

## Lead/acid battery technology

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### Abstract

Following the schedule of previous Asian Battery Conferences, the Proceedings closed with an expert panel of battery scientists and technologists who answered questions put by the assembled delegates. The subjects under consideration were as follows. *Grid alloys*: grain structure of lead–calcium and lead–calcium–tin alloys; dross problems; control of calcium content; cast-on-strap; terminal-post attack; porosity/acid-wicking problems; effect of silver; lead–cadmium alloys. *Lea.y oxide*:  $\alpha$ -PbO $\beta$ -PbO ratio; influence on plate-processing and battery performance. *Paste-mixing and curing*: influence of amorphous material. *Plate formation*: black/powdery plates; effect of acid concentration; charge level. *Valve-regulated batteries*: mass balances; grid thickness; shelf life. *Battery charging*: overcharge effects; fast charging; temperature effects; string configurations; sodium sulfate additive.

**Keywords:** Lead/acid batteries; Grid alloys; Lead oxide; Paste mixing; Curing; Formation; Valve-regulated batteries; Charging

### 1. Grid alloys

*1.1. Question: What methods produce fine-grained lead–calcium and lead–calcium–tin alloy grids?*

R.D. PRENGAMAN

#### *1.1.1. Increase the calcium content*

The additional calcium (up to ~0.10 wt.%) increases the number of grain boundaries and inter-dendritic areas where the cellular precipitation reaction takes place. Above 0.10 wt.% Ca, precipitation of primary Pb<sub>2</sub>Ca from the melt decreases the initial as-cast grain size. These primary particles serve as sites for the further initiation of fine grains. Calcium contents above 0.08 wt.% will cause increased corrosion and reduction of the mechanical properties of the final aged material. The reduced mechanical properties, along with the finer grain size, can result in increased grid growth during battery service.

#### *1.1.2. Add aluminium*

The aluminium acts as a deoxidizer and prevents calcium loss. It precipitates from solution prior to the solidification of the lead alloy and thus serves as sites for the nucleation of

fine grains. The finer grains are obtained at any calcium or tin content. Higher aluminium contents give finer-grain structures. Finer grains produced by aluminium additions, however, do not seem to have the same adverse effects as finer grains produced by higher calcium contents.

#### *1.1.3. Decrease the mould temperature and solidify rapidly*

Colder moulds give more areas to initiate nucleation. The rapid solidification decreases the inter-dendritic spacing and provides more areas for initiation of the precipitation reaction.

#### *1.1.4. Deform the material by rolling*

Rolling lead–calcium alloys causes a break-up of the initial, cast grain-structure and re-orientates the grains in the rolling direction. Deformation by a reduction ratio of 4:1 is required to complete the break-up. Higher reduction ratios result in finer, more elongated, grain structures. The rolling increases significantly the mechanical properties of the alloys, greatly increases the creep resistance of the material, and reduces the corrosion and growth rates. In binary or low-tin alloys, however, the increase is lost to recrystallization. The effects are most pronounced in low-calcium (<0.07 wt.% Ca)–high-tin (>0.7 wt.% Sn) alloys.

*1.2. Question: What methods produce coarse-grained lead–calcium and lead–calcium–tin alloys?*

R.D. PRENGAMAN

*1.2.1. Decrease the calcium content*

In lead–calcium binary alloys, the grain size is inversely proportional to the calcium content. Large grains are obtained at calcium contents below 0.04 wt.% Ca. These alloys have been used for years to provide grids with low corrosion and low growth rate for wet, standby-power batteries. The very large grain size provides very few grain boundaries for corrosion and, consequently, growth is limited. Penetration of grain boundaries may be a problem with thin grids.

*1.2.2. Keep the Sn:Ca ratio above 9:1 in Pb–Ca–Sn alloys*

In lead–calcium–tin alloys, fine grains are produced by the movement of grain boundaries in the cellular precipitation reaction. This reaction occurs at low Sn:Ca ratios. At ratios of 9:1, or above, the precipitation reaction changes to a continuous reaction that ends in  $\text{Sn}_3\text{Ca}$ , and no change in grain size occurs. The original cast grain size is the final grain size. Higher tin contents above an Sn:Ca ratio of 9:1 only increase the grain size by a small amount. Calcium contents of 0.10 wt.%, or above, where primary  $\text{Pb}_3\text{Ca}$  precipitation occurs, can reduce the grain size. Thus, the calcium content should be restricted to 0.08 wt.% Ca, or below. The higher tin content and change in precipitate chemistry and morphology cause a dramatic increase in mechanical properties, particularly a decrease in creep rate (decreased growth). Higher tin contents also decrease the corrosion rate of the grids.

