Swets [9] carried out the first of a series of investigations into compounds related by structure to PbO₂. This work introduced a new compound, lead metantimonate, PbSb₂O₆. It was noted that structural parameters of the latter were similar to those of α -PbO₂, but were quite dissimilar to those of β -PbO₂, suggesting that PbSb₂O₆ may exist with α -PbO₂ through an epitaxial relationship. Thus, it was postulated that PbSb₂O₆ forms during discharging and then, during subsequent charging, facilitates the formation of α -PbO₂. In addition, it was suggested that PbSb₂O₆ might inhibit the participation of α -PbO₂ in the discharge process. These ideas could not be supported by experimental evidence.

In a later study, Hill [10] presented a more detailed crystallographic comparison of PbSb₂O₆ and the two forms of lead dioxide. This further underlined the similarities between α -PbO₂ and PbSb₂O₆. In addition, since PbSb₂O₆ has relatively weak inter-layer bonding, it was thought that the compound could act as a stress-relieving agent if present in the corrosion layer surrounding the grid. Structural aspects of the relationship between antimony and the two forms of lead dioxide were examined by Caldara *et al.* [11]. For thin layers (electrochemically deposited on a gold substrate) of both forms, it was shown that antimony modifies greatly the crystal morphology of α -PbO₂, but has only a minor effect on β -PbO₂. In addition, the ratio of O to Pb in the alpha form was extremely sensitive to the presence of antimony up to 0.2 wt % Sb. The authors did not report any incidence of new phases, such as PbSb₂O₆, in the deposits analyzed. At the time of writing this review, no experimental demonstration of lead metantimonate in lead/acid battery materials has been reported.

The aggregate-of-spheres model

As already noted, some of the earliest work on PCL suggested that the effect might be due to morphological and/or compositional changes in the

active mass. Since then, however, interest in this area has waned with most attention being paid to phenomena occurring in and around the corrosion layer. Recently, Winsel *et al* [12] have taken a fresh approach to events taking place in the bulk of the positive material. They have proposed a model for the structure of the active mass of the positive plate, known as the 'aggregate-of-spheres' ('Kugelhaufen') model, and have argued that it offers an explanation for PCL.

The Kugelhaufen model grew out of investigations into the sintering of metal powders and suggests that a porous electrode, such as the lead/acid positive electrode, can be described as a three-dimensional series of spherical particles. The small areas of contact between particles, essential for electrical conductivity, are termed 'neck zones'. Thermodynamic differences between the lead dioxide in these neck zones and that comprising the bulk of the material form the basis of the model's predictions. Specifically, it is advocated that the neck material is more stable thermodynamically and is therefore 'protected' during redox processes in which the porous electrode participates. With reference to the lead/acid positive plate, this difference in stability is explained in terms of variations in the actual oxygen content of the lead dioxide present in each zone. That in the neck zones is claimed to be relatively oxygen-poor and, hence, is more likely to be α -PbO₂. The model asserts that diminution of positive plate performance is caused by an increase in the resistance of the active material due to the formation of smaller neck zones.

With regard to the phenomena that cause PCL, it is suggested that the latter is described better as 'relaxable insufficient mass utilization' (RIMU). This description includes the term 'relaxable' because affected plates may be 'treated' for a decrease in mass utilization (i.e., drop in plate capacity) so that a recovery of performance takes place. The conditions under which RIMU is observed do not, however, cover many of the important experimental conditions under which PCL is known to occur, the proposed equivalence of RIMU and PCL is, therefore, not justified. Nevertheless, a consideration of the model and its predictions is instructive because, as mentioned earlier, it focuses attention on plate degradation phenomena that are, by definition, more insidious and, therefore, more difficult to detect and overcome.

Winsel *et al* [12] cited earlier work from their laboratories [13] in which it was shown that the resistance of the positive plate material in their special 'Eloflux cell', as measured between two small platinum probes located some distance from the grid, increased as plate capacity decreased during charge/discharge cycling. A slightly greater increase in resistance occurred in the course of each discharge and coincided with the rapid decrease in positive plate potential that accompanies the end of discharge. According to the model, this should be due to appreciable shrinkage of the neck zones and/or conversion of neck material to lead sulfate. The former will only proceed to a small extent under conditions of discharge, thus rendering the latter as the major occurrence. Presumably, the irreversible formation of lead sulfate in the neck zones could, therefore, play an important role in instances of capacity loss.

