When is capacity loss in lead/acid batteries 'premature'?

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Abstract

Elucidation of the principal mechanism that underlies premature capacity loss (PCL) in lead/acid positive plates has always been hampered by the notion that different forms of PCL are responsible for severe and mild instances of capacity loss. Recently, though, studies focused on the conductivity of the porous mass have provided a clear, universal explanation for all examples of PCL. The evidence required to link the differing views has come from charge/discharge cycling of specially designed plates in which expansion of positive material can be restricted in a controlled fashion. In particular, two findings have bridged the gap between failure at the interface (PCL-1) and failure in the bulk material (PCL-2): (i) plates subjected to extreme conditions of service can cycle at constant capacity for long periods, despite the presence of 'barrier-layers'; (ii) loss of conductivity in the porous material close to the current-collector can explain severe and rapid capacity loss. On examination, the latter situation is characterized by a localization of lead sulfate in the region close to the current-collector, in line with previous reports of 'preferential discharge'. The capacity loss for any plate/cell configuration can now be placed on a continuous scale — the rate of loss is determined by the degree to which the configuration, and conditions of service, are able to control the decrease in conductivity of positive material close to the current-collector. Development of positive plates for advanced lead/acid batteries must consider strategies for maintaining conductivity through management of the combined effects of expansion and redistribution of positive material.

Keywords: Lead/acid batteries; Capacity loss; Compression; Conductivity; Porosity

1. Background: terminology and confusion

The phenomenon that is now usually referred to as premature capacity loss (PCL) has occupied researchers in the lead/acid battery field for at least 30 years [1]. Initially, PCL was known as the 'antimony-free effect' [1,2]. This was mainly because the first cases arose from the catastrophic failure of batteries in which the positive plates based on antimonial (Pb–Sb) alloys were replaced by examples of the emerging binary lead–calcium (Pb–Ca) alloys. At that stage, PCL was indeed premature. Typical cycling data from work at the US Naval Research Laboratories [3] showed that while Pb–Ca positive plates failed within 10 cycles on the standard US test for submarine batteries, Pb–Sb equivalents exhibited constant discharge capacity over an extended period. Since then, however, the problem of PCL has, unfortunately, become less clearly defined. The main reasons for this are:

(i) the cycle-life of positive plates is a function of the concentration of antimony in the grid — plates based on Pb–Sb grids are not immune to PCL;

(ii) some of the problems with early Pb–Ca plates were due to poor mechanical properties — new alloys and procedures have improved this situation;

(iii) improved plate-processing and battery-manufacturing methods have generally lowered the susceptibility to PCL.

As a result of these developments, the cycle-life of positive plates now often falls somewhere between the extremes noted in early work. What, then, do we classify as 'premature' capacity loss?

At present, there is no simple answer. Rather, the widely held view is that there are two forms of premature capacity loss: (i) PCL-1, a more severe form of capacity loss that is due to processes in the interfacial region between the grid and the porous material; the formation of so-called 'barrier-layers' is a common synonym for PCL-1; (ii) PCL-2, a less severe loss of capacity that is attributed to failure of the bulk porous material; both the 'gel–crystal' concept [4] and the 'aggregate of spheres' model [5] are examples of explanations for PCL-2. The idea of classifying the different forms of capacity loss was first proposed by VARTA Batterie AG [6], for all types of positive plates, and also by Giess [6], in a scheme devoted to the different forms of the 'antimony-free' effect. Later, these ideas were adopted and developed
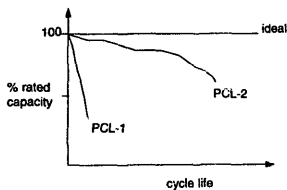

Fig. 1. Typical capacity-cycle plots for PCL-1, PCL-2, and ideal cycling service.

further by the Advanced Lead–Acid Battery Consortium (ALABC), as a result of discussions held by the ALABC PCL Study Group [6,7]. Fig. 1 illustrates the PCL-1/PCL-2 scheme, in terms of behaviour under cycling duty, along with 'ideal' cycling behaviour.

Certainly, this system of classification has facilitated discussion of the many examples of PCL. At the same time, however, it has also entrenched the notion that there are two distinct forms of PCL and, moreover, that there are two underlying mechanisms. This second issue is responsible for much of the confusion that is now associated with the investigation of PCL. Work conducted at CSIRO in ALABC Project AMC-003 has aimed to remove this confusion through the investigation of all aspects of positive plate degradation. As will be seen, the most important result of this work is that we now have strong evidence that there is, in fact, one basic mechanism that determines all forms of PCL. The key to the identification of this mechanism arises from a consideration of the factors that are known to extend significantly the cycle-life of positive plates.

In a recent publication [8], we discussed the relative contributions of a range of factors to the loss of capacity of positive plates. Particular attention was paid to the role of physical processes, such as expansion of the plate material. It was noted that expansion, and a number of related factors, exerts a strong influence over the retention of discharge capacity. A summary of the most important aspects of previous work, by other researchers in this area, is given below.

(i) *Stack pressure.* Deep-discharge cycle-life can be extended greatly by maintaining a cell group under compression [9–14]. Takahashi et al. [9] have shown that the minimum level required is ≈ 40 kPa.

(ii) *Retention of porous material.* The provision of physical support to retain material that would otherwise shed from the plate produces a marked increase in cycle-life, in addition to the increase gained by maintaining high compression [14].

(iii) *Internal expansion/contraction of porous mass.* Expansion of the positive plate during discharging, and contraction during charging, is well documented [9,11,14–16]. A limited amount of data indicate that the degree of expansion usually exceeds the degree of contraction, so that a net expansion occurs during cycling [15,16].

(iv) *Temperature.* At least one study has reported [14] that, under some conditions, the relationship between mate-

rial expansion/contraction and state-of-charge is the opposite to that expected (see above). This inversion of expansion behaviour is associated with appreciable changes in the internal temperature of the cell.

(v) *Packing density.* When finely-ground lead dioxide is packed into an empty tubular plate electrode, the resulting structure only becomes fully functional if the powder is packed above a certain minimum density [17].