*1.2.3. Reduce the aluminium content, reduce dross and inclusions*

The aluminium added to deoxidize the alloy and prevent calcium loss must be kept at a low level to reduce the nucleation of fine grains. Dross or impurity particles in the lead, as well as trapped air, can also serve as nucleation sites and can produce finer grains. Cleaner alloys and casting produce higher mechanical properties and, thereby, less growth. The absence of holes or dross at grain boundaries increases corrosion resistance.

*1.2.4. Use a high metal temperature, high mould temperature, and smoked mould*

Slow solidification in a mould with few areas of grain nucleation results in enormous cast grains in low-calcium or high-tin alloys. It is possible to produce grains that extend over several grid wires and that may be as large as 3–4 cm in any direction. Grains of such size are totally resistant to

growth and are highly resistant to corrosion, except at the grain boundaries.

*1.3. Question: Losses due to dross may increase substantially when moving production from high- to low-antimony lead (grain refiners 1.5 wt.%) and, finally, to Pb–Ca alloys. Why does this occur? What system/procedures should be adopted to minimize dross make? What is a reasonable objective for dross loss (%) with both low-antimony and calcium alloys? Are there any advantages/disadvantages in using fluxes, sawdust, coal, etc., on the lead surface?*

E.M. VALERIOTE

Additions of grain refiners, such as selenium and sulfur, do increase the oxidation rate of liquid lead and, thereby, increase dross formation. Thus, efforts to minimize oxygen access are required.

Another cause of excessive dross formation for low-antimony–lead alloys is the very low solubility limits in molten lead of these grain refiners. Selenium and sulfur form high melting-point inter-metallics of  $\text{PbSe}$  ( $T_m = 1076^\circ\text{C}$ ) and  $\text{PbS}$  ( $T_m = 1103^\circ\text{C}$ ) which have densities that are lower than molten lead. Excess of grain refiners in the form of inter-metallic particles in the melt will float to the melt surface. These particles tie-up liquid lead and result in excessive dross formation.

For Pb–Ca alloys, the situation is different. Calcium is easily oxidized because of its high affinity for oxygen. A small amount of  $\text{CaO}$  skin could tie up a large amount of lead and form excessive dross. Oxygen is capable of scavenging all the calcium in a lead alloy. Whenever the melt is stirred, calcium will be exposed to oxygen and, thus, will be oxidized.

Procedures to minimize dross make are as follows:

(i) Measures to reduce oxidation of the melt, such as: use protective gas shroud or reducing atmosphere; disturb the melt surface as little as possible; minimize open lead-line.

(ii) Specific measures for different alloys:

- Low-antimony lead:
  1. avoid using an excessive amount of grain refiners
  2. minimize temperature variation of the melt to avoid precipitation of inter-metallics
  3. use Cominco battery technology: the Multi-Alloy Caster™ does not require grain refiners to cast any lead alloy
- Lead–calcium:
  1. add a small amount (0.03 wt.%) of aluminium
  2. cast immediately after melt preparation; long waiting encourages the oxidation of calcium and dross formation
  3. avoid melt agitation

The advantage of using flux, sawdust and coal, etc., on the lead melt surface is to provide a reducing atmosphere and, thereby, to reduce oxidation.

**1.4. Question:** Aluminium is now a popular additive to calcium alloys for casting positive and negative grids. Other than helping to control calcium content during use, are there any benefits, e.g., grain refinement, in the finished product? Conversely, are there any disadvantages, such as increased grid corrosion and integrity problems at the grid-lug/strap interfaces?

E.M. VALERIOTE

Aluminium is usually added to lead–calcium alloy baths to protect the alloy from oxidation during casting. This is also beneficial in helping to maintain desired calcium levels.