While the increase in the resistance between two platinum probes in the bulk material amounted to less than an order of magnitude, that measured between one of the probes and the plate grid was greater again by a factor of three. Thus, the probe-grid resistance reached a very high value during discharging. Yet, as soon as the discharge current was terminated, the resistance decreased to less than 50% of the peak value. This behaviour was noted for plates in good condition, but the same may not be true for aged, well-cycled plates for which an increasing portion of the high 'discharge resistance' may persist into subsequent plate operation. Overall, these results indicate that electrical resistance within the positive plate is dominated by the region that includes the grid corrosion layer. Thus, the resistance of material in the bulk of the active mass may increase, but this increase will be significant only once the resistance of the bulk material approaches that of the corrosion layer.

Another recent study of positive active mass structure bears an interesting relationship to the aggregate-of-spheres work. Pavlov *et al* [14] have examined the effect of elements, such as antimony, on the restoration of structure to pulverized positive material. Tubular positive electrodes were constructed by packing finely ground positive plate material, from a freshly formed plate, into the annular space surrounding a lead, or lead alloy, spine. The electrodes were then subjected to charge/discharge cycling. The regeneration of an effective active mass structure was indicated by a substantial increase in cell capacity. The latter was found to be extremely sensitive to the density of plate material within the tube, below 3.80 g cm^{-3} no recovery of capacity took place.

The effect of several metal ions in the electrolyte on the rate of recovery was also assessed. It was shown that only bismuth exerted a beneficial effect, while both antimony and arsenic inhibited the recovery of capacity. With respect to antimony, this result appears to contradict that of Winsel *et al* [12] who noted a partial recovery of capacity when a plate suffering RIMU was soaked at length in battery electrolyte containing antimony. In further observations, however, Pavlov *et al* [14] go on to show that when antimony, or one of the other elements, is present in the lead spine of the tubular electrode a significant recovery of capacity occurs during charge/discharge cycling. The most obvious explanation for this result is that the regenerative effect is localized in the region adjacent to the grid and that metal ions present in solution (with the exception of bismuth) are not able to penetrate to this level of the plate. The documented [15] adsorption of antimonial species by lead dioxide is evidence in favour of this argument.

Thus, one of the main conclusions from this work is that antimony contributes to reformation of an effective active-mass structure and that the focus of this effect appears to be in the region adjacent to the grid. Of course, this conclusion is based on data that were obtained under a unique set of conditions; are they relevant to the normal operation of lead/acid batteries? In other words, are the restorative properties of antimony effective at the micro level within the active mass, thereby reducing the impact of

degradative processes as they occur? Clearly, the answer to this question would be the solution to PCL, at least in terms of the role played by antimony. Perhaps an extension of these studies, involving calcium- and/or tin-based alloys, would provide even more useful information on PCL.

Bare metal electrodes

In the search for a clarification of the role of antimony, several attempts have been made at reducing the complexity of the system under investigation. Undoubtedly the most common approach has involved the substitution of actual positive plates (tubular or pasted) with so-called bare metal electrodes. Of the large number of publications that can be cited in this area, several have endeavoured to relate their findings to the issues of PCL. The key aspects arising from these studies are discussed here.

Cyclic voltammetry was used by Sharpe [16] in an extensive study of the electrochemical behaviour of Pb–Ca–Sn and Pb–Sb alloys. Based on a detailed examination of voltammetric curves in the region of the $\text{PbO}_2/\text{PbSO}_4$ couple, the author contended that the inclusion of antimony in the lead electrode retards the formation of $\beta\text{-PbO}_2$. Substantiation of this important conclusion was difficult because identification of oxidation products was based solely on the observed voltammetric behaviour. This task is always problematic, due to the presence of a range of lead compounds (e.g., PbO , PbSO_4 , PbO_2 , and intermediate oxides). In a subsequent work [17], similar voltammetric experiments were expanded to include a range of antimonial lead alloys (up to 8.2 wt % Sb). Again the complexity of the responses ruled out a simple description of the processes taking place. Thus, while the presence of antimony in the lead electrode clearly modifies both the voltammetric and chronoamperometric responses, this cannot be related easily to any change(s) in the electrochemical processes for the two forms of PbO_2 .

In other electrochemical investigations of bare metal electrodes, Arifuku *et al.* [18, 19] used secondary ion mass spectrometry (SIMS) to determine the distribution of antimony in the corrosion layers of antimonial lead alloys. Electrodes made from Pb–4.9 wt % Sb alloy were cycled potentiostatically between 0.9 and 1.65 V (versus $\text{Hg}/\text{Hg}_2\text{SO}_4$) and then held at 1.12 to 1.60 V for fixed periods of 15 or 30 min. Analysis of the corrosion layer revealed that the concentration of antimony was approximately twice that in the alloy and fell away in a linear fashion to be almost zero at the surface of the layer. The accuracy of this result was reduced greatly, however, by uncertainty in the data acquired from the region between the corrosion layer and the substrate metal. No clear relationship between the maximum level of antimony and the oxidation potential could be inferred.