(vi) *Resistance.* Direct correlations have been demonstrated between increased resistance of the bulk porous material and loss of discharge capacity [5,9,18–20].

Overall, it appears that the relationship between compression and the volume occupied by the porous positive material is a major determinant of cycle-life. At the heart of the benefit is the fact that compression minimizes the progressive expansion of positive material. As expansion takes place, porosity increases, while apparent density decreases. (Apparent density is defined as the mass of porous material divided by the total occupied volume (including pores/voids).) The reason for the fundamental significance of expansion is that it is linked directly to the properties that determine the extent of material utilization. In simple terms, expansion of a porous electrode (of which the lead/acid positive is a typical example) causes a decrease in conductivity through the electrode and this ultimately limits utilization. The key relationship between conductivity/resistance and expansion has been demonstrated for lead dioxide porous electrodes [9] and for nickel oxide electrodes [21].

While compression has a strong effect on cycle-life, it is still not known how the magnitude of this effect compares with that of other factors which influence positive plate behaviour. This study seeks to address this important issue through extension of an approach developed in earlier work [8]. Specifically, by controlling the progressive expansion of porous positive material, it has been possible to rank the relative importance of a number of performance-determining factors, including, of course, compression. Ultimately, this has allowed the formulation of a set of conclusions that apply to all examples of PCL.

2. Experimental methods and materials

Studies of the effects of restraining material expansion were conducted on small, pasted positive electrodes. A schematic representation of the design is shown in Fig. 2. Each electrode is based on a special epoxy casting into which a recess (diameter: 10 mm) is machined. A thread is cut on the narrow end of the electrode assembly, so as to accommodate a plastic (polypropylene) retaining cap with the corresponding internal thread. As shown in Fig. 2, this design allows a disc-shaped separator to be positioned between the cap and the porous material. A disc of pure lead (the 'grid') is provided with an electrical contact and then sealed into the bottom of the recess. A typical motive-power positive paste is prepared and then forced into the recess. Once the cap is in
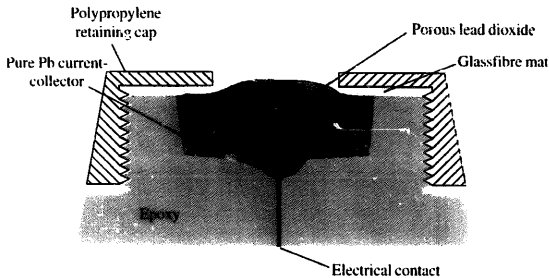
Fig. 2. Schematic diagram of pasted positive electrode for cycling studies.

place, the volume occupied by the active mass is restricted to a large degree, although, as shown in Fig. 2, some expansion of the porous material still takes place (v.i.).

Curing was performed at 50 °C and 100% RH for 24 h, followed by drying at the same temperature for 4 h. The formation procedure was conducted at constant current and involved passing 300% of the theoretical charge requirement over a period of 64 h. This time included two rest periods, each of 4 h. The negative electrodes were constructed from cut-down, pure-lead grids, to give at least twice the positive electrode area. They were prepared with a typical negative paste. Electrodes were formed and cycled in an excess of 5 M H_2SO_4 by means of equipment built in the CSIRO laboratories. Discharging was then conducted at the 5 h rate, to 100% depth-of-discharge (DOD), until constant capacity was reached. The overcharge factor during this phase was set at ≈ 20%. The discharging current was then adjusted, over several cycles, to a value near the 1 h rate. Once the required current had been ascertained, the overcharge factor was raised to ≈ 50%. The charging current was set at one-tenth of the discharging current, with no upper voltage limit.

At the completion of service, positive electrodes were prepared for examination by thorough washing in distilled water (until the washings were substantially free of sulfuric acid) followed by drying in an oven for several hours at 70 °C. Small samples of active material from selected electrodes were removed for X-ray diffraction (XRD) phase-analysis (v.i.). These samples were ground finely and then transferred with ethanol on to a zero-background plate for analysis. Positive electrodes were mounted in Araldite K99 epoxy. Samples were then cut and polished (down to 1 μm diamond paste) prior to further examination.

Scanning electron microscopy (SEM) was undertaken on a JEOL (Tokyo, Japan) Model JSM-25S III microscope that was operated at an accelerating voltage of 25 kV. Epoxy-mounted cross sections, from the small pasted electrodes, were coated with carbon and imaged at a working distance of 48 mm. Electron probe microanalysis (EPMA) of positive electrode samples was conducted with a JEOL (Tokyo, Japan) Model JXA-8900R Superprobe electron microprobe.

This instrument utilizes both wavelength-dispersive and energy-dispersive modes and was operated at an accelerating voltage of 15 kV and a nominal beam current of 50 nA. Each point analysis was fully quantitative with matrix correction. Quantitative determination of phase composition was undertaken by means of XRD. Diffraction patterns were recorded on a Philips (Eindhoven, Netherlands) Model PW3710 diffractometer that was fitted with a Cu Kα X-ray source. The source's generator was set at a tension of 40 kV and a current of 40 mA. Intensity data were recorded in 2θ = 0.050° steps. Calculations of phase abundance were based on peak areas.

3. Results and discussion

Several examples of the pasted positive electrode shown in Fig. 2 have now been subjected to deep-discharge cycling service. In line with preliminary cycling data [8], the charge/discharge performance of these electrodes has been remarkable. All examples have yielded in excess of 100 cycles (to 100% DOD) at the 1 h rate at virtually constant capacity. In all cases, utilization of positive material has been around 20% or greater; examples with relatively thin layers of material operate at close to 30% utilization, without loss of capacity. This level of performance is obtained despite the fact that the conditions of service have been chosen so as to enhance the loss of capacity. To this end, the following features have been incorporated into these cycling studies:

(i) the current-collector of each electrode is pure lead;
(ii) both negative electrode material and electrolyte (5 M H_2SO_4) are present in excess;
(iii) charging is conducted at a comparatively low rate (one-tenth of the 1 h rate) with no limit on the upper voltage;
(iv) the overcharge factor is maintained at around 150%.

