Manufacturing and operational issues with lead-acid batteries

D.A.J. Rand[a,*], D.P. Boden[b], C.S. Lakshmi[c], R.F. Nelson[d], R.D. Prengaman[e]

[a]*CSIRO Energy Technology, P.O. Box 312, Clayton South, Victoria 3169, Australia*
[b]*Hammond Expanders Division of Hammond Group Inc., 2323 165th Street, Hammond, IN 46323, USA*
[c]*Pasminco, P.O. Box 175, Boolaroo, NSW 2284, Australia*
[d]*Recombination Technologies, 909 Santa Fe Drive, Denver, CO 80204, USA*
[e]*RSR Technologies Inc., 2777 Stemmons Freeway, Suite 1800, Dallas, TX 75207, USA*

Abstract

An expert panel replies to questions on lead-acid technology and performance asked by delegates to the Ninth Asian Battery Conference. The subjects are as follows. *Grid alloys*: effects of calcium and tin levels on microstructure, corrosion, mechanical and electrochemical properties; effect of alloy-fabrication process on mechanical strength and corrosion resistance; low dross-make during casting of lead–calcium–tin alloys; future of book-mould casting; effect of increasing levels of silver; stability of continuously processed grids at high temperature. *Negative-plate expanders*: function of lignosulfonates and barium sulfate; benefits of pre-blended expanders; optimum expander formulations. *Valve-regulated batteries*: effect of oxygen cycle; optimum methods for float charging; charging and deep-cycle lifetimes; reliability testing. © 2002 Elsevier Science B.V. All rights reserved.

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1. Grid alloys

1.1. Question: How do calcium and tin levels in the lead alloy affect the microstructure and properties of grids? (C.S. LAKSHMI)

1.1.1. General metallurgical background

1.1.1.1. Microstructural control. The properties and behaviour of metallic materials originate from their internal structure. Many properties, such as mechanical strength, corrosion and creep, are dependant on the microstructure. Alloys with desired properties can be achieved by tailoring the microstructure, either by controlling the composition or by processing. For example, the addition of elements such as selenium, copper or arsenic refines the grain structure of lead–antimony grids, while the addition of tin to lead–calcium grids increases their mechanical strength. Ways of controlling the microstructure by (physical) processing include deforming the grids by a rolling operation and casting the grids at varying rates of cooling. A typical microstructure consists of a number of crystals or grains, see Fig. 1. These grains join one another at the grain boundaries. Each grain is a single crystal with a periodic array of atoms. In the grain boundary regions, there is lack of atomic periodicity. The structures of these grain boundaries have a strong influence on the bulk (physical, mechanical and chemical) properties of the material. For instance, by increasing the area of grain boundaries, the grain size decreases and the mechanical strength increases. At elevated temperatures, however, grain boundaries enhance creep.

1.1.1.2. Plastic deformation. When a material is rolled, it becomes plastically deformed. This deformation breaks up the grain structure and leads to finer, more elongated grains which are aligned in the direction of rolling. Due to this directionality of the grains, the mechanical strength will be higher in the rolled direction than in the perpendicular direction. Thus, rolling results in improvements in the mechanical strength and the creep resistance of the grids. The deformed material will have high internal stresses. On annealing, the internal stresses in the deformed material will aid the formation of new crystals by a recrystallization process. The final microstructure and the resulting properties depend on the extent of rolling and alloy composition.

1.1.1.3. Corrosion. The corrosion characteristics of alloys are determined by both the structure and the composition. Since grain boundaries are chemically more active,

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* Corresponding author. Tel.: +61-395-45-8500; fax: +61-395-62-8919.
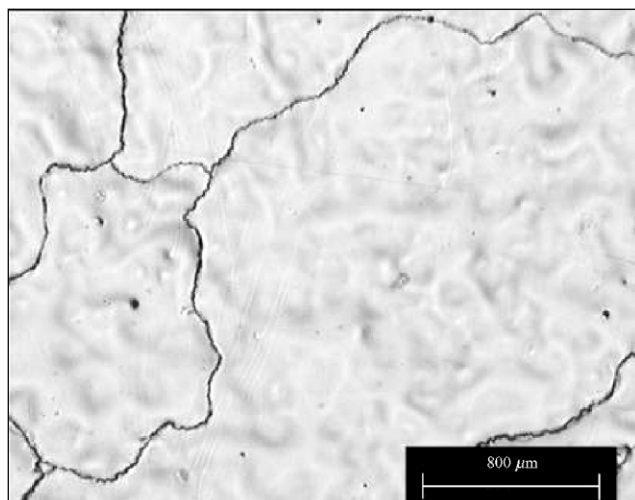*E-mail address:* david.rand@csiro.au (D.A.J. Rand).

Fig. 1. Typical microstructure of metallic materials.

corrosion occurs preferentially at the grain boundaries and this results in intergranular corrosion. The grain boundary area is greater for small grains and, hence, corrosion occurs uniformly throughout the surface. For large grains, there are only a few grain boundary regions and thus corrosion can penetrate deep into the material and give rise to catastrophic failure.

1.1.2. Effects of calcium and tin on grid microstructure

For a gravity-cast grid with the composition Pb–0.06 wt.% Ca–0.6 wt.% Sn, the microstructure would consist of medium-sized grains, Fig. 2(a). If the level of calcium is increased in this alloy, but the same level of tin is unchanged, the grain size becomes much smaller, as shown in Fig. 2(b) for a grid of Pb–0.13 wt.% Ca–0.6 wt.% Sn. On the other hand, if the level of tin is increased, but the level of calcium is kept the same, then the grain size increases significantly. This is clear from Fig. 2(c) for a grid of Pb–0.06 wt.% Ca–1.5 wt.% Sn. Thus, the grain size increases with increasing tin content and decreasing calcium content. It has also been found [1,2] that the grain size depends on the Sn:Ca ratio. The microstructures of low-tin, high-calcium alloys will be fine grains with serrated grain boundaries. In contrast, the microstructures of high-tin, low-calcium alloys will be coarse grains with smooth (regular) grain boundaries.

1.1.3. Effects of calcium and tin on grid corrosion

In lead–calcium–tin alloys, corrosion occurs preferentially along the grain boundaries. Corrosion resistance improves with increasing grain size. Since the grain size is found to decrease with increasing calcium content, it can be expected that the corrosion rate will increase concomitantly. On the other hand, if the level of tin is raised, then the grain size increases and hence there is a corresponding decrease in the rate of corrosion [1,2]. When the grain size becomes too large, however, the grids become susceptible to penetrating corrosion and may lead to catastrophic failure.

1.1.4. Effects on mechanical properties of grids

The age-hardening behavior of lead–calcium–tin alloys is found to depend on the ratio of tin to calcium concentration
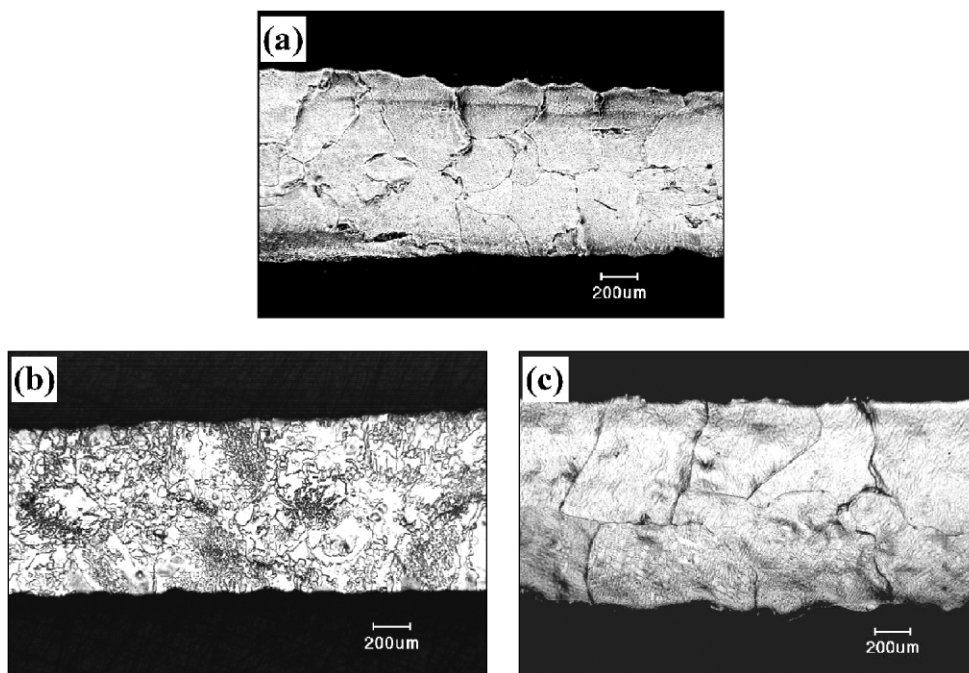

Fig. 2. Micrographs showing effects of calcium and tin additions on microstructure: (a) Pb–0.06 wt.% Ca–0.6 wt.% Sn; (b) Pb–0.13 wt.% Ca–0.6 wt.% Sn; (c) Pb–0.06 wt.% Ca–1.5 wt.% Sn.

in the alloy. For high-calcium–(low-tin) alloys with ratios below 9, hardening occurs very rapidly with the formation of stable Pb_3Ca precipitates. By contrast, low-calcium alloys with ratios above 9 exhibit very low initial values of hardness. This initial slow rate of hardening is followed by a rapid rate of hardening, with the formation of $(Pb,Sn)_3Ca$ or Sn_3Ca precipitates. Both the yield strength and the creep resistance are found to improve with increasing tin levels [1,2]. The improvement in the mechanical strength is again due to the change in precipitation mode from Pb_3Ca to $(PbSn)_3Ca$ with increasing tin levels.

1.1.5. Effect on electrochemical properties

Tin in the alloy decreases oxygen and hydrogen gassing at the positive and negative electrodes, respectively. Tin has also been found to decrease the thickness of the passivation PbO layer [3].
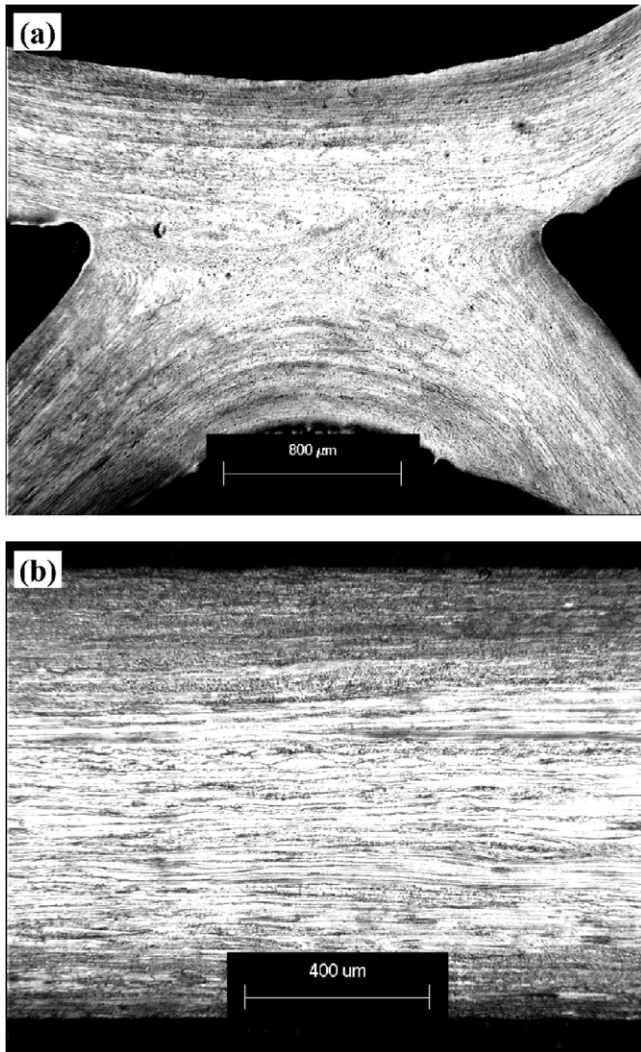
1.2. Question: How does the structure of continuous-cast/ rolled and expanded-metal grids differ from that of gravity-cast grids? What effect will this have on their mechanical strength and corrosion resistance? (C.S. LAKSHMI)

There are several continuous grid-production techniques, as follows:

(i) In the wrought strip expansion method, lead–calcium–tin alloy is rolled into a strip and the rolled sheet is slotted and expanded to form a continuous ribbon of grids.
(ii) In the cast-expansion method, a continuous strip is cast slotted, and then expanded to produce the grids.
(iii) In the Conroll^{TM} technique, molten metal is fed to a casting shoe which slides on a rotating drum. The continuous grid strip is subsequently rolled to obtain very thin grids.
(iv) A stamped grid is made by stamping or punching the grid from a continuous sheet of either a rolled or a continuous-cast lead material.