As part of an extensive study of the behaviour of pure lead and a range of antimonial lead alloys under cyclic potential regimes, Mahato [20] also studied the distribution of antimony in the corrosion layers of oxidized electrodes. By contrast with the SIMS studies [18, 19], this work determined that the abundance of antimony was lower than in the substrate alloy (6 wt % Sb), the highest value was close to 4 wt %. The analyses were carried

out by means of an electron microprobe. This work also described an interesting relationship between the thickness of a so-called 'inner' corrosion layer (that develops during cyclic potential sweeps of each electrode) and the grid composition. Antimonial electrodes containing either 1 or 3 wt % Sb produced inner corrosion layers that had almost the same thicknesses after around 5000 cycles. On the other hand, pure lead electrodes yielded layers that were initially as thick as those on the antimonial alloys, but became much thinner over the same number of cycles. Finally, the effects of antimony on both the morphology of the corrosion products (lead dioxides) and on the nature of the interface between the latter and the electrode metal (substrate) were discussed in terms of visual differences. It was suggested that the presence of antimony enhances the adhesion both between particles of lead dioxide and between the metal (grid) and the adjacent corrosion layer.

Electrochemical studies of lead and lead alloy electrodes have yielded many interesting results, yet the relevance of these to problems experienced in actual lead/acid batteries is limited by two factors. First, solution conditions (pH and sulfate concentration) in the vicinity of the corrosion layer will differ greatly in the two situations. Second, when a metal electrode is surrounded with a mass of paste that is essentially rigid, the forces exerted within the corrosion layer will be modified. This, in turn, reduces the significance of observations concerning the physical appearance of material in this region.

Phenomena at the grid/active-material interface

Probably the most recurrent theme in any discussion of PCL is the notion that a layer of an insulating compound, or compounds, forms around the current collector in a lead/acid cell, and that this layer prevents the full utilization of active material and eventually causes failure. By comparison with the theories discussed so far, which have centred largely on relatively subtle changes in the bulk of the active mass, 'barrier' layers are able to provide a straightforward explanation of PCL and a considerable amount of supporting data has been reported. With regard to the composition of barrier layers, lead sulfate and tetragonal lead monoxide (α -PbO) are cited most often as the main components. The involvement of both compounds is usually discussed in terms of a model in which a layer of lead sulfate acts as a perm-selective membrane and thereby creates conditions that are of sufficient alkalinity to allow the formation of α -PbO. This model was advanced and studied some years ago [21, 22].

The first detailed analysis of the relationship between insulating barriers and PCL was reported by Tudor *et al* [23–25]. Cells based on typical lead–calcium positive plates were subjected to the submarine cycle and autoradiographic techniques were used to determine the distribution of key elements in the positive plate material. In the first stage of the work [23], addition of radioactively labelled sulfuric acid (^{35}S , β^-) allowed location of the regions in which sulfate compounds accumulate within the plate materials. For a series of identical cells, failures occurred after periods ranging from 2 to 24 weeks. Autoradiography indicated that all failures were associated

with an accumulation of a sulfur-containing species in the region adjacent to the grid. It was stated that this species was lead sulfate, although it should have been noted that other compounds, or mixtures of compounds, could have given the same images.

In an attempt to extend the cycle lives of these cells, additions of phosphoric acid were made to the cell electrolyte. A significant improvement in cycle life was indeed achieved and it was shown that sulfur-based compounds did not deposit at the grid/porous-material interface. In order to quantify this effect, additions of radioactively labelled phosphoric acid (^{32}P , β^-) were made to selected cells following several months of service on the 23/1 regime. Examination of plate cross sections revealed that phosphate was taken up by most of the positive material during charging of the cell and liberated during subsequent discharging. The clarity of the phosphorus autoradiographs was, however, inferior to that obtained from experiments with labelled sulfuric acid, and this made evaluation of the phosphorus distribution adjacent to the grid very difficult.

In the following two stages of the investigation [24, 25], evaluation of the effects of phosphoric acid on the performance of lead-calcium cells was expanded to include different plate thicknesses and paste densities. The results confirmed those of the earlier work in showing that phosphoric acid modified the distribution of sulfate compounds in the positive plate material, in a way which prolonged cycle life. There was, however, one disadvantage: available cell capacity was reduced. This finding has been noted since by other workers and will be discussed in detail later in this review.