The inclusion of the last two features is based on the comprehensive investigations by workers at VARTA Batterie AG into the influence of charging parameters on capacity loss [22]. They showed that a variety of positive plates exhibit significant capacity loss within only a few cycles under a regime such as that outlined above. The principal conclusion

from the CSIRO cycling studies is that pasted positive elec-trodes have yielded significantly longer cycle-lives than would be expected under such severe conditions of service. The only way in which these electrodes differ from conven-tional positive plates is in the presence of a tight-fitting cap that covers a major part of the electrode material. On the basis of the literature referred to earlier, the excellent performance is attributed to the constraint that is afforded by the retaining cap. In order to explain the benefits of this strategy, we first take a closer look at the composition and morphology of materials from these electrodes.

During service, the porous material underwent appreciable expansion and this resulted in distortion of the glass-fibre mat that was held under the retaining cap (Fig. 2). This is seen as a prominent bulging of the material, through the aperture in the cap. The amount of distortion was opposed by the glass-fibre mat which, though stretched, remained intact over the bulge. There was no shedding of positive material from any of the electrodes. For cells that were removed in the charged state, the phase composition of the positive material was predom-inantly β-PbO$_2$. As expected, the large amount of overcharge applied to all cells ensured almost complete charging of the positive material.

In order to illustrate the behaviour of these pasted elec-trodes, two examples (denoted '1-h' and '3-m') were removed from service at the end of discharge. Electrode 1-h completed 104 cycles at the 1 h rate and Fig. 3 provides back-scattered SEM images for this electrode. The cross section

was taken through the middle of the electrode so as to expose the full width of the sample. The main image (Fig. 3(a)) reveals the overall extent of expansion of the active material, while Fig. 3(b) highlights the variation in porosity seen in the material. From examination of these and a range of other images, it was concluded that the porosity of the material closest to the current-collector (approximately one-third of the total) was apparently lower than the remainder. As will become clear in subsequent discussion, this observation has important implications in terms of maintaining good conduc-tivity between the bulk material and the current-collector.

As well as providing detail on porosity in electrode 1-h, Fig. 3(b) shows that material near the current-collector (lower part of image) has undergone an appreciable amount of cracking and separation of layers. In particular, one rela-tively wide crack actually extends across most of the width of the sample (Fig. 3(a)). It is worth mentioning that the mounting of this electrode in epoxy was carried out before the retaining cap was removed. In this way, any stresses, e.g., due to expansion/heating of epoxy during mounting, are sup-pressed to a large degree; sample preparation should make little, if any, contribution to the cracking seen during post-service examination. (By comparison, samples from com-mercial flat-pasted plates are normally 'unsupported' during the mounting procedure because removal from the container takes away any constraint associated with the packing of the cell group.)

Closer to the grid, the corrosion layer becomes more com-pact. Fig. 3(c) provides a typical view. The morphology of this region can be classified into: (i) a thin, very dense layer of material immediately adjacent to the grid; EPMA analyses returned an average composition of PbO$_{1.15}$ along with traces of sulfur; (ii) a less compact, thicker layer of material, the average composition of which was PbO$_{2.05}$S$_{0.2}$; (iii) material with an open, porous form that is part of the layered formations seen in the lower part of Fig. 3(b), elemental analyses indicated mainly lead dioxide, PbO$_2$. The elemental composition of (ii) is most likely consistent with a mixture of PbSO$_4$ and lead oxides (PbO$_{1.6}$). Lead sulfate was also found in a variety of discrete forms throughout the corrosion layer, as indicated in Fig. 3(c).

In order to determine the distribution of sulfur (as lead sulfate) throughout the electrode, EPMA mapping was con-ducted. This provided information on the extent of discharge in different regions of material. Fig. 3(d) shows a qualitative map of sulfur abundance in which any concentration of sulfur above background is assigned a shade of grey, while points with sulfur below background are represented by black. Although the distribution of lead sulfate throughout the mate-rial is quite widespread, there is a clear bias towards the outer (electrolyte side) portion of the plate. This reflects the fact that utilization of inner plate material is dependent on diffu-sion of sulfuric acid from the bulk electrolyte. In addition, comparison of Fig. 3(d) with the corresponding back-scat-tered electron image (Fig. 3(a)) shows that the regions of
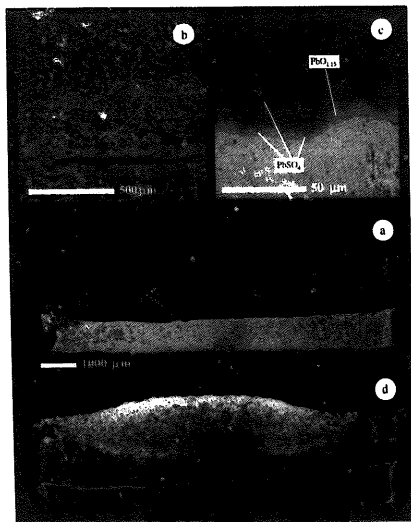
Fig. 3. Cross-sectional analysis of electrode 1-h: (a)–(c), back-scattered SEM images, and (d) qualitative EPMA map of sulfur abundance.

largely un-discharged material are distinguished by relatively low porosity. This will also tend to limit utilization.

When removed from service, electrode 1-h was still delivering close to its initial capacity, the electrode was in a healthy condition. And yet, examination of the electrode revealed features that are commonly noted in failed positive plates. What appears initially to be a paradox is, in fact, the first part of a general explanation of capacity loss. It allows us to assign a 'degree of significance' to some of the often-cited causes of plate failure. In particular, analysis of electrode 1-h highlights three aspects of the so-called 'barrier-layer' mechanism (PCL-1): (i) a high concentration of lead(II) oxides close to the grid; (ii) a relatively high concentration of sulfur (as $PbSO_4$) in the corrosion layer; (iii) extensive cracking of the corrosion layer, co-planar with the surface of the grid. Importantly, though, none of these features affected the performance of the electrode. We must conclude, therefore, that each of them is benign. We must also conclude that the constraint applied to the positive material is more powerful in maintaining capacity than is the sum of the severe conditions of service in promoting loss of capacity.