Users of aluminium have reported enhanced fluidity and early age-hardening characteristics, as well as reduced drossing. Batteries with Pb–Ca–Sn–Al alloys behave much like conventional Pb–Ca alloys. Small aluminium additions do not change significantly the physical or mechanical properties of the alloys, and the handleability should be as good, or better, than that of conventional Pb–Ca alloys. Corrosion rates of aluminium-bearing Pb–Ca alloys are similar to those of the corresponding non-aluminium alloys. On the other hand, corrosion characteristics can be more uniform and less variable, because it is easier to maintain the preferred calcium levels when oxidation losses are minimized.

In principle, aluminium additions should refine the grain structure. This is because aluminium has a very low solubility in molten lead so that solute partition during solidification will result in aluminium enrichment ahead of the solidification front. This could reduce the growth rate of the existing solid grains and allow new solid grains to form ahead of the interface in the melt. Such an effect is not always obvious. There are some anecdotes, but little evidence in the literature, of grain-refining effects of aluminium. Researchers at the University of Nancy [1], however, have observed grain refinement for 0.01–0.08 wt.% Al. Prengaman [2] states that aluminium decreases the amount of suspended calcium oxides and, thus, reduces casting defects. Prengaman [2] describes aluminium grain-refining effects and shows comparative structures of Pb–Ca alloys with and without tin. Finally, he asserts that aluminium prevents severe penetrating corrosion by refining the structure of Pb–Ca alloys with high tin content. For example, Pb–0.06wt.%Ca–0.6wt.%Sn, can have large grains that are susceptible to penetrating corrosion in the absence of aluminium. Prengaman [3] has further reported that the bonding between Pb–Ca lugs and Pb–Sb straps is improved by the addition of aluminium to the Pb–Ca alloy.

**1.5. Question:** What is the recommended COS alloy for joining: (i) low-antimony grids in flooded cells; (ii) calcium grids in flooded cells, or (iii) calcium grids in valve-regulated (VRLA) cells?

R.D. PRENGAMAN

For both low-antimony and calcium grids in flooded-electrolyte lead/acid cells, the recommended alloy is 3 to 4 wt.%

Sb with adequate arsenic and tin to give an exceptionally strong strap. This alloy has sufficient antimony to produce enough low-melting eutectic to form a good bond with lugs of either low-antimony or lead–calcium. The alloy should also contain a nucleant (such as copper or selenium) to prevent cracking of the strap during through-the-partition welding. The higher antimony content gives better welding and exceptional rigidity to the inter-cell joints. The arsenic level should be about 0.10 to 0.20 wt.%, while the tin should be in the same range, but can be as high as 0.4 wt.%. In these alloys, the tin in the strap or grid lug will not influence the corrosion of the joint.

For calcium grids in valve-regulated lead/acid (VRLA) cells, the recommended alloy is Pb–2wt.%Sn. The alloy should contain very low impurity levels of antimony, arsenic, nickel, or selenium. These elements are gas formers on the negative and can cause negative-strap and grid corrosion in AGM versions of VRLA batteries if they reach unacceptable levels of 0.005 wt.% or more. To provide an adequate bond when using 2 wt.% Sn as a COS alloy, many manufacturers pre-coat the grid lugs with a low melting-point, lead–tin solder, e.g., 50wt.%Pb–50wt.%Sn, prior to the COS operation. A thin coating on the grid lug will join with the strap alloy to produce a good bond without excessive heating of the grid lug.

**1.6. Question:** Is there an optimum alloy for use with lead inserts to prevent sulfation and blackening of terminal posts during service?

R.D. PRENGAMAN

Blackening and sulfation of terminal posts (positives) are caused by leaking of acid, or access of acid to the positive terminal. Virtually any lead–antimony alloy will blacken anodically when exposed to sulfuric acid and a charging current; the surface is covered with PbO<sub>2</sub>. Lead–antimony and lead–calcium–tin alloys with high tin contents will not blacken under normal conditions when not exposed to acid. This is because the major oxide formed on alloys containing > 0.5 wt.% Sn is tin dioxide, and this material is transparent.

**1.7. Question:** Which alloy should be used to reduce porosity/acid-wicking in the following production methods: (i) gravity casting; (ii) pressure diecasting, and (iii) cold forging?

R.D. PRENGAMAN

Gravity-cast parts of good quality normally require a lead–antimony alloy with sufficient nucleants to produce a sound battery part. The parts should be produced from a lead–antimony alloy with > 3 wt.% Sb. The mould should be designed for a large riser and sprue system, or should be vented through its sides to remove trapped air that might cause porosity. Low-antimony alloys (1–2 wt.% Sb) should be avoided because the casting may have inadequate mechanical properties to be

handled properly and these alloys have maximum freezing ranges that can cause gas entrapment during solidification.