Tudor *et al* [23-25] showed that the technique of autoradiography is useful in tracking the distribution of sulfur in the plate material. However, many of the images were of poor resolution, so that spatial assignments were difficult to establish. In particular, autoradiography does not seem to distinguish between regions of higher-than-average sulfur concentration and regions in which the same compound(s) may have formed continuous 'barriers'. This is, of course, the key issue in any explanation of PCL based on the growth of a barrier layer around the grid.

From examination of the corrosion behaviour of a variety of lead alloys, Weininger and Siwek [26] provided more evidence for the deposition of lead sulfate in the region adjacent to the grid. Pasted plates based on lead-calcium, lead-calcium-tin and lead-antimony alloy grids were subjected to constant potential (float) service equivalent to 2.25 V/cell. The distribution of sulfur in plate cross sections was mapped by analysis of electron microprobe data. For lead-calcium plates, the region near the grid was found to contain an appreciable accumulation of lead sulfate, relative to that in the bulk of the active material. Although the deposit was clearly neither continuous nor particularly thick, it was present only for lead-calcium plates. No evidence of sulfate accumulation was detected in plates based on antimonial lead and lead-calcium-tin alloys. It is worth noting that the grids employed in this work were produced by expansion of wrought lead alloy strip, compared to the cast material used in most of the other studies cited. Given that grain

structure and size influence corrosion and leaching processes at the grid/active-material interface, fabrication methods for grids are likely to be important determinants in promoting the incidence of PCL. Nevertheless, the work of Weininger and Siwek provided another indication that positive plates with binary lead-calcium grids are somehow susceptible to the build up of lead sulfate in the corrosion layer. Furthermore, it was found that incorporation of tin prevented this occurrence. This study did not, however, address the behaviour under cycling conditions, thus reducing its relevance to the discussion of PCL.

From investigations of the performance of lead/acid batteries under simulated electric vehicle service, Barrett *et al* [27] presented results from scanning electron microscopy (SEM) and electron microprobe studies of positive plates. The latter were based on grids with 2 wt % Sb and were sampled at various stages of life. It was shown that the only noticeable changes in structure or composition of plate materials were found in the corrosion layer. Evidence from microprobe analyses conducted on a healthy, cycled positive plate indicated that thin, discontinuous regions of a sulfur-rich phase(s) were present in this layer and that these regions were larger at failure. Elemental analysis of the constituent material showed that it was probably a complex mixture of oxides and sulfates of lead, together with a trace of some antimonial species. Curiously, these high-sulfur regions, formed early in cycle life, could not be imaged by SEM, rather they appeared to be associated with cracks that were concentric with the corrosion layer surrounding the grid. Analyses for antimony with the microprobe revealed that concentrations of this element were high at many locations near the grid and became lower further into the bulk of the active material in line with earlier studies (*vs*). The abundance of antimony was low in the regions of high sulfur content. It should be noted that, by today's standards, the grid antimony content of 2 wt % Sb adopted in this work has been used successfully in lead/acid batteries for deep-discharge cycling duty. Yet, it would be fair to say, also, that the same antimony content falls in the 'grey' region of alloys that may, or may not, give rise to PCL depending on other parameters of manufacture.

Research at Yuasa Battery Co Ltd on PCL was mainly directed towards investigation of the composition and microstructure of the region between the positive grid and the adjacent active material. In the first of two studies, sponsored by ILZRO (International Lead Zinc Research Organization), attention was focused on the phase distribution and morphology of the active material [8]. The second, larger work [28] consisted of a systematic evaluation of the effects of antimony on material in the positive plate and included the issue of barrier-layer formation.

Pasted plates based on grids containing 0 to 4 wt % Sb were subjected to a cycling regime that consisted of discharging at approximately $C_6/6$, followed by charging with an overcharge factor of 130% [28]. Results showed that cycle life (to less than 50% of initial capacity) was proportional to antimony content, in an almost linear fashion. Cycle life was poor for plates

based on 0 and 1 wt % Sb grids, yet the rate of capacity loss, once a decline in performance had begun, was only slightly greater than that observed for cells with higher antimony content. An important observation for the low-antimony plates was that the rate at which the voltage dropped at the end of discharge increased markedly during the service life. It was stated that this finding was made often in antimony-free cells that failed prematurely.