In order to learn more about the strength of the effect, we now consider the results obtained for another electrode, 3-m. After completing a similar number of cycles as electrode 1-h, at the 1 h rate, 3-m was subjected to nearly 200 cycles ($\approx 70\%$ DOD) at the 3 min rate. In addition, the retaining cap of electrode 3-m was loosened slightly (by 1/2 turn) at the completion of formation; this allowed the material to expand by a small additional amount compared with that of electrode 1-h. Despite the extra period of service, the performance of electrode 3-m remained at the initial level. It was removed from service in the discharged state. In common with electrode 1-h, the view at lowest magnification (Fig. 4(a)) shows appreciable variation in the porosity of different regions of the sample.

In particular, large pores and voids are noted in the region close to the grid (Fig. 4(b)). This highly porous, open form of material is also a feature of the corrosion layer (Fig. 4(c)). As for electrode 1-h, the thin, compact layer next to the grid was shown to consist mainly of lead(II) oxide. EPMA analyses returned an average composition of $PbO_{1.06}$. For electrode 3-m, however, the layer was discontinuous. For approximately half the width of the sample, in the centre of electrode 3-m, the layer of PbO was either absent, or present only in discrete tracts.

The distribution of sulfur (as $PbSO_4$) throughout electrode 3-m is shown in Fig. 4(d). (Again, any concentration of sulfur above background is assigned a shade of grey, while points with sulfur below background are represented by black.) By comparison with electrode 1-h (Fig. 3(d)), the distribution of lead sulfate is much more localized. The highest concentrations lie in a relatively narrow, dense band, close to the grid. This distribution is substantially different from that seen in fresh/healthy plates. At high rates of discharge, it is known that conversion of lead dioxide to lead sulfate takes place mainly in the outer regions of the porous material,
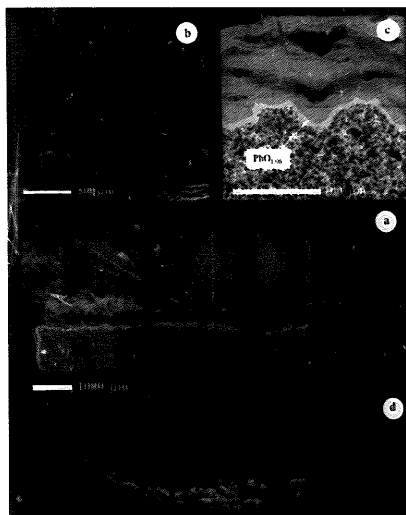

Fig. 4. Cross-sectional analysis of electrode 3-m: (a)–(c), back-scattered SEM images, and (d) qualitative EPMA map of sulfur abundance.

close to the bulk electrolyte. For electrode 3-m, however, discharge occurred preferentially in a band well within the positive mass. The most likely explanation for this shift in location of discharge is that the greater porosity now present close to the grid provides a substantial reservoir of electrolyte which helps to sustain discharge for longer.

While increases in the porosity of the positive material, especially close to the grid/corrosion layer, are often found during the examination of cycled positive plates, they are generally not viewed as a direct indication of capacity loss. In fact, though, such increases in porosity actually represent critical degradative change in the electrode structure. The reason is that as positive material expands, its porosity increases while its conductivity decreases. Accordingly, the conductivity of the material close to the grid in electrode 3-m is probably lower than in the corresponding region of electrode 1-h, where porosity remained relatively low. It is worth restating, however, that no sign of capacity loss was observed for electrode 3-m. Clearly, the increase in porosity had not reached a critical value before removal from service.

Had the increase in porosity of the material of electrode 3-m continued, it is easy to see that electrical contact would eventually have been broken between the grid/corrosion layer and the bulk of the porous material. At that stage, significant capacity loss would have been noted because the bulk of dischargeable material would have been effectively 'disconnected' from the current-collector. With this information, as well as the findings drawn from electrode 1-h, we

conclude that restraint of positive material expansion is by far the greatest factor in determining plate cycle-life and that the mechanism by which plates lose capacity is directly related to changes in material conductivity. In order to develop a complete description of this mechanism, consideration is now given to the processes that affect conductivity within the positive plate.

3.1. Factors that influence the conductivity of a porous electrode

As discussed earlier, expansion exerts a direct effect on conductivity through an increase in porosity. Fig. 5 provides a simplified, two-dimensional view of how this might occur at the 'microstructural' level. Individual particles of lead dioxide are represented by a polygonal shape. These polygons are grouped into a trigonal arrangement which, on repetition, yields a honeycomb-like lattice that serves as a two-dimensional projection of the lead/acid positive plate. Conductivity through the plate is initially high because neighbouring particles make a maximum number of contacts (Fig. 5(a)). With the introduction of expansion (Fig. 5(b)), however, there is a dislocation that results in a decrease in the number of interparticle contacts. Hence, conductivity falls.
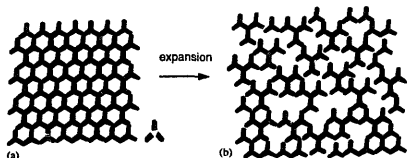
This idealized view of plate structure illustrates the importance of particle 'connectivity' at a basic level. From here, we now examine the way in which this principle determines the charge/discharge performance of an entire plate. This information is obtained by considering the behaviour of positive material on a larger scale. It is necessary, therefore, to take into account the well-known 'macrostructural' characteristics of the plate and how these change during cycling.

Workers at Bell Laboratories [23,24] have provided perhaps the best illustration of how the structure of the positive plate changes during cycling. Through extremely precise use of SEM, Yarnell and co-workers [23,24] were able to follow changes in the morphology of positive material during service, from formation to failure. Fig. 6 provides a schematic view of the observations described by the Bell group [2]. The shape labelled 'formed' represents an aggregate of very small lead dioxide particles. These particles are seen as very small dots that 'fill in' the shape of the aggregate. A portion of the aggregate is also shown in detail. At this level, the fine structure is represented by the scheme that was introduced in Fig. 5 (above). The aggregate is the base, or repeating, unit of the structure of the positive active-mass. We note also that the aggregate is hollow and that the inner volume of the resulting pore is accessible to electrolyte.