Pressure die-casting should be produced from lead–antimony alloys that contain only a few nucleants. The lead enters the mould at high pressure in the form of droplets or streams with high turbulence and, hence, virtually no nucleants are required since many small lead crystals are formed very rapidly. Excessive amounts of nucleants may trap air in the mould and, thereby, promote porosity.

In order to eliminate porosity in pressure die-cast operations, the mould should be filled with oxygen prior to injecting the metal. In this case, the lead alloy will react with the oxygen to produce PbO, SnO<sub>2</sub> or CaO (when Pb–Ca–Sn alloys are used) as finely-divided particles in the metal. Since there is no nitrogen in the mould, once the oxygen is consumed, the part should be virtually pore-free. In this process, either Pb–Sb or Pb–Ca–Sn alloys may be used. Without oxygen, die-casting of Pb–Ca–Sr alloys is difficult due to the entrapment of air bubbles within CaO films that form around the outside of the bubbles. This can lead to porous battery parts. If Pb–Ca–Sn alloys are used, care must be taken to burn adequately the post to the Pb–Ca bushing.

Since VRLA batteries operate under pressure during oxygen recombination, it is more important to prevent loss of gases through porous top terminals than is the case in conventional (flooded-electrolyte) batteries. Cold-forged parts may provide this requirement.

Lead–antimony alloys are extremely strong and creep-resistant in the cast form, but become very weak when they are deformed, such as in cold forging. The working destroys the cast; the reinforcing particles of the eutectic are stiffened and spread throughout the part. The cast part is hard and does not deform well. A cast 3 wt.% Sb alloy with a yield strength of 55.2 MPa is reduced to 16.3 MPa in the wrought form, while the creep resistance decreases by more than three orders of magnitude.

Lead–calcium–(1.2–1.8 wt.% Sn) alloys, on the other hand, are very soft initially but become significantly stronger and more creep-resistant when the parts are worked significantly. A deformation of about 4:1 will yield, immediately after working, a fine-grained battery part of exceptional corrosion resistance and strength. Moreover, the part will become stronger with age.

*1.8. Question: It has been suggested that if 100 ppm of silver is added to a lead–calcium–tin alloy, there may arise a problem with the oxygen overpotential. How serious is this problem?*

K. PETERS

Silver does effect the oxygen overpotential, but this is not expected to be serious at a level of 100 ppm.

J.E. MANDERS

Many minor elements at low levels do exert effects on battery gassing rates. Clearly, there is much work to be done on how to measure these effects to determine the permissible

levels for minor elements. This is especially applicable to the use of soft lead.

R.D. PRENGAMAN

The American Society for Testing and Materials (ASTM) has recently completed a new standard specification, *ASTM B 29-92*, for refined lead to be used in the manufacture of lead/acid batteries. This specification takes into account some of the elements that are not normally considered, such as tellurium and nickel, and limits antimony and arsenic to the same reasonably low level, (i.e. 0.0005 wt.%) so that the lead is suitable for valve-regulated lead/acid batteries.

*1.9. Question: Are lead–cadmium–tin alloys better than lead–calcium–tin counterparts for positive grids in valve-regulated lead/acid batteries?*

R.D. PRENGAMAN

My company will not make lead–cadmium–tin alloy. In my opinion, it is a nasty alloy and should not be produced for the industry. Thus, it is not recommended.

## 2. Leady oxide

*2.1. Question: What is the mechanism for the development of  $\alpha$ -PbO and  $\beta$ -PbO in Barton-pot and ball-mill leady oxides? What are the levels of  $\alpha$ -PbO and  $\beta$ -PbO in the leady oxides?*

L.T. LAM

During oxide production,  $\alpha$ -PbO and  $\beta$ -PbO are formed via the following reactions:



The lead particles are oxidized to  $\alpha$ -PbO by the inlet air and some of the  $\alpha$ -PbO is converted to  $\beta$ -PbO. Reaction (2) only occurs when the temperature of the process is high because the transition temperature of  $\alpha$ -PbO to  $\beta$ -PbO is around 480 °C.