Several other tests were conducted on the above plates and the results can be summarized as follows:

(i) the degree of buckling of the positive plate, due to the stresses of charge/discharge, was greater by a factor of ten for pure lead plates compared to 4 wt.% Sb equivalents;

(ii) there was no clear relationship between the amount of material shed from the positive plate and the grid antimony content,

(iii) samples of material from the corrosion layer of each type of plate (0, 1, 2, 3 and 4 wt.% Sb) were of equal hardness early in the cycle life but became harder in the pure lead plate relative to the others prior to the end of life.

The first point has limited importance because such effects are determined largely by the configuration of the grids and the method used for their manufacture. Finding (ii) is consistent with the observation that plates affected by PCL nearly always appear to be in good condition, discussion of the extent of material shedding is, therefore, inappropriate. Finally, observation (iii) provides the basis for speculation that harder material in the corrosion layer would be more prone to cracking, with a concomitant loss of electrical contact.

Perhaps the most significant feature of the Yuasa work was the observation that the concentration of acid in the electrolyte could influence both the incidence and the severity of PCL. This aspect was examined further at Yuasa by Nakashima and Hattori [29]. These authors adopted a similar approach to the previous work in a comparison of plates based on grids of Pb-0.07wt.%Ca-0.5wt.%Sn alloy with an antimonial (4 wt.% Sb) equivalent. Under deep-discharge cycling conditions at $C_5/5$, the cycle life of the Pb-Ca-Sn plates decreased with increasing acid strength and was almost a linear function of concentration in the range of 1.10 to 1.20 sp gr. Below 1.10 sp gr, the performance declined abruptly due to extremely severe grid corrosion, while at sp gr. > 1.20, failure was best described as being due to PCL since no signs of plate degradation were apparent. These tests were conducted in a relatively large volume of electrolyte that, even at the lowest concentration (1.10 sp gr), provided a twofold excess of the theoretical requirement of sulfuric acid.

When the amount of acid available was restricted further (by reducing the volume of electrolyte) the cycling performance was improved, except at the lowest concentration, in which case grid corrosion again dictated the course of cell life. Thus, positive plates that were susceptible to PCL could be 'protected' against the effect through modification of both the strength and quantity of electrolyte. Clearly, the concentration of sulfuric acid within

the plate material during discharge is an important determinant in the discussion of PCL. Unfortunately, this result does not represent the solution to PCL because restriction of electrolyte causes a significant reduction in the available capacity. Indeed, Nakashima and Hatton [29] showed that, for electrolyte of 1.28 sp gr, extended charge/discharge service could be maintained, but only at a capacity equal to approximately 60% of that in an excess of electrolyte. This drop in capacity was explained in terms of greatly reduced specific surface area and coarsening of the material structure in the positive plates.

Further investigation of plates that failed prematurely revealed deposits of a compound in the region between the grid and the active material. The compound appeared yellow under illumination by polarized light and, by comparison with other studies, the authors concluded that it was α -PbO. Another feature noted during discharging of these plates was the concentrated formation of lead sulfate in the region of active material nearest the grid. By comparison, plates with Pb-Ca-Sn grids that did not exhibit PCL showed an even distribution of lead sulfate throughout the material. These results were interpreted in the same terms as those advanced by both Ruetschi [21] and Pavlov and Jordanov [22]: an accumulation of lead sulfate generates conditions in solution that are conducive to the formation of compounds such as α -PbO. Without supporting evidence, it was stated that the electrical properties of α -PbO and/or PbSO₄ restrict cell performance.

Giess [30] reached a similar conclusion in his work on the role of tin in grid alloys used for lead/acid cells. According to this study, PCL can be attributed to at least two distinct phenomena: (i) inhibition of the discharge of PbO₂ when the concentration of certain antimonial species in the electrolyte falls below a critical level (the antimony-free effect), (ii) passivation of the current-collector surface by a poorly conducting compound when the amount of tin in the grid/spine alloy is insufficient (the tin-free effect).

Focusing on the latter, it was shown that the potential of a tubular positive plate based on a tin-free Pb-0.05wt%Ca alloy rose greatly during constant current charging after a deep discharge. Similar, though less dramatic, rises were also seen for a tin-free Pb-1.5wt%Sb alloy under the same conditions. By comparison, electrodes based on a Pb-0.05wt%Ca-0.6wt%Sn alloy did not exhibit any abnormal elevation of potential during charging. In parallel with these investigations of actual battery plates, bare specimens of the same alloys were subjected to potentiostatic oxidation. The results showed that tin reduced the rate of corrosion (measured by weight loss) and suppressed the formation of α -PbO. SEM investigations of the corroded tin-free specimens showed that the latter compound formed as thick layers under an outer layer of lead sulfate. This recalled earlier theories of insulating barriers around the grid [21, 22]. It should be noted that experimental evidence (based on XRD data) of α -PbO adjacent to the current collector was only provided for the case of bare metal electrodes held under potentiostatic control. No data were reported for examinations of the material from the tubular plates.