As illustrated by the sequence in Fig. 6, Yarnell et al. [23] found that, during discharge, lead dioxide is consumed from the inner surface of the aggregate and the product, lead sulfate, crystallizes on the outer surface. During the following

Fig. 5. Idealized, two-dimensional representation of expansion in a porous particulate system.

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[2] It is worth noting that this and subsequent representations of positive material structure are used only for the purposes of illustration. The shapes and forms depicted have been chosen primarily to convey the salient features of the discussion. There is no evidence to suggest that the properties illustrated here are specific to the experimental conditions used in the work at Bell Laboratories.
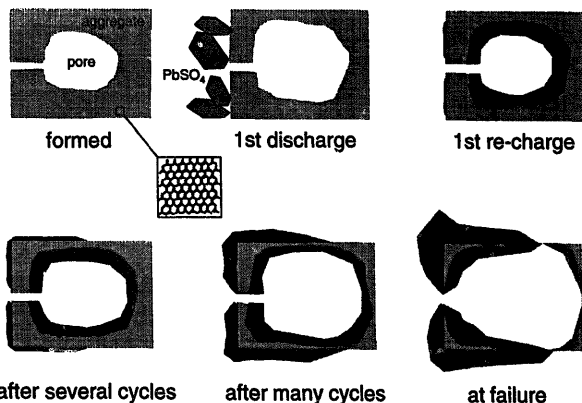

Fig. 6. Schematic representation of changes in electrode structure during charge/discharge cycling. Aggregate material of lighter shade has not taken part in charge/discharge while darker material has been re-deposited during charging. (After Yarnell and co-workers [23,24].)
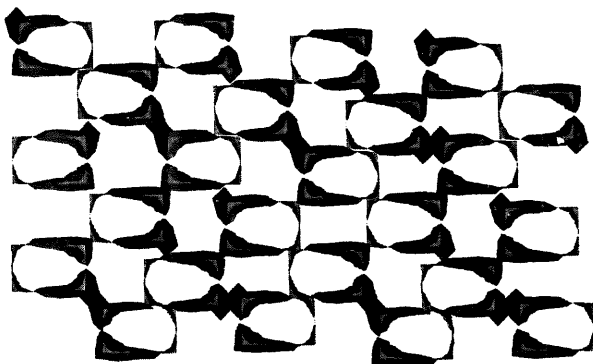
Fig. 7. Two-dimensional representation of electrode structure, based on the morphology depicted in Fig. 6, after extensive charge/discharge cycling.

charge, most of the lead dioxide is deposited in the original location, inside the pore. Importantly, though, it was found that a small portion of the material remained on the outside of the aggregate. In this way, there is a gradual accumulation of lead dioxide outside the original structure. From these studies, Yarnell and co-workers [23,24] concluded that this redistribution of lead dioxide results ultimately in collapse of the aggregate structure.

In fact, for an electrode that is comprised of a network of aggregates of the type shown in Fig. 6, significant changes would be noted in the properties of the electrode — especially conductivity — well before the actual collapse of the structure. Fig. 7 illustrates this point by means of a simple two-dimensional arrangement. We see that pathways for current flow are not uniform through the network. Rather, at this late stage in cycle-life, the conductivity of the structure is now critically dependent on regions where the 'walls' have become very thin. As the thinning proceeds: (i) portions of the network will become isolated, due to limited conductivity of the 'bridging' regions, and (ii) large-scale disruption to the network will occur (with concomitant fall in conductivity), because of the expansion forces during each discharge). Therefore, redistribution and expansion of positive material work together to lower the conductivity of the plate.

The impact of any fall in conductivity is noted during the discharge of the plate, because conductive material (PbO_2) is progressively removed from the network, through conversion to $PbSO_4$. A schematic representation, based on the arrangement shown earlier, is provided in Fig. 8. First, we see that discharge reduces conductivity through a lowering of the number of inter-particle contacts and, hence, the number of conductive pathways through the electrode (Fig. 8(b)). Individual crystals of lead sulfate are not shown because they would be relatively large on this scale and, according to Yarnell and co-workers [23,24], they deposit on the external surface of aggregates (of which the view

shown in Fig. 8 is only a small portion). Next, we recall the effect of expansion at this level of structure (Fig. 8(c)), i.e. dislocation of particles and small clusters of particles. Clearly, the combination of these two effects (Fig. 8(d)) can reduce significantly the number of pathways through the structure. The result is a substantial loss of conductivity that becomes more critical as discharge proceeds. The final question to be answered is whether the changes in conductivity are of a magnitude that can influence plate performance.

In descriptions of the behaviour of the lead/acid positive electrode, it is usually assumed that the conductive path (network of particles) through the electrode remains intact, both during the course of each discharge, and throughout cycling service. This assumption is based on the belief that, although plate conductivity falls during service, other factors exert greater limiting effects on the utilization of positive material.
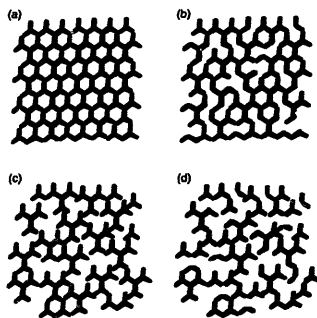

Fig. 8. A two-dimensional representation of electrode microstructure: (a) initial/healthy state, charged; (b) healthy state, discharged; (c) cycled state showing signs of expansion, charged, and (d) close to failure, showing effects of both (b) and (c).