Fig. 3. Microstructures of rolled and expanded-metal grids: (a) Pb–0.08 wt.% Ca–0.2 wt.% Sn; (b) Pb–0.04 wt.% Ca–1.6 wt.% Sn.
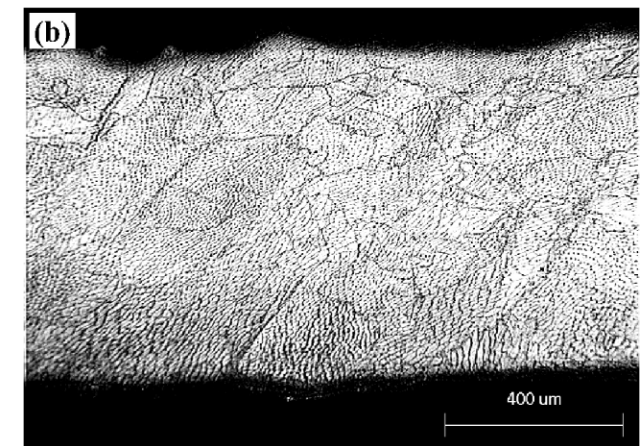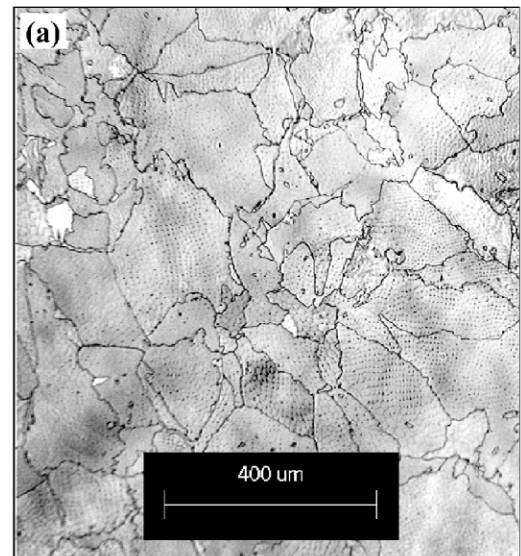

Fig. 4. Microstructures of cast-strip expanded grids of Pb–0.06 wt.% Ca–0.3 wt.% Sn; (a) lug region; (b) grid wire.
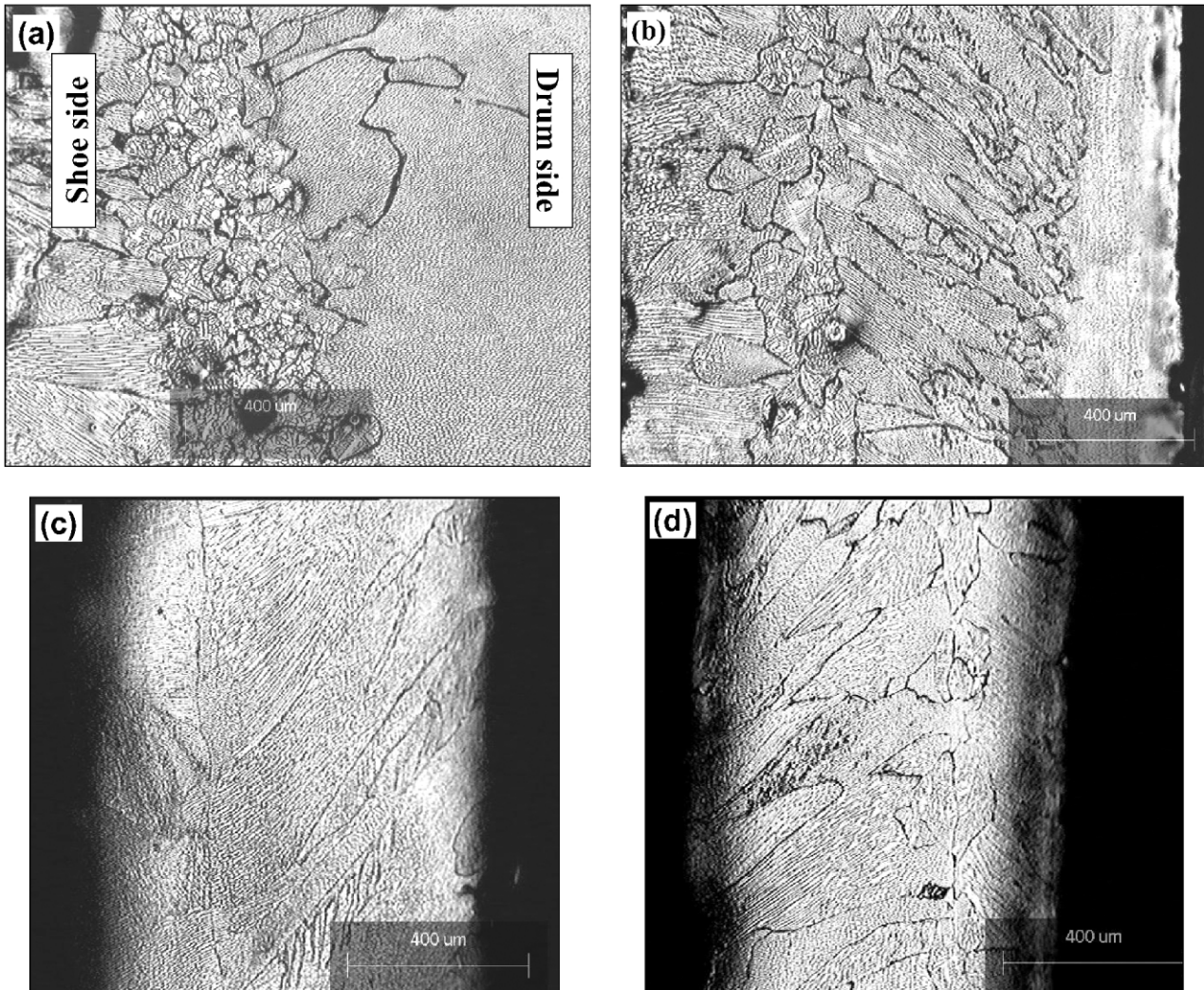
Fig. 5. Micrographs showing evolution of microstructures (perpendicular to plane of the grids) in Conroll^TM process (a) as-cast grid, (b), (c) and; (d) show consecutive microstructures arising from subsequent rolling process. (Grid composition: Pb–0.05 wt.% Ca–2 wt.% Sn.)

The extent of rolling and the alloy composition determine the final microstructure and the resulting properties of the grids. Therefore, there are significant differences in the microstructures of the grids made from the above-mentioned techniques.

1.2.1. Microstructures

The typical microstructure of an expanded-metal grid (from wrought-metal strip) is shown in Fig. 3(a). In contrast to the normal gravity-cast grid (see Fig. 2), no distinct grains are visible. As a result of the rolling process, the normal grain structure has been broken to give a laminar, textured structure. Even for an alloy containing high-tin, the microstructure appears similar, as shown in Fig. 3(b).

In the cast-strip and expanded-metal grids, the grain structure is similar to that of conventional gravity-cast grids, Fig. 4(a), with discrete grains. The grains are orientated in the direction of expansion for a grid wire, as shown in Fig. 4(b).

The microstructures of the Conroll^TM grids (perpendicular to the plane of the grid) from the as-cast condition to the subsequently rolled grids are presented in Fig. 5. In an as-cast grid from a Wirtz continuous caster, Fig. 5(a), the grains show a distinct variation across the section of the grid, with smaller grains on the shoe side and larger grains on the wheel (or drum) side. This variation in grain size is due to significantly different cooling rates on the two sides of the grid (with smaller grains at higher cooling rates). On subsequent rolling of this cast grid, microstructural evolution occurs, Fig. 5(b). With just a couple of passes, some orientated grains develop. On the drum side, the grain structure has been broken. With further rolling, the grain size becomes more uniform across the section of the grid, Fig. 5(c) and (d), with no variation on either side of the grid. The improvement in homogeneity of the grain structure has occurred as a result of the recrystallization process. The orientation of the grains indicates the direction of rolling.
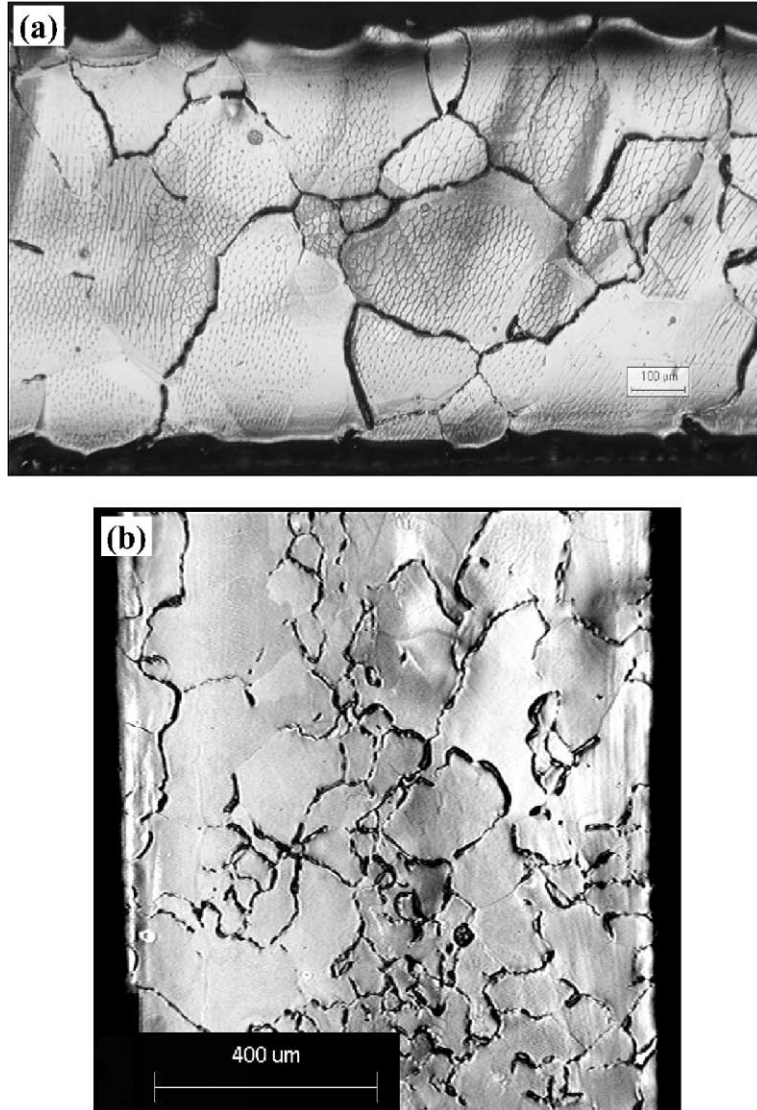
Fig. 6. Micrographs of Pb–0.6 wt.% Sn grids: (a) stamped; (b) Conroll[TM].

The microstructures of lead–tin grids produced by the stamping and the Conroll[TM] techniques are shown in Fig. 6(a) and (b), respectively. At this composition, the grids tend to recrystallize and hence the grains across the cross-section appear equi-axial in both the cases. The size of the grains depends, however, on the extent of rolling. In gravity-cast grids, the grains are normally equi-axial and their sizes differ based on the composition (as discussed in Section 1.1).

1.2.2. Properties

The rolling process improves the mechanical strength of lead–calcium–tin alloys [4]. Since the grain structures of the grids differ with the method of manufacture, the corrosion behaviour is also dependant on the composition and the extent of rolling during manufacture. The corrosion morphology of a rolled and expanded grid is shown in Fig. 7. As discussed earlier, the microstructure of the rolled and expanded grid consists of very fine textured grains. Hence, there is very uniform corrosion, mainly at the surface. In wrought-expanded grids, however, the probability of stress-corrosion cracking exists.

Rolled and expanded grids exhibit uniform surface attack without any significant intergranular component. Stamped or punched grids are relatively stress-free and hence are more resistant to stress-corrosion cracking. On the other hand, for the cast-strip and expanded grid, corrosion is intergranular. Therefore, in this case, corrosion penetrates into the grid, Fig. 8. A gravity-cast grid experiences an intergranular type of corrosion, see Fig. 9.