Chang [31] has provided a clear demonstration of premature capacity loss from a comparison of cells based on Pb-0.09wt %Ca-0.3wt %Sn and Pb-3.0wt %Sb grids. Cycling duty was employed in which discharging was carried out at $C_5/5$, to 100% depth-of-discharge, followed by charging to 115% of the capacity removed. For cells in which no provision was made for retention of the positive material (i.e., no wrapping of plates and no plate stack pressure), the cycle lives for Pb-Ca-Sn cells were less than one fifth of those for the Pb-Sb equivalents. Moreover, the rate of capacity loss, once performance had begun to decline, was significantly greater in the former. The longevity of non-antimonial test cells was improved by (i) incorporation of stack pressure, (ii) increased paste density, (iii) increased plate thickness. Nevertheless, the benefits, in terms of cycle life, were modest and involved a reduction in available capacity. Thus, the longevity of plates based on Pb-Ca-Sn grids could be enhanced, but only by adopting protective measures that led to a reduction in energy density.

Detailed examinations of plate composition and microstructure were carried out on samples taken at various stages of service life. The results showed that PCL was associated with the preferential discharge of active material in the region immediately surrounding the corrosion zone, as contended by Nakashima and Hattori [29]. It was argued that lead sulfate formed a continuous layer around the grid and prevented further discharge of plate material. Furthermore, this concentrated deposition of lead sulfate was also regarded as the eventual cause of failure in antimonial cells subjected to the same cycling regime. The key difference was that in the latter cases, discharge of material adjacent to the corrosion layer only occurred after extensive utilization of material in the bulk of the active mass. In the Pb-Ca-Sn cells, discharge next to the corrosion layer took place before any appreciable utilization of material remote from the grid. It was also noted that cracking of the material in the corrosion zone, concentric with the grid wire, was both more extensive and more severe for non-antimonial cells and that lead sulfate crystal growth was rapidly established in the resulting fissures.

Overall, Chang's results showed that PCL was most notably associated with the preferential and premature discharge of the material located in the outer regions of the corrosion layer, in contact with the positive material. The observation of widespread cracking in the latter region, early in the cycle life, suggested that acid ingress was important in the mechanism of PCL. The effect was not alleviated by modification of plate processing (i.e., curing, formation, etc.). It should be noted, though, that one variable of plate production was not controlled in this study, the two grid types used were manufactured by different processes. Pb-Ca-Sn grids were produced by the expansion of cast strips of the alloy, while the antimonial grids were cast in a book mould. Despite being similar with respect to overall dimensions, the known metallurgical differences between grids produced by the two processes are potential sources of divergence in behaviour.

Valeriotte *et al.* [32] noted the same issue in their investigation of the deep-discharge cycling characteristics of plates based on a variety of grid

types. In this case, however, charge/discharge at $C_5/5$ (100% depth-of-discharge) did not invoke PCL in any of the alloy/grid configurations (both antimonial and non-antimonial) studied. While this may be explained by certain features of the experimental regime, it is interesting to note that evidence was provided for the presence of the barrier-forming compounds α -PbO and PbSO₄. Importantly, neither of these was observed to have formed a continuous layer around the grid in the samples examined; these results could, therefore, be regarded as providing support for the barrier layer theory.

Appraisal of contributing factors

Active material

Early work on PCL demonstrated morphological differences between positive material taken from plates based on antimonial and non-antimonial grids and suggested that these explained the large variation in plate performance. Of all the relationships advanced in explanation of PCL, this would probably be the most difficult to substantiate because the parameter of plate performance being targeted – the structural integrity of the active mass – is a fairly nebulous quantity that does not lend itself to quantification.

From around the same time came the interesting, though apparently anomalous, results regarding the effect of antimony on the distribution of lead dioxide between its two crystalline forms (α -PbO₂ and β -PbO₂). Since then, several studies have shown that antimony can indeed modify the morphology of lead dioxide and that α -PbO₂ is more susceptible to this effect. Whether a process that mainly affects the alpha polymorph is significant in terms of plate performance depends on the role of this compound in the positive material. It is well known that, although relatively high levels of α -PbO₂ may be present after plate formation, the fact that this compound will not be produced from lead sulfate during charging of the plate, sees its abundance fall significantly within a few charge/discharge cycles. Nevertheless, measurable quantities are known to persist through long periods of deep discharge service, and this suggests that α -PbO₂ resides mainly in the 'backbone' structure of the positive active mass, protected from high concentrations of acid. If this is indeed the case, then any factors that influence the abundance and/or morphology of α -PbO₂ would certainly be expected to also affect the integrity of the positive active mass.