Indeed, under common discharge conditions, electrolyte diffusion and/or blocking of the electrode surface determines the extent of material utilization [25]. In light of the discussion presented here, though, there are important exceptions to this generalization. First, Euler et al. [26] and Metzendorf [27] have shown that a decrease in conductivity can actually limit the discharge, but only at very high levels of positive material utilization. At close to 70% utilization, Metzendorf [27] demonstrated an abrupt decrease in conductivity that was consistent with the rapid fall in voltage at the end of discharge. Importantly, these studies provided a theoretical framework (in terms of both percolation theory and effective medium theory [26,27]) from which values of conductivity were determined. For example, the sharp fall in conductivity in the final stage of discharge is due to the removal of a conducting pathway throughout the plate; the so-called 'percolation threshold'.

It is important to note that Metzendorf's results were obtained for healthy positive plates [27]. In the very early stages of positive-plate life, under normal discharge conditions, it seems certain that conductivity through the plate does not limit discharge. During charge/discharge cycling, however, a decrease in the degree of contact between constituent particles, due to expansion and redistribution of material, means that conductivity can become a significant factor at normal levels of material utilization. Regions of the plate where expansion and redistribution are appreciable are regions in which the utilization during discharge can reach levels where conductivity falls to critically low levels. At this stage, portions of plate material can be effectively disconnected from the main structure/network. The important issue of the actual location of the decrease in conductivity is discussed in Section 3.2.

Having now discussed in detail the importance of interparticle contact, it is appropriate, in concluding this Section, to consider the influence of the actual configuration and shape of the particles on the ability of the plate to withstand the breakdown of conductivity associated with expansion. Crucial in this regard is the demonstration by Metzendorf [27] that the percolation threshold is a function of the number of points of contact between a particle and its nearest neighbours. An increase in this 'coordination number' lowers the threshold and, thereby, allows a greater level of material utilization. Concomitantly, a plate with this characteristic will also be able to tolerate greater expansion prior to loss of conductivity (and capacity). This principle offers two ways for improvement in plate performance. First, control over the shape of lead dioxide crystals would allow the coordination number to be raised; clearly, long, acicular crystals would be advantageous. Second, conductive additives, which should be effective at high levels of material utilization, should be produced in a shape that maximizes coordination number. As noted by Euler et al. [26], this idea is well illustrated by the use of carbon fibres in manganese dioxide electrodes.

3.2. Location of changes in conductivity

At this stage, we have described two processes (expansion and redistribution) by which positive plate capacity can fall, through decreases in the conductivity of plate material. On the basis of this quite generalized mechanism, we must now explain why the rate of capacity loss in PCL is found to vary over a wide range. There are two factors that govern the rate of fall in plate material conductivity. First, and more obvious, is the speed with which expansion and redistribution are allowed to occur. In terms of relatively rapid capacity loss, redistribution is probably not significant; work at Bell Laboratories suggests that its effects only become important after many cycles. By comparison, expansion can occur during relatively short periods of service. Furthermore, the use of very low compression would obviously enhance the rate of expansion.

The second factor that determines the rate of capacity loss is the location within the plate where the fall in conductivity occurs. As noted earlier, in the discussion of results for electrode 3-m, if expansion of material is localized close to the current-collector, then discharge of the material in this region can isolate most of the bulk outer material. In this way, changes in the properties of a small portion of the plate material exert a major effect over the behaviour of the whole structure. The drawing provided in Fig. 9 attempts to illustrate the explanation. Here, the increase in porosity is restricted to a small portion of the material (14% by mass) close to the grid. This region is shaded grey. As Metzendorf [27] has shown, once material utilization reaches around 70%, discharge will be limited by a sharp fall in conductivity through the material. In the situation represented by Fig. 9, this conductivity limit will be reached when only 10% of the total plate mass has been converted to lead sulfate. Moreover, 86% of the plate is now not accessible to discharge because there is no conducting pathway to the grid. (In reality, discharge of material is never 'completely' localized, as shown here, because the first small fraction of discharge, unaffected by diffusional limitations, will always be distributed throughout the bulk of the plate.) The localization of discharge means that appreciable changes in plate behaviour are seen at quite low overall values of material utilization. Therefore, through an increase in porosity, severe capacity loss can develop rapidly because only a relatively small fraction of the total material need be affected.

The tendency to 'open up' the internal regions of the plate structure is inherently self-perpetuating. Regions of greater porosity will undergo more extensive discharge, compared with neighbouring denser material, and this, in turn, will enhance expansion of the former regions. As a result, the limit of conductivity will be reached more quickly. This is of great significance to the performance of positive plates under electric-vehicle cycling conditions, because the amplification of capacity loss will be more severe for high rates of discharge, as required during peak vehicle loads. At such rates, i.e. on the timescale of minutes), discharge is localized to a
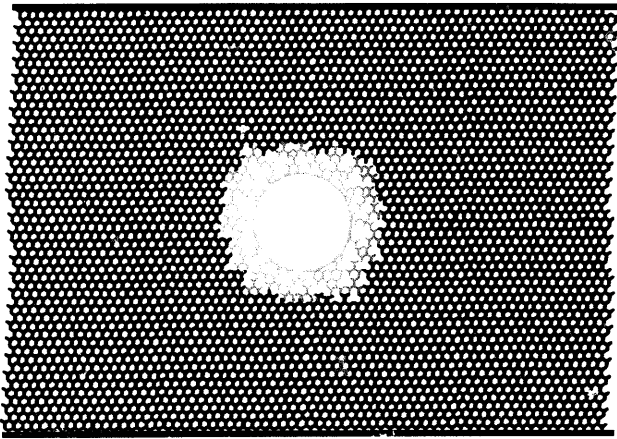
Fig. 9. Idealized view of the effect of localization of discharge on the utilization of plate material. Grey shading indicates increased porosity and localized discharge.

relatively small volume of the plate. This, in turn, concentrates the expansive forces associated with discharge into the same small region and results in greater disruptive forces.