In summary, continuous grid-production techniques provide a better means of controlling the microstructures and achieving superior mechanical strength, creep resistance and corrosion resistance. The extent of rolling and composition determine the final microstructure and the resulting properties of the grids.
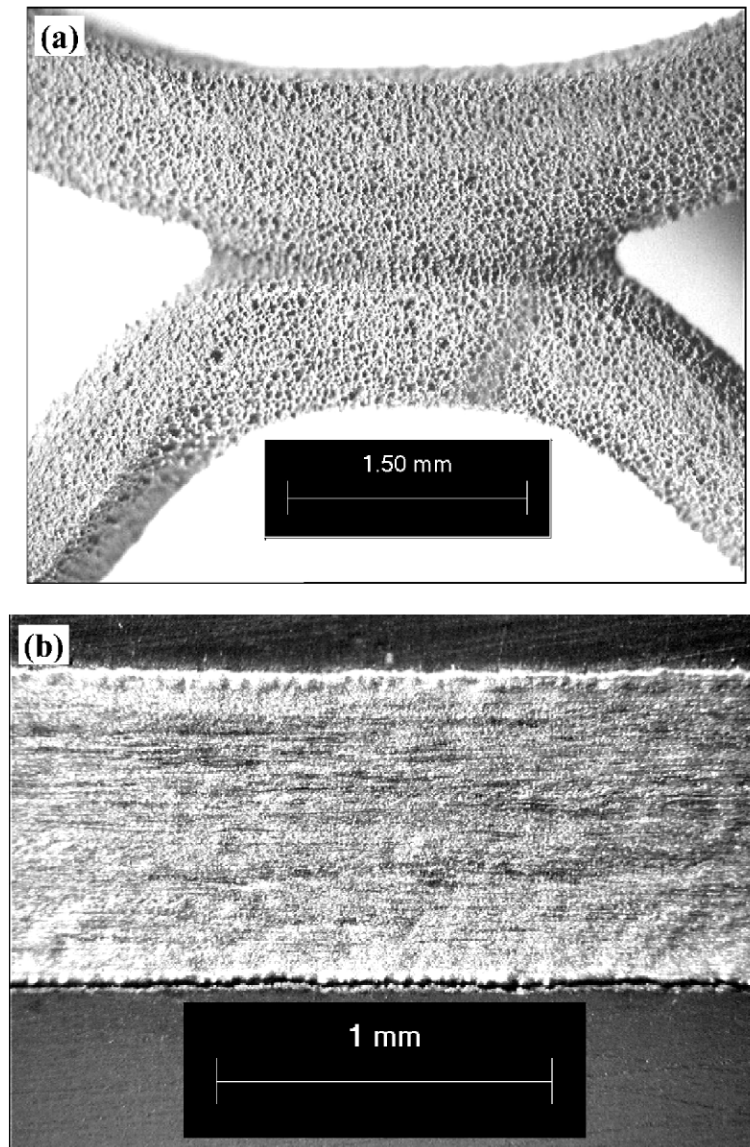
Fig. 7. Corrosion morphology of rolled and expanded grid of Pb–0.08 wt.% Ca–0.9 wt.% Sn; (a) grid wire intersection; (b) grid wire in cross-section.

1.3. Question: What are the means for achieving low dross-make during the casting of lead–calcium–tin alloy grids? (C.S. LAKSHMI)

Dross is a product of oxidation of calcium and molten lead in the grid casting operation. Since the dross is difficult to separate from the metallic lead, this will increase the wastage of lead. Excessive dross-make also leads to operating problems, such as clogged feedlines, poor quality grids, etc.

The amount of dross produced during grid casting depends on various factors, such as: (i) the aluminum content in the melt; (ii) temperature of the melt; (iii) pot or pump turbulence; (iv) the de-drossing procedures and other handling methods used. Depending on how well the above factors are controlled, the amount of dross could vary from a low of 2 wt.% under optimized conditions to as high as 9 wt.% in non-optimized conditions [5].

1.3.1. Effects of temperature and aluminum content

The most important step in minimizing dross is to include aluminum in the range 0.015–0.030 wt.% in the grid alloy. Aluminum forms a stable oxide skin that locks out air and prevents any further oxidation of calcium and lead. Since aluminum has low solubility in lead (see Fig. 10), it is important to maintain its level by maintaining the melt at appropriate temperatures.

In grid casting, the loss of aluminum from the melt can occur only when the temperature of the pot is held too low (below 490 °C). At these temperatures, the solubility of aluminum in lead is too low and hence gives rise to a thick (or heavy), mushy (or sticky) dross of metallic lead. Calcium is also similarly lost and the feedlines become clogged.

For calcium alloys, even at properly set temperatures (in the range 490–505 °C), it is important to monitor the various operating temperatures at regular intervals. In reality, the
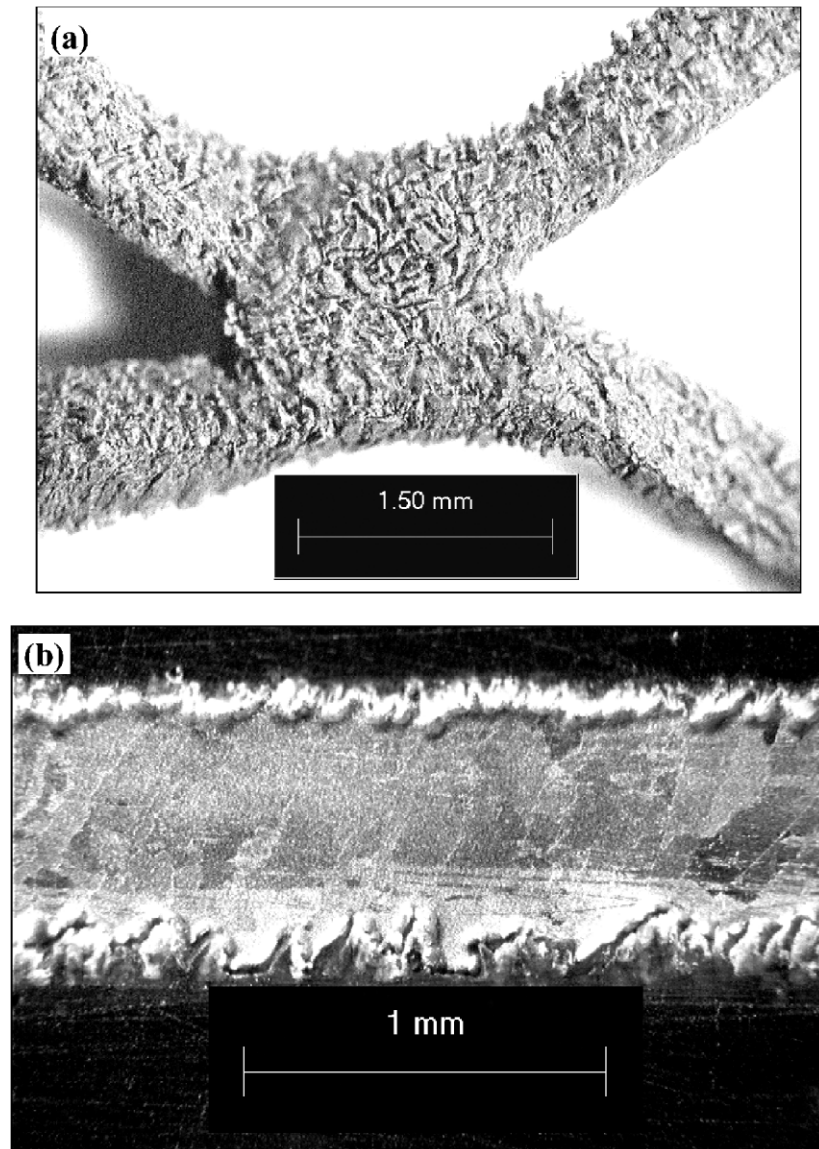
Fig. 8. Corrosion morphology of cast-strip and expanded grid of Pb–0.06 wt.% Ca–0.3 wt.% Sn; (a) grid wire intersection; (b) grid wire in cross-section.

temperature of the pot can vary significantly due to the return of the scrap, the addition of cold ingots to the bath, etc. Even low temperatures for short periods can give rise to severe problems.

On the other hand, when the temperature is too high, the rate of drossing is accelerated. This is because the rate of oxidation of lead itself increases rapidly at high temperatures. Also, as the solubility of aluminum increases with increasing temperature, the amount of rich–rich compounds increases. This reduces the amount of aluminum available for the formation of a protective oxide film on the surface of the melt. This, in turn, causes extensive oxidation of calcium and tin and hence more dross formation.

Whilst the grid caster is idle, e.g., for up to a day, it is important not to turn down the temperature of the pot. Such practice avoids the loss of aluminum that would occur on lowering the temperature. It is also preferable to retain a layer of dross on the melt surface so as to limit the access of oxygen.

1.3.2. De-drossing and agitation

De-drossing or the removal of dross from the pot should be carried out as infrequently as possible. This is because keeping a pad of fine dross on the surface protects the metal from further oxidation. While removing the dross, the operator should ladle the dross from the top of the pot and shake and tap to drain the molten lead out as much as possible. Proper operator training and procedures are essential to achieve low metallic contents in the dross. If the method of de-drossing is improper, the dross will be lumpy with as high as 70–80 wt.% entrapped metal and will include high levels of aluminum. With proper procedures, the dross will be powdery with 20–25 wt.% entrapped metal.
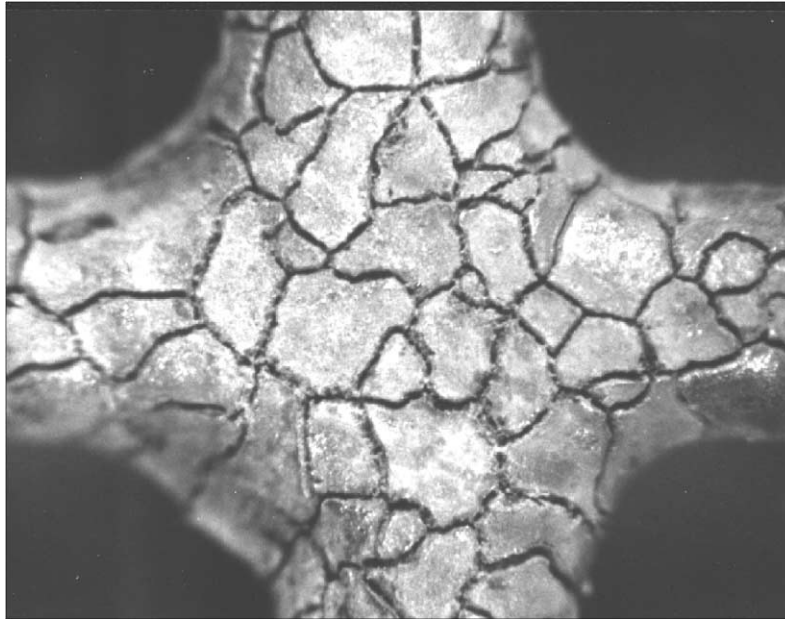
Fig. 9. Corrosion morphology of gravity-cast grid of Pb–0.06 wt.% Ca–1.0 wt.% Sn.

The returning trim scrap always causes agitation and increase dross production. In order to minimize dross, the agitation should always be kept to a minimum.

1.4. Question: What is the future of book-mould casting when the change is made to 36 V automotive batteries? (R.D. PRENGAMAN)

The 36 V batteries planned for use in the new electrical systems for automobiles will most likely be valve-regulated lead-acid (VRLA) designs. Japan Storage Battery, for example, has developed a 36 V battery using book-moulded grids.

The major questions regarding book-moulded VRLA batteries are given below.

(i) Do the plates have uniform compression cell-to-cell?
(ii) Does each cell have the same saturation of electrolyte?

Fig. 10. Solubility of aluminium as function of temperature.

(iii) Can the grids be cast in thin cross-sections required for the high-power requirements?
(iv) Can the grids and subsequent plates be produced with sufficient consistency for a three-fold increase in the number of cells?

1.4.1. Requirements for book-mould cast grids

The book-mould cast grids must use corrosion-resistant lead–calcium–tin–silver alloys. The thin grids will require more precision in casting grids without defects. This will require higher precision in the control of the metal temperature and mould temperature to prevent trapped air and possible hot cracks in the grids.

The grids must be cast to high dimensional tolerances. The normal tolerances of ±0.05 to ±0.075 mm will not be acceptable in a 1 mm thick grid. This would represent 5–7.5% variation in grid thickness. To achieve high reliability of cells, a variation of no more than 1% will be required [6]. This would be only ±0.01 mm in a 1 mm thick grid.