The other means by which some feature of the positive material structure or composition could determine plate behaviour is embodied by the aggregate-of-spheres model. In this, it is argued that the stability of material in the neck zones, relative to that in the bulk particles, is a key determinant of positive plate performance. The implication that α -PbO₂ is more likely to reside in the former is consistent with the abundances that are typically recorded for this phase. Both this and the previous argument imply that a certain level of α -PbO₂ must be present for adequate charge/discharge cycling.

performance Furthermore, observations of enhanced formation of α -PbO₂ in the presence of antimonial species [33] would, on this basis, help to explain the superior performance of plates based on antimonial alloy grids

Corrosion layer

While models that describe the behaviour of the entire active mass are able to provide plausible explanations of capacity loss, evidence continues to suggest that the process, or processes, that cause PCL are active mainly in the region where corrosion products from the grid meet the bulk of the porous positive material The corrosion layer is of course adjacent to the primary source of elements such as antimony, calcium and tin, thereby ensuring that it is exposed to higher concentrations of these species, and their derivatives, than elsewhere in the plate The material in this region is also likely to experience electrolyte of lower acidity Thus, the α -PbO₂ β -PbO₂ ratio is generally higher here than in the bulk of the active mass, and, as a result, it may be concluded that α -PbO₂ also has an important role in an explanation of PCL based on properties of the corrosion layer Most attention, however, has focused on compounds that are essentially non-conducting, such as PbSO₄ and α -PbO, and the degree to which either, or both, of these can isolate the grid from the active mass These ideas form the basis of what is probably the most favoured explanation of PCL, yet evidence gathered to date is largely circumstantial and often contradictory

The latter feature is well illustrated by a discussion of the instances in which deposits of α -PbO have been reported in corrosion layers of positive plates Few workers have been able to identify such deposits with a high degree of certainty (e.g., by means of XRD analysis) Many have made this assignment on the basis of visual evidence from optical microscopy This approach is at best qualitative (determination of purity is difficult even with advanced analytical techniques) and has led to vague descriptions of α -PbO as a yellow or orange material under plane-polarized light A region of such material may well contain an appreciable quantity of α -PbO, so as to account for the observed colour of the deposit, yet an amount of another compound such as lead dioxide may also be present thus rendering the material harmless with respect to processes of capacity loss Valeriotte *et al* [32] have highlighted this issue with their observations of thick, corrosion layers of yellow–orange material in some of the samples taken from freshly formed, healthy plates Thus, there is some controversy in this area of research Nevertheless, the perceived importance of discerning the phase composition of corrosion layers, in attempts to explain PCL, has prompted many detailed investigations, employing a range of techniques

Analysis by means of SEM, XRD, electron microprobe and other methods has demonstrated the presence of PbSO₄ and/or α -PbO in and around the corrosion layers of samples affected by PCL In some cases results have shown that deposits of these compounds have formed continuous layers around the grid Even this observation is by itself of limited significance, though, without direct evidence of the properties of these layers and their

effect(s) on plate performance. Specifically, layers of material suspected of behaving as electrical barriers must be shown to be acting in this way, *in situ*. Weininger and Siwek [26] expressed similar comments following their observations of lead sulfate in corrosion layers of Pb–Ca based plates. To date, very few studies have addressed this issue. Of these, Giess [30] has provided an indication of how a non-conducting compound, such as α -PbO, may affect the polarization of the positive plate through investigation of charge-acceptance characteristics. A similar theme was followed by Doring *et al* [34] in their work on passivation during storage of lead/acid cells at open circuit. Both of these works concentrated on the beneficial properties of tin (either in the grid alloy or plated onto the grid) with respect to prevention of passivation. The presence of tin is clearly an important modifying factor of the incidence of PCL, but it does not represent a complete solution to the problem. Several other factors must be taken into consideration, namely (i) the extent of utilization of positive active material, (ii) the concentration and/or quantity of sulfuric acid in the electrolyte, (iii) the charging regime.

There is much anecdotal evidence to suggest that PCL can be avoided by increasing the relative amount of positive material. Increases in plate thickness and paste density are known to have the same effect. Chang [31] has to some extent quantified these relationships.