The localization of discharge close to the grid is commonly known as 'preferential discharge' and excellent descriptions of this phenomenon are available [28,29]. It is widely thought that preferential discharge is simply a result of factors that increase the amount of electrolyte in regions close to the grid. Such factors alone cannot, however, be the primary explanation for the inability of the outer, bulk of material to undergo discharge. Rather, the driving force for preferential discharge, as described above, is the loss of a conductive path through to the outer regions of the plate. In fact, the same mechanism also accounts for the type of plate failure commonly described as 'barrier-layer' formation. This is because, in terms of experimental findings, there are no features that distinguish the phenomenon of preferential discharge from the barrier-layer model of plate failure. For example, work at Yuasa in the early 1980s revealed the presence of both a continuous layer of PbO around the grid and a high concentration of PbSO$_4$ in the corrosion layer at the end of discharge [28]. What is called a barrier-layer is, actually, a highly localized form of preferential discharge.

The discussion of capacity loss has now returned to a theme raised at the outset: what is the significance of events and features that are found in, or near to, the corrosion layer? Again, as earlier, we are able to conclude that the various forms of barrier-layer, by themselves, exert no significant effect. Rather, they are indicators of more serious changes in plate morphology, such as increased porosity near the grid. Previously, these indicators were the only detectable features that could be labelled as 'causes' of severe capacity loss. As

seen in the examination of electrode 1-h (Fig. 3), though, 'barrier-layers' can also be found in healthy positive plates. The real cause of the problem lies in the behaviour of the porous material in the immediate surroundings. In his review of the 'aggregate of spheres' model of capacity loss, Meissner [2] also stressed that any changes in morphology/composition that take place in the corrosion layer play only a secondary role in the events that cause capacity loss.

Overall, it can now be stated that the severity of capacity loss falls on a continuous scale. This means that instances of plate failure do not have to be classified into the categories of PCL-1 ('rapid' capacity loss) or PCL-2 ('gradual' capacity loss). Instead, the position on the scale where a particular cell lies is determined by the rate at which the porosity of the porous material reaches a critical value, at which conductivity is compromised. In terms of battery design, the magnitude of this rate is determined by a combination of several factors. As discussed in an earlier report [8], the most significant of these are: (i) the 'spring' characteristics of the separator, which define the ability to maintain a certain level of compression within the cell; (ii) the paste density, because it defines the starting value of porosity, and (iii) the strength of the grid, in resisting the forces of the expanding positive mass.

3.3. Events close to the grid: loss and expansion of material

Having underlined the critical importance of conductivity in the portion of material close to the current-collector, some comment is now required on why this region is susceptible to the increases in porosity that ultimately limit conductivity

and cause plate failure. Ruetschi [30] has suggested that factors such as charge/discharge currents and temperature may be responsible, through their effects on the rate of dissolution/precipitation of PbO_2. From examinations of cycled positive plates, he coined the term 'porosity inversion' and noted that it contributes to extensive utilization of material close to the grid [30]. Ruetschi contends that migration of PbO_2, allowed by the mobility of soluble intermediate species, results in a redistribution of material away from the inner regions of the plate.

As discussed earlier, Yarnell and co-workers [23,24] have demonstrated, unequivocally, that PbO_2 in positive plate material is susceptible to a redistribution process. That work implied, however, that the effects of redistribution were localized to individual aggregates of lead dioxide particles. In other words, the effects are short range and refer to movement of lead dioxide over small distances. By contrast, the results presented in this work (*v.i.*) provide evidence of movement over much longer distances. This is an important feature of the redistribution process because it helps to explain the development of increased porosity within the positive plate. As will be shown, the long-range movement appears to be a physical process in which particles of lead dioxide are carried through the porous structure. By comparison, short-range movement is probably best described as a solution-related process, due to the diffusion of soluble intermediate species.

Evidence of long-range movement of positive material can be found in the SEM images for electrodes 1-h and 3-m. Figs. 3 and 4 show that the material in the outer regions, nearest to the electrolyte, appears to have a relatively high packing density, i.e. low porosity. Inspection at higher magnification indicates that the porosity of these regions is on a smaller dimensional scale, compared with the bulk of the material. Fig. 10 provides a typical view. The main feature that defines this 'micro-porosity' is the presence of many small particles of material in the voids between relatively large aggregates
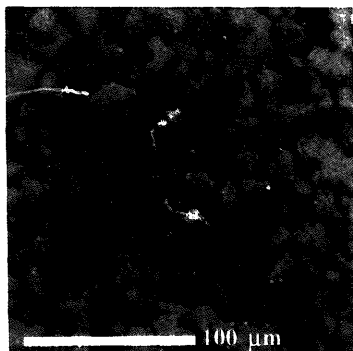

Fig. 10. Back-scattered SEM image of porous material in the outer (near bulk electrolyte) region of electrode 3-m.

of material. The latter appear to constitute the backbone, or macrostructure, of the electrode. The small particles are generally loosely packed in the voids. Particles of similar size and morphology were also found in other regions of the electrode, but with much less abundance. The impression that is conveyed by such micrographs is that of fine particles of material moving through the porous matrix, towards the outer edge of the sample.

Progress beyond the confines of the porous structure is hindered by the layer of glass-fibre matting pressed against the outside of the electrode. With continued cycling, though, very fine material is clearly visible in the bulk electrolyte, outside of the electrode body. This observation, made on electrodes that are still in service, confirms the existence of a process that is of great significance to long-term cycleability. Since the volume within which the positive material is confined remains virtually constant, the migration of material out of the porous system will cause the porosity of the remaining structure to increase. Eventually, this process will cause the conductivity of inner regions of the electrode to fall to a critically low value.

The driving force for this migration of lead dioxide is most likely composed of: (i) diffusion of intermediate lead species, as mentioned above, and (ii) convective transport associated with oxygen gas production at the completion of charging, gradients in acid concentration and thermal gradients. Certainly, the very high level of overcharge adopted in this study would have enhanced the contribution from gas evolution. In any case, it seems that the behaviour described by means of Figs. 6 and 7 must now be modified so as to allow for the net movement of material away from a particular aggregate. Furthermore, consideration must also be given to the form in which lead dioxide is deposited during each charging phase. The clear implication from the preceding discussion is that the lead dioxide produced under certain conditions is more susceptible to being dislodged and then transported through the pore system. Recently, Lam et al. [31] provided evidence that improved positive plate cycle-life observed under pulsed-current charging may be due to minimization of lead dioxide crystal size. From the discussion presented here, an additional component of this effect may be due to the formation of lead dioxide that is more adherent to the underlying backbone material. As a final comment on the processes labelled 'redistribution', it should be noted that the magnitude of their effect on capacity loss is much smaller than that due to expansion. This is clearly demonstrated by the preservation of discharge capacity in electrodes 1-h and 3-m, under conditions that promote redistribution, but where expansion is controlled to a large degree.