To produce the low grid-to-grid variation required for uniform compression, new materials which extend cork life must be developed. The grids must be produced to not only thickness tolerances but also weight tolerances. The thickness tolerances can be achieved by the use of planishing dies. A planishing die compresses the cast grid frame and wires to a uniform thickness prior to trimming. Wirtz has produced planishing dies for many years which can dramatically reduce the thickness variation of book-mould cast grids to $\pm1\%$ or lower. Planishing dies can give a three-sigma increase in grid thickness reproducibility.

In addition to thickness variation, the weight variation of the grids is also important. Thicker grids planished to thinner cross-section will decrease slightly the cross-section of the open space in the grid which will be occupied by the active
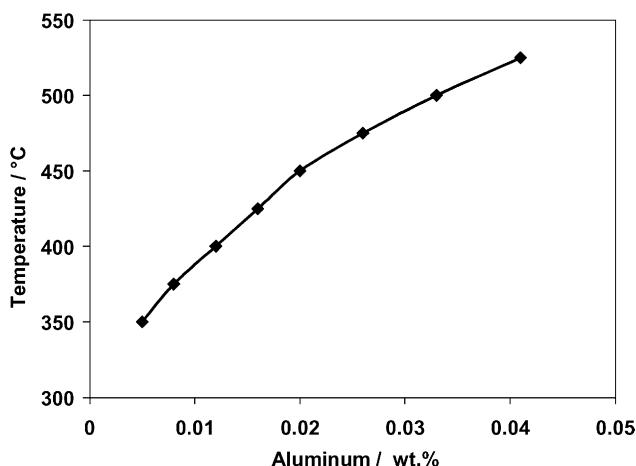
material. To reduce the grid-to-grid variation, individual grids must be weighed. Although this seems impossible, such a procedure was in operation at a European battery plant over 10 years ago. There is nothing that will drive a battery company to produce improved grid dimensions and weight than reprocessing what seem to be perfectly good grids which are light or heavy.

Once high dimensional tolerance grids are produced, they must be pasted to uniform thickness and weight. Most likely, this ±1% variation cannot be attained on a belt paster. Rather, an orifice paster will be required. Not only must the paster be precisely controlled but the variation in paste density, water content, acid:oxide ratio and penetration must be better controlled from batch to batch. To reduce corrosion of thin grids, the plates must be well cured to produce a good, adherent bond between the grid and active material.

1.4.2. Spiral-wound cells

Book-mould casting can also produce grids for spiral-wound cells. The process is more difficult than the production of flat-plate grids. Spiral-wound cells generally employ much softer lead–tin grid alloys without calcium to serve as an element to strengthen the grids. Grid distortion during casting is a potential problem.

Grids for spiral-wound cells must be of a larger size than conventional grids. Since the grids must be produced with multiple lugs, conventional grid mould designs must be modified to permit trimming of the cast grid. All other aspects of grid casting discussed above—such as control of the dimensions, weight and squareness of the grids, as well as control of paste thickness and weight—must also be performed.

Despite the attractions of continuous processes which can produce tighter tolerances such as roll-expanded, Cominco cast or extruded-expanded, Wirtz Concast™ or Conroll™, conventional book-mould casting can produce grids for both flat rate and spiral-wound cells to high tolerances required for 36 V batteries.

1.5. Question: What are the effects on battery materials of: (i) silver in new lead–calcium–tin–silver alloys and (ii) higher silver content of recycled lead? What is the effect of increased silver content on the active material of the battery and how can It be overcome? (R.D. PRENGAMAN)

1.5.1. Effect of silver in grid alloys

Silver causes a marked improvement in the corrosion resistance as well as the creep resistance of lead–calcium–tin alloys used for positive grids. Sufficient silver dramatically reduces grid growth in positive grids at elevated temperatures. The reduction in grid corrosion as well as grid growth has led to the construction of heat-resistant automotive batteries with significantly longer lives than batteries without silver. This is important as higher underhood temperatures produced by aerodynamic styling and higher engine

temperatures have served to reduce battery life in those parts of the world with hot climates.

To a small extent, silver increases immediate as-cast strength which, in turn, improves handling of low-calcium–tin–silver grid alloys. Silver in amounts over 0.02–0.025 wt.% can, however, can lead to cracking in book-mould cast grids. The silver can form a low melting point eutectic with the tin additions to the alloy. Grids from these alloys may not completely solidify until temperatures are reached which are 20–40 °C lower-than-normal alloy solidification temperatures. Thus, either silver or tin can lead to cracked grids. This was the primary reason for low-tin contents (0.05–0.6 wt.%) in the first lead–calcium–tin–silver alloys that were used for positive grids which had high-silver contents (0.035–0.050 wt.%).

Silver is also used by one battery manufacturer in the USA to increase the corrosion resistance of lead–antimony alloys which are employed to prevent corrosion and leakage at the side terminals of automotive batteries. The amount used (1 wt.% Ag) makes this battery the highest silver-containing design produced today.

In general, silver-containing alloys are extremely corrosion-resistant. As a result, battery companies have had considerable trouble in attaching the active material to the grids during curing. Book-mould cast grids can be steamed or heat treated at elevated temperatures to develop an oxidation layer on the grid surface prior to pasting. Such a layer can facilitate the adhesion of the active material to the grid by attachment to the PbO surface which is already present.

For corrosion-resistant lead–calcium–tin–silver grids produced by Cominco expanded, rolled-expanded, Wirtz Concast™ or Conroll™ processes, it is virtually impossible to produce a PbO layer on the surface of the grid prior to pasting. As a result, failure of these batteries often occurs by paste shedding instead of positive grid corrosion, even at elevated temperatures. Special paste mixes with higher paste density and higher alkalinity are required to corrode these highly corrosion-resistant grids and produce a good bond between the grid and positive active material.

1.5.2. Silver content in recycled lead

The addition of silver to the positive grids and to the alloys used for side terminals has had a dramatic effect on the silver content of recycled lead. Over the past 5 years, there has been a dramatic increase in the silver content of recycled lead. Data produced by RSR battery-recycling plants in the USA for the actual average silver content from 1996 to 1999 are presented graphically in Fig. 11 [7]. The graph also includes projections for the silver content of recycled lead from 2000 to 2003 based on the number of silver-containing automotive batteries produced during the years 1996–1999. The results show that, from an average of about 17 ppm silver in the early and mid 1990s, the silver content of recycled lead has increased to about 20 ppm in 1996, 21 ppm in 1997 and 22 ppm in 1998. This is most likely
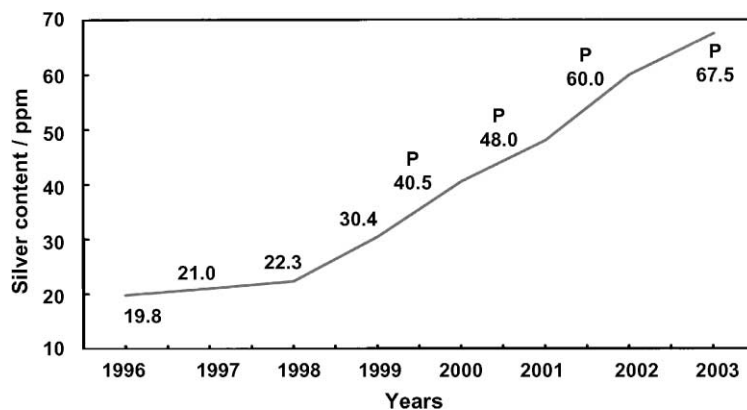
Fig. 11. Increase in silver content (actual and projected) in recycled lead at RSR battery-recycling plants in the USA.

due to recycled plant scrap from battery manufacturers using silver-containing alloys, as well as from some early battery failures.

In 1999, the recyclers experienced a dramatic jump in silver content from 22 to over 30 ppm. This coincided with the failure of the first wave of lead–calcium–tin–silver positive grids produced in 1995–1996. There was another jump in silver content of recycled lead to over 40 ppm in 2000, which caused many difficulties within the battery industry in the USA.

There are many variations in silver content in battery manufacturers' specifications for pure-lead to be used as battery oxide or grid materials for automotive batteries. The silver content is generally 25–50 ppm and is well above the normal levels of about 17 ppm. In 2000, many battery manufacturers raised the silver content of their specifications to 50 ppm which corresponded to the US-ASTM specification for lead. Based on the predictions of the curve in Fig. 1, however, the 50 ppm level is likely to be reached in late 2001 or early 2002 and will rise to 67 ppm in 2003. A level of 90–100 ppm could eventuate by the end of the decade.

1.5.3. Effects of higher silver content in pure-lead

Silver decreases the rate of oxidation of lead in Barton pots which leads to decreased production. The decline in the rate of production is substantial and may reach 8–10% at levels of 50 ppm and above. More important is unstable operation of Barton pots due to variable silver content in the lead fed to the reactor from batch to batch. Ball-mill production appears to be less affected, although lower production and higher recycle rates have been reported. Silver acts to reduce the rate of oxidation of lead in oxide manufacturing in a manner similar to that which protects the silver-containing positive grids from oxidation (corrosion).

To overcome the effects of reduced production in Barton pot operation when using lead with a higher silver content, many companies have added antimony to the lead prior to introduction into the Barton pot. In general, the antimony is added in an amount approximately equal to that of the silver content of the lead. Thus, a material with 20 ppm silver utilizes an addition of about 20–30 ppm antimony. At the higher silver contents presently seen in the USA, viz., about 48 ppm, the antimony required would be about 50–60 ppm. Even higher amounts would be required in later years. The addition of high amounts of antimony would present gassing problems for the batteries as antimony would be transferred to the negative active material.

The adverse effect of antimony might be overcome by the addition of surface-active agents to the negative active material to absorb the antimony as it is transferred. Such agents have been tested in Project B-005.1 of the Advanced Lead-Acid Battery Consortium (ALABC) and have served as a trap for antimony until they become saturated. At levels of 50–100 ppm antimony in the active material, these additives should not become saturated with antimony and should be able to trap it before excessive gassing occurs. Zinc has been shown to reduce gassing in lead-acid batteries by the addition of 0.1–0.3 wt.% $ZnSO_4$ to the electrolyte. Such an addition dramatically reduces the gassing current, even at higher potentials.

During the curing process, the free-lead in the paste mix is oxidized to PbO and converted to $PbSO_4$, tribasic lead sulfate, or tetrabasic lead sulfate. Silver also decreases the rate of oxidation of the free-lead in pasted plates during curing. Battery companies have had to modify their curing practice to assure satisfactory reduction in free-lead in the final plates. Free-lead in the formed plates can lead to significant self-discharge of fully charged batteries upon storage.

The effect of silver on the gassing behaviour of batteries has been reported [8]. In this work, minimal gassing was observed when the silver content was kept at 100 ppm or below in the active material. The ALABC is studying the effects of silver and other impurities of the active material in Project N3.1. Other ALABC work has reported that silver is transported from the positive active material and the corrosion layer to the negative active material. Thus, if the active material of both positive and negative plates contains 50 ppm silver, within a few cycles after formation, the positive plate will contain 1 ppm or less and the negative plate will contain 100 ppm.

It may be thought that the transfer of such a large amount of silver would dramatically increase the generation of hydrogen if the silver were a significant generator of hydrogen. Lawrence [8] has reported, however, that there is no significant increase in the $H_2:O_2$ ratio of the gas generated under the J240 testing regime at 75 °C, despite significant amounts of silver in the negative active material. The $H_2:O_2$ ratio is 1:2, which indicates higher O_2 evolution than hydrogen evolution, even with 450 ppm silver in the active material (900 ppm in the negative active material).

There may be a 'silver lining' to the problem of high-silver content in the active material. At the same doping levels seen in the testing of automotive batteries, silver has been shown to have a positive effect under DIN cycle-life duty. Silver contents of 100 and 450 ppm in the active material give significantly higher cycle-life than similar batteries with zero or 50 ppm silver. This may be due to the higher conductivity of the negative plate when the lead is coated with small amounts of silver. The improvement in cycle-life only occurs when sufficient silver is present.

1.5.4. Summary of silver effects

  (i) The level of silver entering the recycling stream from silver-containing batteries is not likely to be reduced significantly.
 (ii) Silver does not appear to be as much a problem as first envisioned, even at high levels up to about 100 ppm.
(iii) Silver increases O_2 evolution more than H_2 evolution.
 (iv) The addition of antimony can stabilize the production rates of oxide at high-silver levels.
  (v) Additives to the negative active material that serve as antimony traps may negate the effects of antimony additions.
 (vi) Addition of zinc may suppress the negative effects of antimony.
(vii) Silver may be beneficial in improving the performances of cycling batteries.