As stated earlier, changes that yield a significant increase in cycle life do so with a reduction in available capacity. The same reasoning applies to the increases in cycle life that are recorded for positive plates in cells that contain phosphoric acid. From early detailed studies on the effect of phosphoric acid on Pb–Ca positive plates [23–25] to quite recent work [32], any benefits in terms of extended service lives have been offset by lower capacity. Structural and chemical effects of phosphoric acid have been reviewed recently [35], and a number of processes that modify positive plate behaviour have been proposed. Overall, any step that leads to a drop in capacity is, in effect, simulating a reduction in the depth of discharge, thereby extending the cycle life of the cell.

Studies in which the amount of sulfuric acid has been an experimental variable have demonstrated that this parameter has a significant bearing on the incidence of PCL. As might be expected, results have shown clearly that the prevention of PCL, by limitation of the quantity of acid present, is associated with less available capacity, utilization of positive active material is less than in the case of an unrestricted supply of acid. Nevertheless, the structural and compositional changes that accompany this modification are worthy of further investigation. For instance, if it was shown that operation of lead/acid cells in acid deficiency induced improved adhesion between grid and porous material, then perhaps the same result could also be achieved by some other means, without a drop in energy density.

Many investigators have noted the influence that the charging regime has on the incidence of PCL. Valeriotte *et al* [32] did not observe any instances of PCL under conditions where no control was exerted on the top-

of-charge (*TOC*) voltage reached by each cell. By comparison, studies that utilized the submarine cycle, which features a relatively low *TOC* voltage (2.35 V/cell), gave clear demonstrations of rapid capacity loss. It is not suggested, though, that there is a simple relationship between PCL and *TOC* voltage, the magnitude of the charging current is also an important factor.

Gibson *et al* [36] have provided a dramatic example of the differences in behaviour that can accompany changes in the method of battery charging. This work compared the performances of automotive battery plates based on 5 to 6 wt % Sb, 2.3 to 2.8 wt % Sb and 0.08 to 0.09 wt % Ca alloys. Each alloy contained tin at a typical level. Discharging was conducted at the cold-cranking rate, and was followed by charging at either a constant voltage of 2.67 V/cell, or a constant current of 0.1 C_{20} . In the former case, calcium-based cells were still in good condition after 20 cycles, while both types of antimonial cells failed (through grid corrosion) well before this mark. Under constant current charging, no calcium cells progressed past the first cycle, yet the positive plates from these cells appeared to be in excellent condition. Cells with antimonial positive plates survived up to nine cycles and grid corrosion again determined the end of life. The same disparity between calcium and antimonial alloys was evident in deep-discharge cycling ($I_{\text{discharge}} = C_{20}/20$, 100% depth-of-discharge) with constant-current charging. Samples from the positive plates of these batteries were examined by SEM. Imaging of the region adjacent to the grid, from a plate that had suffered PCL, showed that extensive formations of large lead sulfate crystals were present in the vicinity of the corrosion layer. Samples from antimonial cells showed no such formations.

Concluding remarks

A solution to the problem of premature capacity-loss in lead/acid batteries has been a major research objective for over thirty years. A wealth of information on PCL and related topics has been accumulated, yet a full understanding of the effect has proven elusive. Indeed, there is an obvious need for further research in several areas. First, the conditions under which the effect occurs must be established unambiguously. This applies not only to parameters of cell design and operation, such as balance of active materials and charge/discharge regime, but also to the presence of grid alloy constituents such as antimony, tin and calcium. Opinions on the roles of these and other elements still vary widely. The second, and clearly more difficult, task is to obtain more information on the composition and properties of materials in the positive active mass, as they exist during cell operation. In particular, data concerning the electrical conductivity of suspected 'barrier' deposits are crucial to resolving the issue of whether or not PCL occurs primarily as a result of an increase in the resistance of the corrosion layer. This is not to suggest that future investigations should focus their attention on events in either the corrosion layer or the bulk of the plate material. PCL may well

turn out to be a composite effect that involves both parts of the battery plate

For some years now, important trends have been taking place in the market demand for lead/acid batteries. A clear requirement for maintenance-free operation under deep-discharge cycling conditions has established a need for a dramatic reduction, if not the complete removal, of antimony in battery materials. Expanding markets for portable, rechargeable electrical appliances have placed added emphasis on achieving further gains in energy density. As shown in this review, progress in both these areas is being impeded by PCL. Thus, solving the problem of PCL is of paramount importance. With the support of ILZRO, a study of PCL is in progress within the laboratories of CSIRO. The work programme is designed to (i) clarify any aspects of the problem that have led to confusion in previous research, (ii) establish a rigorous explanation of the processes that constitute PCL, (iii) develop procedures that will prevent the occurrence of PCL without any adverse effect on battery performance.

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