As mentioned earlier, temperature could play an important role in the processes that contribute to loss of conductivity in the porous structure. Unfortunately, relatively little information is available on the mechanism(s) of any thermal effects that operate within lead/acid positive plates. Alzieu et al. [14] observed a correlation between an increase in temperature and in expansion of a complete cell group, under

certain conditions of discharge. In simple terms, this would contribute to a loss of capacity. By contrast, Valeriote [7] has shown that appreciable heating effects, associated with the rapid charging of a range of lead/acid cells, are linked with good cycling behaviour.

An important aspect of the discussion of temperature is the recognition that there are three components of heat flow in a cell/battery: (i) the reversible heat effect, due to the change in entropy associated with the electrochemical reactions taking place; (ii) the irreversible heat effect, due to the various overpotentials that are present, and (iii) the resistive heat effect, which expresses heating due to the flow of current through a conductor. While heat is always given out in (ii) and (iii), the effect of (i) is either heating or cooling. For example, Valeriote et al. [32] has calculated that charging of the lead/acid positive plate absorbs heat from the surroundings. Another factor to be considered is that the regions of the plate over which the different heating/cooling effects occur may not coincide. This raises the possibility of differential expansion within the plate under certain operating conditions. Future research on the influence of temperature on plate longevity must aim, therefore, to determine not only the magnitude of any heating effects but also the exact location of these effects within the plate group.

4. A unified view: conductivity-limited capacity loss

Perhaps the most appropriate way of concluding this examination of capacity loss is to consider how the explanation developed here addresses the best-known features of PCL. The first reports of PCL actually coincided with the removal of antimony from certain types of lead/acid battery. The 'antimony-free effect' highlighted the susceptibility of the positive plate to severe, often catastrophic, loss of discharge capacity [1–3]. In time, it became clear that the presence of antimony was not the sole factor responsible for good cycleability. Nevertheless, still today, it seems clear that the most durable cycling batteries have antimonial positive plates.

For many years, studies that focused on the benefits of antimony were hampered by confusion over issues such as barrier-layer formation [3]. By contrast, the explanation presented here allows a straightforward treatment of the effects of antimony. For pasted plates, the superior strength of Pb–Sb grids will be an important factor in resisting the expansion of the porous material. The compression applied to a group of plates is only able to control expansion in one dimension (normal to the plane of the plates). It is the strength of the perimeter member (frame) of a grid that determines how much growth/expansion occurs in the plane of the plate. If such expansion is restrained, and the cell group is held under

compression, then the plate-material volume will be restricted to a large degree and capacity will be maintained.

In the context of conductivity, antimony exerts a second beneficial effect. There is good evidence to suggest that antimony promotes high apparent density (low porosity) in the zone of material close to the current-collector. Results from many studies have shown that antimony, leached from Pb–Sb alloys during charging, modifies the morphology of the surrounding porous material [33,34]. In fact, some of the earliest studies on the effects of antimony demonstrated what now appear to be significant changes in the size and shape of aggregates of lead dioxide crystals [35].

Clearly, battery manufacturers are now faced with a challenge to duplicate these two important effects of antimony, by means of other additives or processes. In the area of improved grid strength, recent progress has been made in the development of new Pb–Ca–Sn alloys that contain small amounts of silver and relatively high levels of tin [36]. With regard to maintaining high apparent density close to the grid, it is conceivable that other elements can be found that have a similar effect or, perhaps, that antimony itself can be utilized in a more controlled fashion, i.e. by removing its deleterious effects. Alternatively, given that the key issue is to preserve conductivity (rather than apparent density per se), it may be possible to deploy a conductive additive in the region close to the current-collector.

The mechanism for positive plate capacity loss that has been developed here represents a unification of the previously disparate views on PCL in lead/acid batteries. The principal conclusion from this mechanism is that the service life of positive plates, under any type of deep-discharge cycling duty, is mainly determined by the stage at which the conductivity, close to the current-collector, falls below a critical value. (While emphasis is placed on the behaviour of porous material close to the current-collector, it is not intended to discount the contribution to capacity loss from the decrease in conductivity that is known to occur throughout the bulk of the material. A conclusion as to the relative importance of conductivity changes in the two regions awaits more experimental data.) Situations where capacity loss is severe (within a few cycles, i.e. PCL-1) occur when a combination of design/manufacturing factors conspire to allow a significant and rapid fall in conductivity. In addition, operation under high rates of discharge also contributes to the severity of the decline in performance.

If, however, the factors that allow conductivity to fall are either removed or attenuated, then capacity will be preserved for longer periods of service. The eventual failure has until now been described as PCL-2. For particularly well-built batteries, this prevention of capacity loss will extend battery life to the point where other failure modes, e.g. grid corrosion) will become dominant. As regards the question: 'When is capacity loss 'premature'?', the simple answer is: 'Never'. What we may now call conductivity-limited capacity loss (CLCL) is as understandable and controllable as any other plate failure mode. Moreover, the basic strategies for main-

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[3] For example, great significance has always been attached to the fact that cycled antimonial positive plates never display distinct layers of (supposedly insulating) 'PbO' next to the current-collector.

taining conductivity above a minimum value are widely known (compression, grid strength, etc.) and batterymakers also have access to a full theoretical treatment of the underlying principles. Indeed, once more is known about the modes of inter-particle contact in positive material, the concepts of percolation theory can be used to model the key parameters of plate performance. This type of approach will be crucial in research that aims to maximize specific energy, especially for the future development of advanced lead/acid batteries for electric-vehicle applications.

Acknowledgements

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