1.6. Question: Can grid materials which are continuously processed (i.e. rolled-expanded, Cominco expanded, Concast^TM, Conroll^TM) survive high-temperature life tests such as the hot SAE J240a procedure? (R.D. PRENGAMAN)

In order for any battery to pass high-temperature life tests, the grid materials must have the following attributes.

1.6.1. Low corrosion rate

Lead–calcium–tin–silver alloys have been developed to serve as alloys for positive grids for lead-acid batteries operated at elevated temperatures. The most important concern is to have a low rate of corrosion. This property is produced by low-to-moderate calcium contents, moderate-to-high-tin contents and the addition of silver. Grids produced from such alloys have exhibited low rates of

corrosion despite elevated temperatures and high rates of oxygen evolution.

1.6.2. Uniform microstructure

The grids must maintain a uniform microstructure. With various grid-manufacturing processes, the microstructures of the grids vary widely. To date, only conventionally book-mould cast grids with large grain size have survived hot life tests. Our recent work has indicated that other grid-manufacturing methods, such as Cominco expanded, can produce grids which can also pass hot life tests. We believe that it is neither the grid-manufacturing method nor the grain structure which is important, but the uniformity of the structure within a grain. In this sub-structure, the grain boundaries contain high concentrations of tin and silver with lower calcium content. When the alloy composition is correct, segregation of these elements makes the sub-grain boundaries virtually indistinguishable from the grain boundaries. If the grain boundaries have nearly the same composition as that of the grains due to sub-grain segregation, the size and shape of the grains are not nearly as important as the uniformity of the segregated structure.

1.6.3. High microstructural stability

The microstructure must remain stable at elevated temperature. To maintain a uniform microstructure, the alloy must contain sufficient tin in order to react with all the calcium present to convert it to Sn_3Ca. If some of the calcium remains unreacted, it will precipitate as Pb_3Ca. Pb_3Ca can only be precipitated behind moving boundaries. As grain boundaries move through the alloy to precipitate Pb_3Ca, they destroy the cast-in segregation and concentrate impurities rather than tin and silver at the grain boundaries.

To produce a stable structure, the alloy must contain an additional tin content above that required to convert the calcium to Sn_3Ca. Because tin and calcium are segregated to different areas of the sub-grains (calcium-centre, tin/sub-grain boundary), the tin must be higher than that calculated to assure the conversion of all calcium to Sn_3Ca. Because of calcium segregation, even low-calcium alloys will require higher than expected tin contents to achieve microstructural stability, particularly at elevated temperatures where grain boundaries are more mobile.

1.6.4. Minimal penetrating corrosion

The grids must have minimal penetrating corrosion to prevent catastrophic corrosion which can result in failed grid members or grid growth. Maintaining the uniformly segregated grain structure throughout the grid, regardless of the grid-manufacturing method, will prevent penetrating corrosion. By reducing or eliminating grain boundary movement by producing Sn_3Ca and providing sufficient silver to restrict creep or boundary movement, grids can be made resistant to penetrating corrosion despite grains which grow completely through the grid cross-section. Thus, grids made via the Cominco cast-expanded or the Wirtz Concast^TM or

Conroll™ processes can yield uniform corrosion profiles on the surface of the grid despite wide variations in grain structure, provided the segregation is maintained.

1.6.5. Resistance to growth

Grid growth is caused by corrosion which penetrates into the grain structure and causes the grid to elongate. Growth is a function of not only the amount of corrosion but also the uniformity of the corrosion product and the mechanical properties of the grid. Non-uniform corrosion, particularly in expanded-metal grids produced from rolled material when subjected to high-temperature life tests, is believed to be caused by the unequal mechanical properties created by the rolling operation which also destroys the cast-in segregation. Despite low rates of grid corrosion, growth occurs. For years, it has been thought that grids require side borders to prevent grid growth. If growth is controlled by alloying to produce a uniform microscopic segregated structure at the surface of the grid in all directions, a side border produced by a book-mould casting may not be required. If the structure changes at elevated temperatures, grid growth can occur in any grid configuration.

1.6.6. Good connection with active material

One of the most important requirements for grids produced by continuous processes to survive the high-temperature life tests is good connection between the grid and the active material and the prevention of disengagement of the paste from the grid. In continuous processes, the grids cannot be pretreated to produce a PbO corrosion film on the surface. Many corrosion-resistant grids using low-calcium–high-silver–moderate-tin alloys resist the corrosion processes which are required to form a PbO_2 layer on the surface for adequate attachment of the active material.

The formation of tribasic or tetrabasic lead sulfate crystals at the grid/active material interface requires corrosion of the grid surface during curing. For optimum attachment of the active material, the grid surface must be alkaline to permit solubility of the lead ions in the water of the paste. Higher calcium contents than are normally used in low-calcium alloys promote conditions of sufficiently high pH to permit the corrosion of the grid surface. Higher density pastes, which employ more water and less acid, also yield active material which is resistant to shedding under high-temperature life tests.

Curing must be continued to low contents of free-lead. The free-lead in the paste mix is more reactive and more readily oxidized than the grid surface. If the plates are improperly cured and contain relatively high free-lead contents, there may not be sufficient water remaining to corrode the grid surface to attach firmly the active material.

1.6.7. Good conductivity

The grid must maintain good conductivity across the grid/active material interface. ALABC-sponsored work has demonstrated that if the grid contains sufficient tin, the corrosion product will not contain significant amounts of the insulating α-PbO. Segregation of tin to the grain and the sub-grain boundaries produces areas of significantly higher tin content than the bulk alloy. These areas can dope the PbO_2 locally to produce uniform, honeycomb-like regions of high-tin content through the corrosion layer. Tin contents of 10 wt.% or more are required to produce a layer which has electronic as well as ionic conduction. Such levels are easily attained in the regions of the grain and the sub-grain boundaries due to segregation of tin. These regions present low resistance paths through the grid/active-material interface to reduce heating, cracking and spalling of the active material. Tin also serves to prevent the formation of passive barrier layers of $PbSO_4$ at the grid/active-material interface that decrease the rechargeability of the grid.

1.6.8. Summary of grid materials

With proper alloy composition, most grid-production processes can produce grids with acceptable high-temperature life. The grids must: (i) be structurally stable and have low rates of corrosion without penetration; (ii) have sufficient tin and silver segregated to the grain and sub-grain boundaries to make all boundaries similar; (iii) be sufficiently corroded to produce a good bond between the grid and the active material.

2. Negative-plate expanders

2.1. Question: What are the functions of lignosulfonates and how do they work? (D.P. BODEN)

Expanders are used in every lead-acid battery produced in the world. Despite this, they are often regarded as mystery substances and knowledge about how they perform their function, the materials used in their production and the correct formulation for a particular battery application is meager.

Lignosulfonates exert physical, chemical and electrochemical effects on negative pastes and active materials. They affect the plasticity of the paste and increase its flow characteristics. This permits less water to be used during paste mixing. Insufficient lignosulfonate will result in a paste that is too stiff, while too much can result in a paste that is sloppy. Depending on the type and quantity of lignosulfonate in the paste, the water ratio may have to be adjusted to achieve the desired paste density and plasticity.

The principal chemical function of lignosulfonates is to inhibit the formation of tetrabasic lead sulfate (4BS) in the paste during mixing and in the plates during curing. Consequently, cured negative plates, regardless of curing conditions, contain no 4BS crystals.

The electrochemical functions of lignosulfonates are as follows:

(i) Lignosulfonates beneficially improve the electroreduction process during plate formation and thus cause
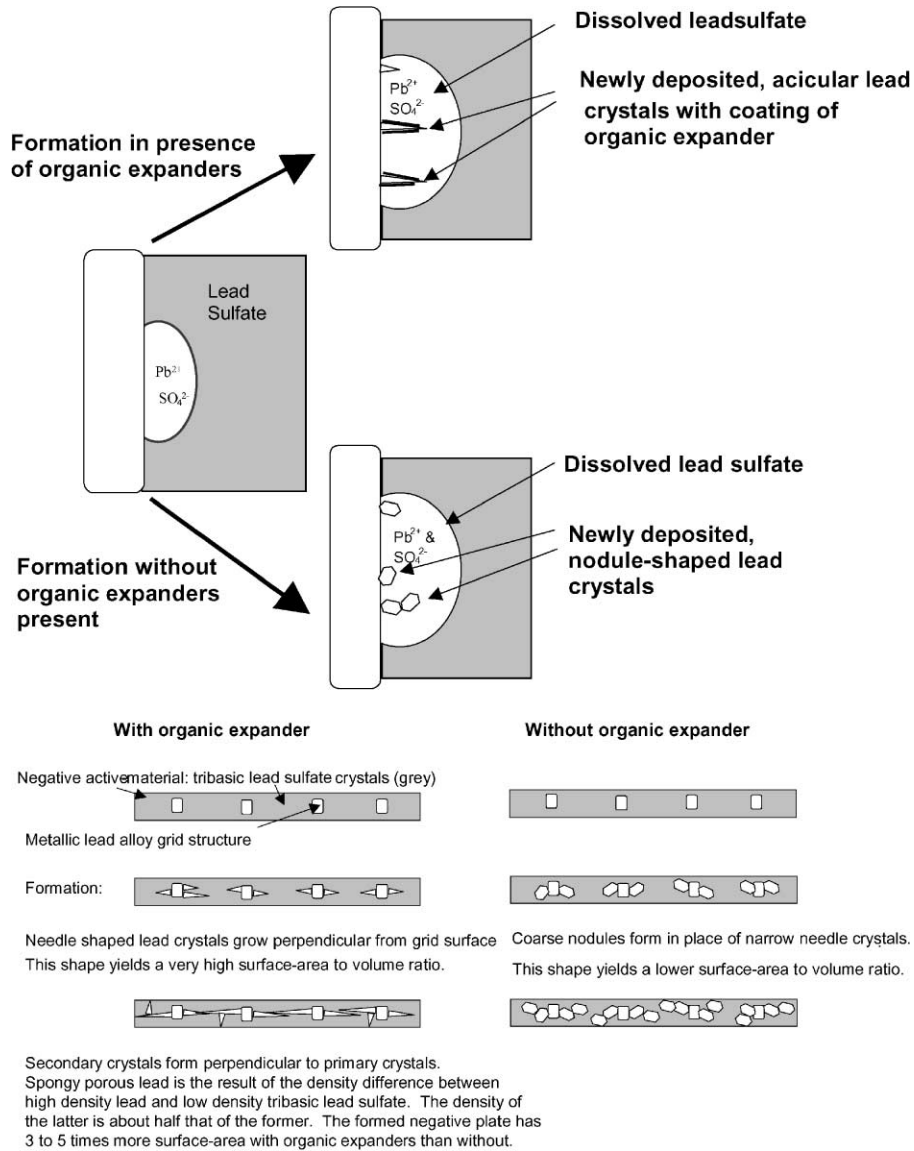
Fig. 12. Diagrammatic representation of the effect of lignosulfonates on the growth of lead crystals during negative-plate formation.

the production of small, finely divided, lead crystal-lites with high surface area and porosity. A diagram-matical representation of how crystals grow during formation of the negative plate in the presence and the absence of lignosulfonates is shown in Fig. 12. When lignosulfonates are present, the lead crystals have a uniform, equi-axial habit. These crystallites are finely branched and have high surface area and porosity.
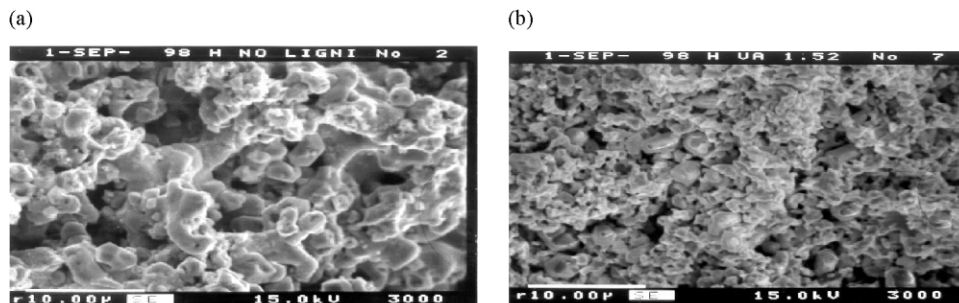

Fig. 13. Morphology of lead crystals in: (a) absence; (b) presence of lignosulfonate (0.5 wt.% Vanisperse A).
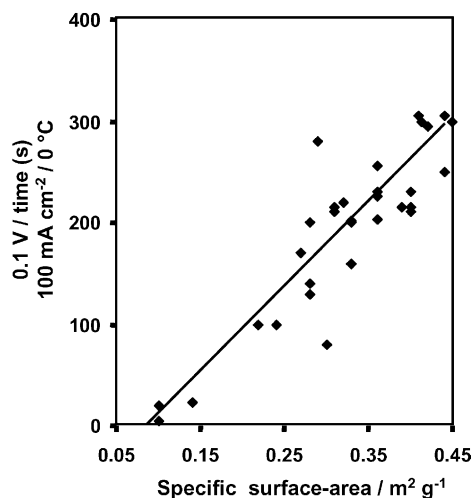
Fig. 14. Relationship between specific surface area and cold-cranking performance of negative active material.

(iii) Lignosulfonates promote the formation of porous, non-passivating, lead sulfate during discharge and thereby delay the onset of solid-state passivation.

(iv) Lignosulfonates preserve capacity during cycling.

During discharge of a negative plate containing lignosulfonate, several phenomena take place simultaneously. An artists rendition of these phenomena is shown in Fig. 15. The lignosulfonate is strongly adsorbed on both the lead metal and the lead sulfate crystals. The dissolved lead ions are complexed by the lignosulfonate and thus allow more lead ions to be produced before surface saturation occurs. This has the effect of increasing the discharging capacity. The adsorbed lignosulfonate on the lead sulfate crystals increases the surface energy and thereby makes it easier for lead and sulfate ions to form new crystals rather than to continue the growth of existing lead sulfate crystals. This produces a finely divided, porous lead sulfate discharge product which is non-passivating. The large adsorbed lignosulfonate molecules cause significant stearic hindrance in the electrical double-layer which inhibits diffusion of sulfate ions to the electrode surface. Precipitation of lead sulfate takes place, therefore, away from the electrode surface, and prevents passivation.

Lignosulfonate molecules are complex structures with several electrochemically-active functional groups. These have been found to affect the performance of negative plates in a number of ways. For example, phenolic hydroxy groups beneficially influence cycle-life, but also have a weak negative influence on capacity and charge-acceptance. Carboxyl groups exert a positive effect on capacity. This indicates that oxylignins should perform better than kraft lignins. Methoxyl groups show a positive correlation with cold-cranking performance. Organic sulfur groups have a negative effect on initial capacity with no discernable effect on cycle-life. Increase in molecular weight appears to reduce initial capacity and has no effect on cycle-life. Chemically-bonded metals show no correlation between capacity or life, but

If no lignosulfonate is present, the lead mass has a dense nodular structure with low porosity and surface area. Scanning electron micrographs which illustrate these features are shown in Fig. 13.

(ii) Lignosulfonates increase the capacity of the negative active material, particularly at high rates and low temperatures. There is a strong relationship between the surface area of negative active material and its cold-cranking performance (see Fig. 14). With increased surface area, more electrolyte comes into contact with the lead surface and thus reduces the effective current density at the reaction sites. Consequently, polarization is reduced and discharge time to the cut-off voltage is increased. The capacity is also enhanced because of the greater inventory of electrolyte in the porous lead sponge. The cold-cranking performance of negative plates which contain 0.5 wt.% lignosulfonate is two-to-three times better than when no lignosulfonate is used.
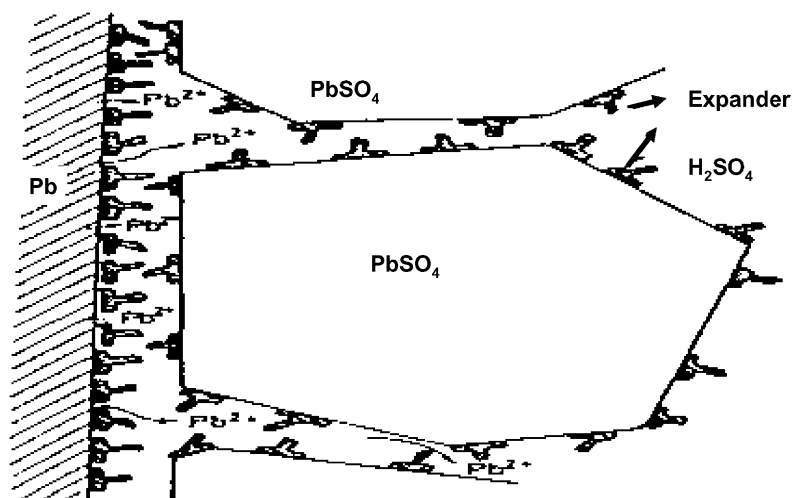

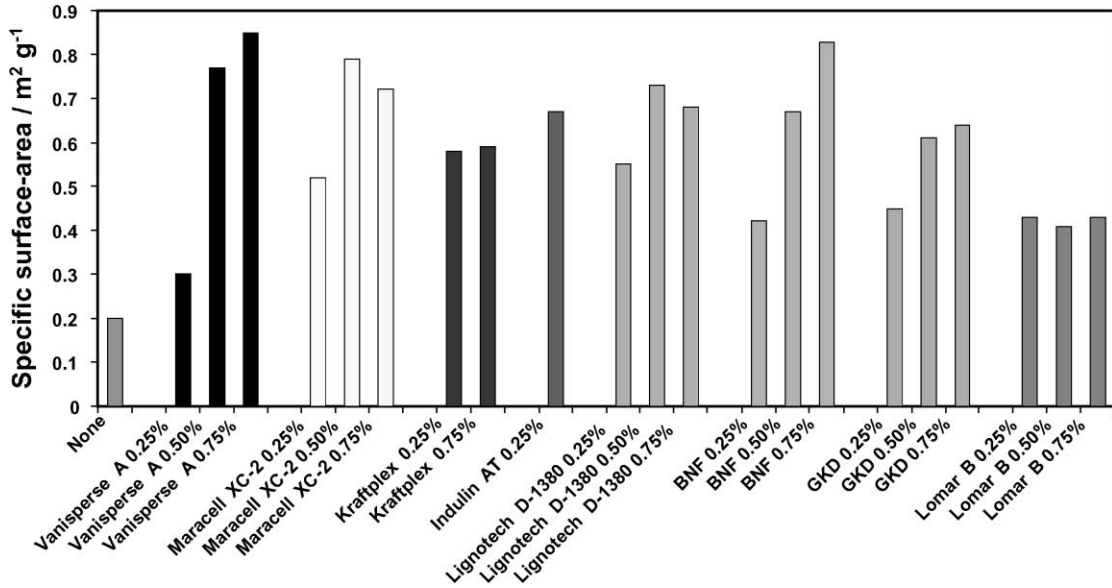Fig. 15. Illustration of phenomena during discharge of negative plate.

Fig. 16. Effect of organic additive on specific surface area of negative active material.

metals as impurities may have an effect on hydrogen over-potential.

The organic additive is very strongly adsorbed on the surface of the lead and causes a significant increase in surface area. Without any organic additive, formed negative active material is dense and has a BET surface area of approximately 0.2 m^2 g^{-1}, while active material which contains 0.5 wt.% Vanisperse A is fine-grained, porous and has a BET surface area of about 0.8 m^2 g^{-1}. The effect of various organic additives on the BET surface area of formed negative active material is shown in Fig. 16. All of the organic additives increase the surface area considerably and, generally, surface area increases further as the concentration of additive is increased. In some cases, the surface area reaches a maximum and then decreases as the concentration is increased.

The effect of the organic additives on the utilization of negative active material is shown in Fig. 17. All of the organics increase the active material utilization compared with plates that have no additive. The greatest effect is obtained from Lomar B. Other organics that give good active material utilization are Kraftplex at a 0.75 wt.%

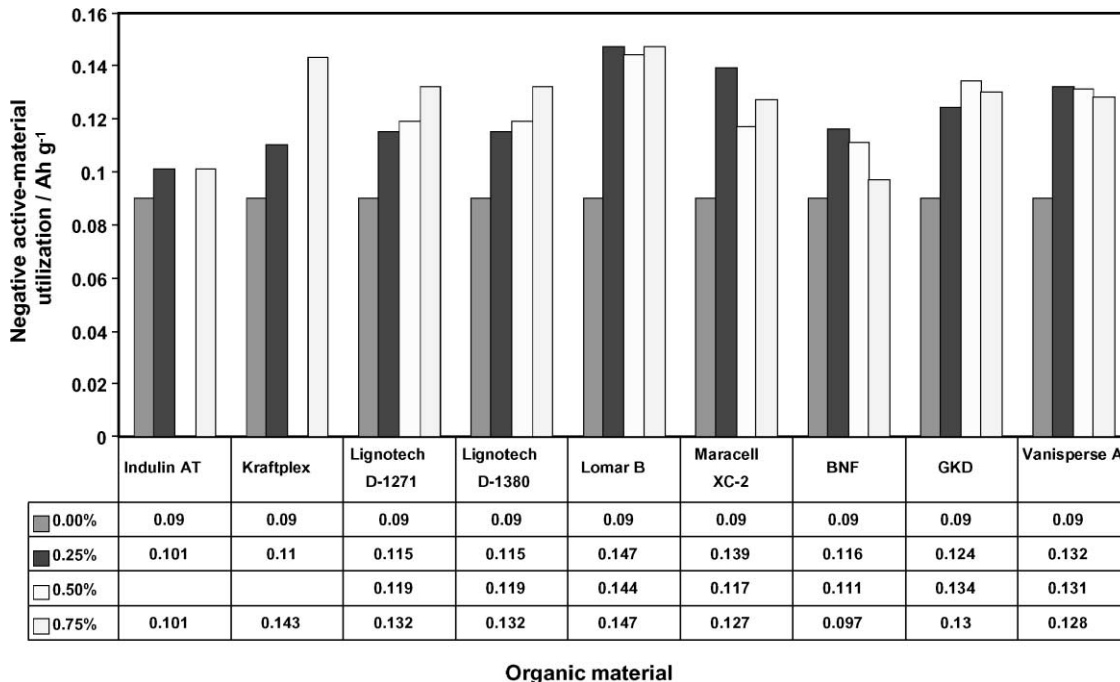|	Indulin AT	Kraftplex	Lignotech D-1271	Lignotech D-1380	Lomar B	Maracell XC-2	BNF	GKD	Vanisperse A
0.00%	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09
0.25%	0.101	0.11	0.115	0.115	0.147	0.139	0.116	0.124	0.132
0.50%			0.119	0.119	0.144	0.117	0.111	0.134	0.131
0.75%	0.101	0.143	0.132	0.132	0.147	0.127	0.097	0.13	0.128

Organic material

Fig. 17. Effect of organic additive on utilization of negative active material.
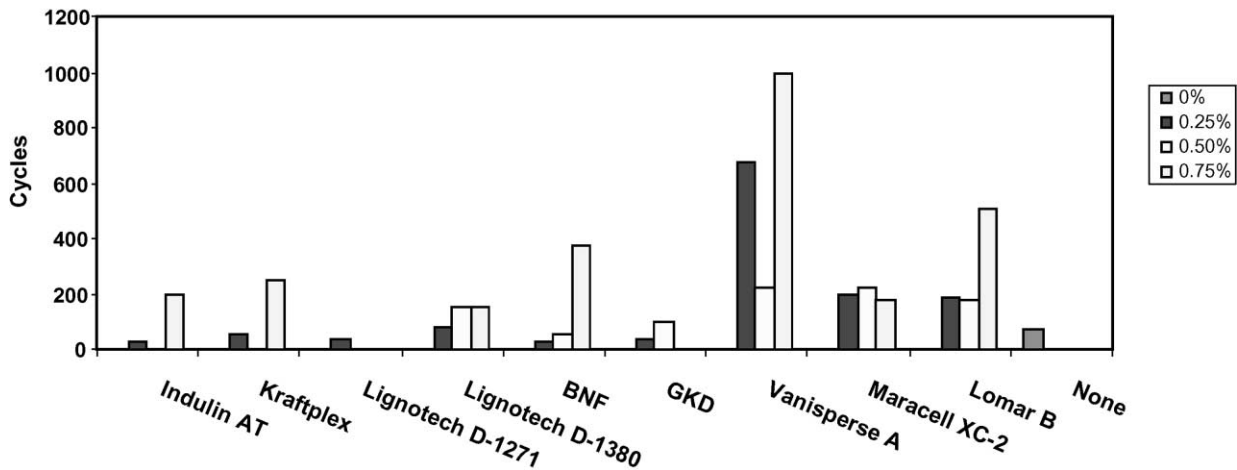
Fig. 18. Effect of organic additive on cycle-life.

dosage rate, Lignotech D-1380 at 0.75 wt.%, Maracell XC-2 at 0.25 wt.%, GKD, and Vanisperse A.

The organic additive also improves cycle-life. Cycle data at the 1 h rate and 100% depth-of-discharge at ambient temperature are presented in Fig. 18. Vanisperse A gives by far the longest cycle-life at 1000 cycles. This is the principal reason why this material is very widely used by the battery industry.

2.2. Question: What function does barium sulfate perform in negative plates? (D.P. BODEN)

Two types of barium sulfate are used in the production of expanders. The most important of these is blanc fixe, which is precipitated from solution and has a median particle size of $1.0 \pm 0.25\ \mu m$. The other form is barytes, which is a milled, naturally occurring, form of barium sulfate. This usually has a median particle size of $3.5 \pm 0.50\ \mu m$. Scanning electron microscope images of blanc fixe and barytes are shown in Fig. 19(a) and (b), respectively.

The principal function of blanc fixe is to prevent passivation of the reacting lead surface with lead sulfate during discharge. Barium sulfate and lead sulfate are isostructural. This close similarity of crystal structure reduces the energy of crystallization and promotes precipitation of lead sulfate on the barium sulfate seed crystals which, thereby, eliminates (or reduces) 'coating' of the lead active mass.

Barium sulfate does not affect the cold-cranking ability of negative plates. Data from cold-cranking tests ($-18\ ^\circ C$) on automotive batteries whose negative plates contain various concentrations of blanc fixe are presented in Fig. 20. There is no change in performance over a barium sulfate range of 0.25–3.0 wt.%.

The cycle-life (SAE J240 test) of automotive batteries is increased as the concentration of barium sulfate is increased and reaches a maximum at between 0.75 and 1.0 wt.% $BaSO_4$, as shown in Fig. 21. Above this, cycle-life decreases gradually with further increase in barium sulfate

concentration. This is the principal reason why expander formulations used at the correct dosage level specify a concentration of barium sulfate in the plate of between 0.75 and 1.0 wt.%.

Barytes is only used in industrial battery expanders. These expanders contain a much lower percentage of lignosulfonate than those used in automotive batteries, as discussed below. Barytes is also added at a higher dosage level. Barytes is used to prevent the concentration of barium sulfate in the plate from exceeding the optimum level of 0.75–1.0 wt.%. Its principal use, therefore, is as an inert extender. There is some speculation that barytes acts as a slow release agent for barium sulfate although this has never been verified experimentally.

2.3. Question: What are the benefits of using pre-blended expanders over adding the separate components directly to the paste mix? (D.P. BODEN)

In North and South America and much of Asia, it has become standard practice to add expander to the paste mix as pre-blended materials in bags that contain the correct amount of additive for the size and formulation of the paste mix. In other areas, particularly Europe, it is still common to add the separate expander components to the paste mix, or to mix the components in the plant before adding them to the mix. The latter practice is costly, increases the risk of mistakes and is unnecessary.

There are numerous advantages to be gained from using a pre-blended package, as follows:

- *Lower cost*: Because of the large volumes of materials consumed, the expander manufacturer purchases these at a lower cost than a typical battery manufacturer. In addition, purchasing expander ready made: (i) eliminates labour; (ii) eliminates equipment; (iii) reduces inventory cost and storage space; (iv) reduces waste disposal; (v) reduces paperwork.
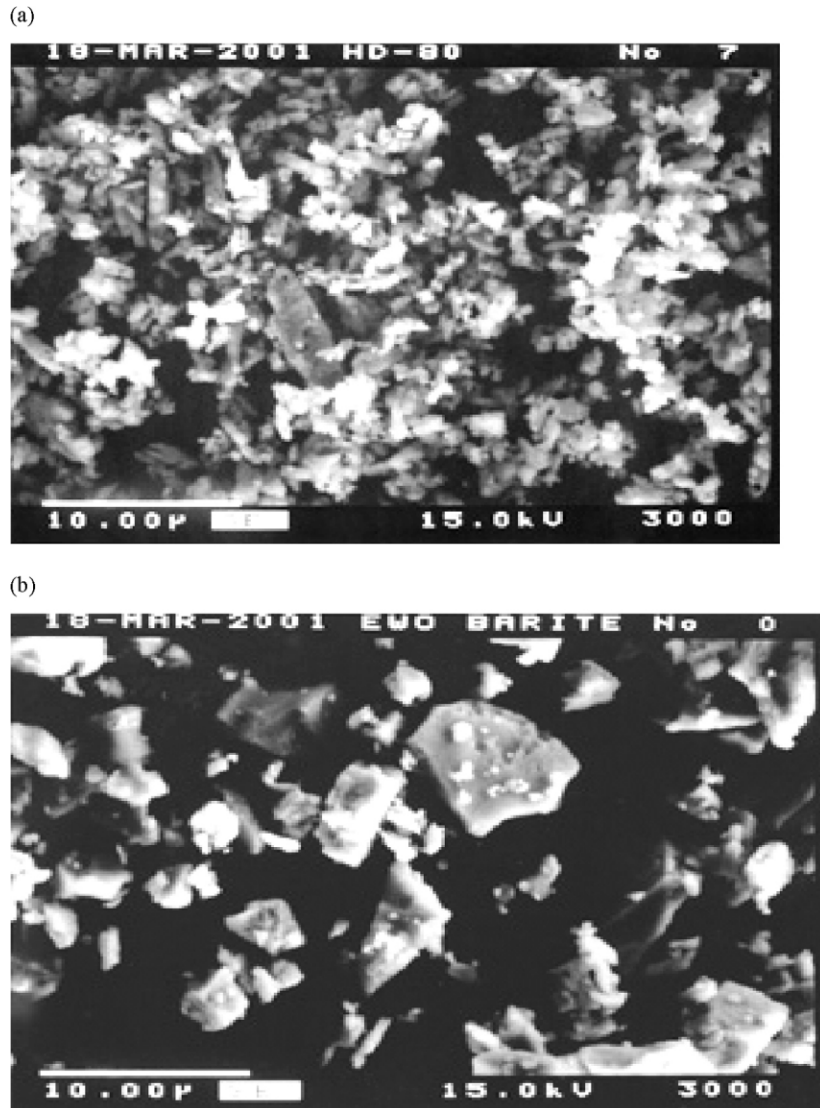
(a)

(b)

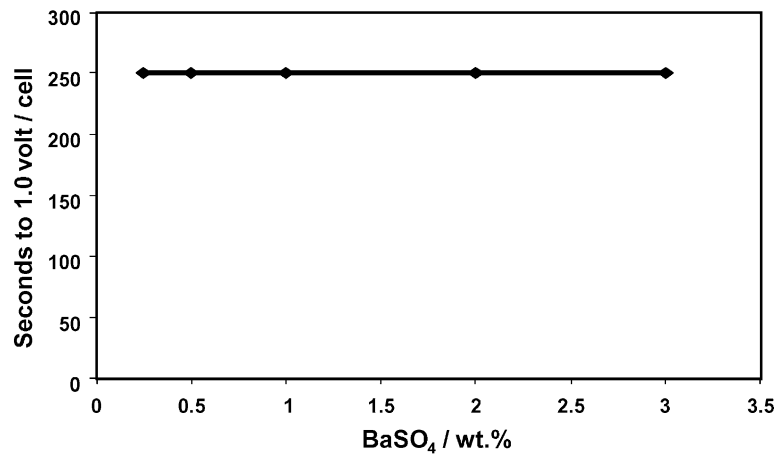Fig. 19. Scanning electron micrographs of : (a) blanc fixe; (b) barytes.

Fig. 20. Effect of barium sulfate on cold-cranking ability of negative plates.
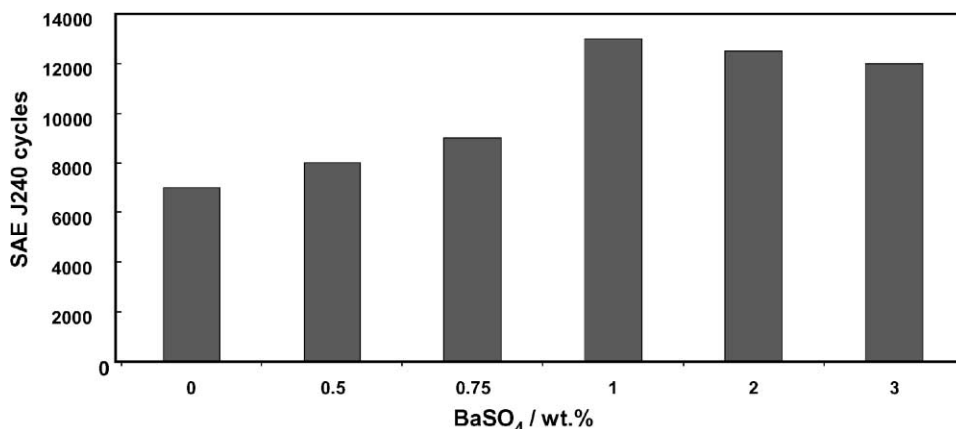
Fig. 21. Effect of barium sulfate on cycle-life of automotive batteries.

- *Improved quality control*: Adding components directly to the paste mix involves risk since it is impossible to determine whether they were weighed or added correctly. Mistakes on the pasting platform will not be detected until they show up as defective batteries. Since 1 kg of expander produces approximately seven batteries, this risk cannot be justified. Pre-blended expanders are tested before they are added to the paste mix. Other quality benefits are: (i) precise control of component weights; (ii) precise control of bag weights; (iii) component analysis; (iv) less ash residue; (v) UV analysis for lignosulfonate; (vi) less impurities.
- *Optimized formulation*: The formulations used by most battery manufacturers have been proven by use over many years.
- *Convenience*: The expander is packaged with the correct weight for the paste mix. All that is needed is to add the contents of the bag to the mix. Flock and other additives can be added to the bag.

2.4. Question: What are the best expander formulations for different types of batteries? (D.P. BODEN)

Typical ranges of expander components used by the battery industry in various applications are shown in Table 1. The expanders used in automotive batteries contain a high percentage of the organic component, approximately 0.3 wt.% in the plate. This gives the negative plate very good high-rate discharge performance at low temperatures. Motive-power batteries, on the other hand, use expanders with a lower organic content and a higher percentage of barium sulfate. This gives a range of 0.06–0.2 wt.% organic and 1.4–1.8 wt.% barium sulfate in the plate. The high level of barium sulfate promotes good deep-discharge capacity and long life.

Telecommunications batteries sometimes use expanders that do not have an organic component. The reason for this is that organics contribute to float voltage variability between cells, which can be a significant problem at low float voltages. Batteries for uninterruptible power supplies (UPSs) contain moderate amounts of the organic additive since they are rated to operate at high discharge rates.

Data for VRLA batteries are taken from expander formulations used by major manufacturers in the USA. There are very wide ranges of components (see Table 1). This indicates that there is still no consensus on the optimum expander for this type of battery. Work carried out at Hammond Expanders has shown that a high level of organic should be used to counter the high compressive forces in these designs and to compress the positive active material. A dosage level of 0.5 wt.% is recommended. The investigations have also shown that the optimum barium sulfate concentration in the plate should be between 0.8 and 1.0 wt.%.

The expanders recommended by Hammond Expanders Division for different classes of batteries are listed in Table 2.

Table 1
Expander formulations and addition rates for various battery applications

Battery application	Component (%)			Addition rate (wt.%)
	Organic	Carbon	$BaSO_4$	
Automotive	25–40	10–20	40–60	0.5–1.0
Motive-power	3–10	5–15	70–90	2.0–2.5
Telecommunications (flooded batteries)	0–10	3–8	80–95	2.0–2.5
UPS	10–20	5–5	70–80	2.0–2.5
Valve-regulated	10–55	0–22	22–85	1.0–2.5

Table 2
Expander selection guide

Application	Recommended types		
Automotive	HE-4640	HE-631	
Motive-power	HE-115	HE-120	HE-1511
Telecommunications	HE-KXLF		
UPS	HE-1160		
Valve-regulated	HE-120	HE-1160	HE-KXLF

These are the most widely used by battery manufacturers at the present time. In summary, expanders have become an essential component of lead-acid batteries. They improve both performance and life for a very low cost. The use of pre-blended materials offers significant advantages in terms of convenience, quality and cost. There is a trend to packaging additional additives (e.g. flock, stearic acid) with the expander in the same bag. This further simplifies the paste-mixing process by reducing the number of operations that have to be carried out by the process operator.

3. Valve-regulated lead-acid batteries

3.1. Question: How does the oxygen cycle affect float and cyclic charging of valve-regulated lead-acid batteries? (R.F. NELSON)

The effects are different for float and cyclic charging but, in both cases, oxygen transport from the positive to the negative plate makes charging of VRLA batteries more difficult than for flooded lead-acid products. In flooded batteries, grid corrosion and water breakdown at the positive with the generation of oxygen gas have no effect upon the negative plate, as virtually all of the oxygen escapes as vented gas. In other words, both plates charge independently of each other and the efficiency of charging depends mostly upon mass balance and the charge efficiencies of the plates.

Due to the partially-saturated nature of the glass-mat separator in VRLA batteries, oxygen transport to the negative takes place—and increasingly so, as the battery ages. This creates problems in charging because the reduction potential for oxygen is well below (i.e. less negative) than the equilibrium potential of the negative electrode. Thus, when oxygen reaches the negative plate in significant amounts, the normal overcharge process of hydrogen evolution is shut off and the plate potential is lowered. In extreme cases, the negative-plate potential can be drawn down to values below open-circuit and the plate becomes partially sulfated. This may be to only a minor degree, but it will be cumulative and will lead to reduced discharge capacities.

Initially, VRLA batteries are 'almost flooded', in that electrolyte saturation levels of the plates and separator are, by design, in the region of ∼95%. This high saturation level makes the creation of gas paths through the glass-mat separator difficult. Thus, in cyclic charging, the effect of the oxygen cycle is minimal because recharge is completed before gas paths are fully formed. As VRLA batteries age, however, the saturation level, particularly in the separator, decreases due to water loss via grid corrosion, gassing and transport through the plastic case and, early on, redistribution of electrolyte from the separator to the plate pores as porosity is developed in the plates. When the saturation level is reduced to, say, ∼85% the creation of gas paths is almost instantaneous or they always exist. At this point, the diffusion rate of oxygen is rapid (for a plate spacing of 1 mm, it will take ∼0.05 s for oxygen to reach the negative plate, at which point it will still have to diffuse through the pore thin film), probably in the order of several seconds in total. With many charging algorithms, the effect is compounded because the lowering of the negative-plate potential causes an increase in the positive potential, which leads to more water breakdown, which generates more oxygen, which further reduces the negative-plate potential and so on, in a vicious cycle.

It is clear from these comments that for proper functioning of the VRLA cell over a long life, the effects of the oxygen cycle must be controlled and moderated. The key appears to be to attenuate the oxygen cycle so that less oxygen reaches the negative plate per unit time. This, of course, will result in higher weight losses during float or overcharge but true 'dry-out' is not normally the life-limiting factor.

3.2. Question: What are some of the effective approaches to float charging of VRLA batteries? (R.F NELSON)

From the standpoint of controlling or moderating the oxygen cycle, there are several approaches to proper float charging of VRLA batteries. These include the following.

- *Time*: Given several months on float, VRLA cells in long strings will equalize somewhat on a standard constant-voltage float charge due to higher-voltage cells losing some water via gassing and thus lowering their voltages (and drawing lower voltages up).
- *Catalysts*: Catalysts allow the negative plate to be adequately polarized and thus, remain fully charged—by taking up much of the oxygen created at the positive and converting it back to water with hydrogen from the negative. This water is then returned to the cell stack.
- *Gelled-electrolyte batteries*: The poorer oxygen-recombination efficiency of gel batteries relative to absorptive glass-mat (AGM) designs (at least initially) has been viewed as a drawback. It may be beneficial on float charge, however, by allowing the negative to polarize more strongly with less oxygen present (for discussion of the meaning of 'polarization' see [9]). Gassing levels are therefore higher and eventually the gel battery will develop sufficient void space such that greater amounts of oxygen transport comparable with those in VRLA batteries will occur.
- *Intermittent charging (IC)*: A high percentage of float current goes into overcharge, with resultant grid corrosion

and gassing which, in turn, give rise to water loss and increases in void volume. IC is a charging technique where full recharge is done periodically (typically 30 min once every 7–10 days), overcharge is minimized, and in each charge process (which is at aggressive, high cyclic, charge voltages) cell equalization occurs in long strings.

- *Wrapped negative plates*: This approach, apparently pioneered by Matsushita, involves enveloping the negative plate with a semi-porous membrane designed to slow down, but not eliminate, oxygen transport to the pores of the plate.
- *Engineered separator pore structures*: Examples of such structures are gel, fine-fibre AGM with high compression, combinations of glass and polymeric membranes and sub-micron non-glass materials such as the Daramic acid-jellifying separator (AJS, a silica-loaded polyethylene material). In different ways, all of these restrict oxygen transport by having very fine pore structures and/or holding electrolyte strongly so that the creation of gas paths is made difficult. Again, polarization (i.e. a shift from the negative-plate equilibrium potential [9]) occurs more strongly due to lower oxygen reduction rates at the negative plate and, thus, the cell remains fully charged. Again, higher weight losses will take place because if oxygen is not being converted back to water at the negative plate it escapes as gas. At the same time, if the negative plate is not depolarized by oxygen from the positive it will be in overcharge and will generate hydrogen gas, which is also vented.

3.3. Question: What is the best way to charge a VRLA battery for maximum deep-cycle lifetime? (R.F. NELSON)

Traditional methods of charging VRLA batteries involve current-limited, constant-voltage charge (so-called 'IU'), or constant-voltage charge with a low-level constant-current finishing step ('IUI' charge) with a relatively high voltage limitation, usually for 1–2 h. Deep-cycle lifetimes of 250–350 are usually achieved; lower cycle numbers are associated with thin-plate VRLA products. The batteries do not fail due to fatal grid corrosion or to excessive dry-out, but rather due to insufficient recharge of the negative plate (which is often heavily sulfated at autopsy). These charging approaches work well when the battery is relatively new and electrolyte saturation levels are high. The plates charge more-or-less independently, much as they would in a flooded lead-acid battery. By the time gas paths have been created and oxygen reaches the negative plate, the recharge process is over and the charge factor is relatively low, i.e. of the order of 1.05–1.10. Most of the overcharge current goes into the normal processes of oxygen and hydrogen gassing and grid corrosion. These processes decrease the separator saturation level.

As the saturation level drops, oxygen transport is facilitated and more of the overcharge current goes into oxygen reduction (so-called 'recombination'). Full recharge can still be accomplished, particularly with the IUI algorithm, but end-of-charge voltages are lowered and the charge factor increases. At some point, the current draw for the oxygen cycle causes the limiting charge factor to be reached before the negative plate is fully charged. Recharge is terminated and the subsequent discharge capacity drops slightly. This process is amplified in following cycles and there is a rapid loss of capacity. If the charge algorithm is not modified the battery is considered as failed.

The problem is not so much the limited amount of over-charge being delivered, but the fact that more and more of it is going into the parasitic oxygen cycle. At some point, the current draw for oxygen reduction exceeds the finishing current level and it is then impossible to complete recharge. Other than instituting design and/or materials changes, the only effective approach is to increase the *rate* of the finishing charge step, not the *amount* of overcharge, i.e. increase the finishing current level. This not only allows full recharge of the negative plate by overpowering the oxygen cycle, but it also keeps the charge factor low by completing recharge rapidly and thus minimizes the amount of charge being drawn by the oxygen cycle.

At some point, the finishing current will be so great that heat build-up becomes the limiting process. For this reason, a technique called 'current-interrupt', or CI, was developed to allow time for heat dissipation between current pulses. This technique uses a rise to a pre-determined end-of-charge voltage for termination. Alternately, if the finishing current is sufficiently high, a fixed charge factor of, say, 1.10 can be used out to several hundred cycles, at which point the charge factor may have to be increased to continue cycling. With this approach, deep-cycle lifetimes of 700–900 were achieved for thin-plate Optima 12 V/50 Ah batteries. Using a variation of this so-called 'partial state-of-recharge', or PSoR, lifetimes of up to 1160 deep cycles were obtained. This approach involves minimizing overcharge even further by performing only partial recharges (97–99% charge return) for nine cycles, followed by a full CI recharge every 10th cycle. Even out to 1160 cycles, lifetime was not limited by grid corrosion or by dry-out but, rather, by heat build-up limiting the finishing current magnitude to a level that could not overcome the oxygen cycle efficiency. Longer lifetimes should be possible with thicker-plate batteries. This work to develop the CI and PSoR/CI algorithms was sponsored by the ALABC in Project B-007.

3.4. Question: Is there a relatively simple diagnostic test for VRLA batteries to determine whether batteries are serviceable, given that measurement of acid relative density and high-rate discharge are sufficient for flooded automotive batteries? (R.F. NELSON)

Clearly, acid density cannot be measured in a 'sealed' product with no free electrolyte. High-rate discharge is useful to determine whether internal connections are intact

and grid corrosion has not become excessive, but in many VRLA applications the battery cannot easily be taken off-line to do this. Over the last 10 years or so, several passive tests have been developed for on-line monitoring of VRLA standby installations but these are not completely satisfactory, largely due to the fact that they do not 'stress' the battery and test the diffusion conditions and active material integrity that exist. In addition, techniques such as conductance testing only correctly identify weak or failed cells or batteries when they are near or below the 80% failure point. Having said this, taking these measurements reproducibly and several times a year (and recording the data!) will provide an historical data base that can be used, with some certainty, to identify modules as they weaken.

Voltage measurements can give some information about the state-of-health of a VRLA module. Open-circuit voltages (OCVs) can identify modules with high weight losses (electrolyte is concentrated, higher-than-normal OCV) and those that experience sulfation of one or both plates (electrolyte is diluted, lower-than-normal OCV). The occurrence of both of these conditions simultaneously can, however, give normal OCV readings, as they counteract one another.

End-of-charge voltages in constant-current operation can indicate a lowering of the electrolyte saturation levels; as saturation levels drop so do end-of-charge voltages. This can also be seen by recording individual cell or module voltages in strings on float; those with relatively high readings will have high saturation levels and those with low readings will be relatively low in saturation. This must be done several times to establish a clear trend, as VRLA cells tend to 'wander' in float voltages over time. Higher-than-normal float currents will also indicate that a battery string is approaching a dangerous condition of generally low saturation levels (and a corresponding tendency to go into thermal runaway).

In cyclic charging using current-limited constant-voltage (CV or IU) algorithms, the current flowing at the end of the charging 'tail' just before termination will also rise gradually as the saturation level falls. While this may be gradual for some number of cycles, it can begin to rise rapidly at some point and result in thermal runaway within the next few cycles. In IUI charging, the charge voltage at the end of the constant-current finishing step can also be used to signal a drop in electrolyte saturation to dangerous levels; as this happens, the voltage during the low-level, constant-current finish will gradually drop. It should be noted that in all of these voltage-measurement techniques data must be collected, analyzed and compared with previous readings and expected behaviour in order to be able to detect meaningful trends. This can easily be done with the use of modern battery-management systems that can collect, store and analyze large amounts of data.

A useful method to observe the general state-of-health in terms of plate pore structures is to record high-rate (10 C or more) pulse-discharge curves (5 s) and, more important, the voltage 'rebound' after the termination of the discharge. Two typical types of curves will be encountered. For a 'strong' battery, the initial drop in voltage upon discharge is followed by a rising voltage up to the 5 s termination point. Following the discharge kick-out, there is a sharp rise in OCV to a value near the voltage before the beginning of discharge. The rising voltage at the beginning of discharge and the sharp voltage 'rebound' are both indicative of an open pore structure and efficient electrolyte supply from the separator reservoir into the plates.

The second case is for a 'weak' battery, i.e. one with a poorly-developed pore structure and/or inefficient electrolyte supply. On the 5 s discharge, the voltage may rise initially and then begin to fall toward the 5 s point or, for a very weak battery, it may fall continuously after the sharp drop at the initiation of discharge. Following termination, the voltage 'rebound' is slow and sluggish. All of this represents poor electrolyte-diffusion conditions due to improper plate pore structures and/or inefficient electrolyte transfer from the separator to one or both of the plates. The latter may be due to very low plate-stack compression which can actually result in a small gap between plates and separator that does not allow electrolyte transfer.

This type of test can be used as an end-of-line measurement following formation or it can be done during service. In the latter case, battery deterioration can be detected by repetitive measurements that are stored and electronically compared with current performance. As it is a short-term test, the battery is removed from service for only a few seconds and thus is not as inconvenient as a full discharge test.

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