In the Barton-pot process for making leady oxide, molten lead is oxidized to  $\alpha$ -PbO by a stream of air at a temperature between 330 and 400 °C. Further heat is generated during the oxidation so that the surface temperature of some of the lead particles can reach over 480 °C. This brings about the conversion of  $\alpha$ -PbO to  $\beta$ -PbO. Thus, the resulting oxide will contain a lower amount of free lead, and a higher level of  $\beta$ -PbO, when the pot is operated at the upper limit of the temperature range. In general, a typical Barton-pot oxide contains 15–27 wt.% Pb, 47–80 wt.%  $\alpha$ -PbO and 5–26 wt.%  $\beta$ -PbO.

Ball mills are run at much lower temperatures than Barton pots, namely, 160 to 190 °C. In this temperature range, generally, zero or only trace amounts of  $\beta$ -PbO are formed. Accordingly, a typical ball-mill oxide contains 15–35 wt.% Pb and 65–85 wt.%  $\alpha$ -PbO.

2.2. *Question: What is the effect of  $\beta$ -PbO on the subsequent curing and formation processes? Moreover, does  $\beta$ -PbO affect the capacity and cycle life of the battery?*

L.T. LAM

Two curing processes are commonly employed in battery manufacturing, namely, low-temperature and high-temperature curing. Both processes are conducted with high relative humidity (RH).

Under low-temperature/high RH conditions, the cured plate contains mainly unreacted  $\alpha$ -PbO and  $\beta$ -PbO, tribasic lead sulfate ( $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O} = 3\text{BS}$ ), and a minor amount of unreacted lead (free-lead). The level of  $\beta$ -PbO in the starting oxide has no major effect on either the phase composition or the morphology of the 3BS-cured material.

Under high-temperature/high RH curing conditions, the cured plate contains mainly  $\alpha$ -PbO and tetrabasic lead sulfate ( $4\text{PbO} \cdot \text{PbSO}_4 = 4\text{BS}$ ), together with a small amount of free lead. The development of 4BS during high-temperature curing can be defined in terms of four main features, namely, induction time, completion time, growth rate and maximum yield (Fig. 1). It is well known that the first three factors are influenced strongly by temperature, humidity and plate thickness, while the maximum yield is limited by the quantity of sulfuric acid solution that is used in the paste formulation. Research in the CSIRO laboratories [4,5] has identified and quantified a further determinant of 4BS production, namely, the level  $\beta$ -PbO in the starting oxide. It has been found that the induction and completion times are decreased, and the 4BS growth rate is increased, when the leady oxide contains up to a certain amount of  $\beta$ -PbO. By contrast, the yield of 4BS is unaffected. In other words, the development of 4BS can be accelerated, but its yield is unaffected, by the presence of  $\beta$ -PbO in the precursor leady oxide.

There are no published data that show the effect, if any, of  $\beta$ -PbO on the plate formation, the initial capacity or the cycle life of batteries. The efficiency of plate formation is dependent upon the type of cured material (i.e., 3BS or 4BS), the

specific gravity of the forming acid, and the temperature and applied current profiles. The initial capacity and cycle life of batteries are also influenced by: nature of the cured state; composition of the formed plates; acid concentration; temperature, and discharge rate. Battery cycle life is further affected by the type, composition and morphology of the grid alloys, the battery design (e.g., compression), as well as by the depth-of-discharge. For batteries produced via the high-temperature/high RH curing route, it has been shown that 4BS-cured plates prepared from the optimum  $\beta$ -PbO content give longer service lives than plates in batteries produced via the conventional curing procedure.

### 3. Paste-mixing and curing

3.1. *Question: Paste-mixing and curing procedures attempt to produce desired quantities of tribasic and tetrabasic lead sulfate. Very little mention is made of the importance, or otherwise, of the amorphous content of the unformed active-material on the structure and performance of the finished plate. Does the amorphous content play an important role in the performance of the active-material?*

E.M. VALERIOTE

There is always some amorphous material in the cured and unformed active-material. It could be as high as 20 wt.%. If an X-ray diffraction phase-analysis is performed on a cured active-material, it would be found that some 10–20 wt.% of the material is unaccounted for in the recorded diffraction pattern. If tribasic lead sulfate and lead monoxide are mixed together in the same ratio as in a cured plate, the plate would be mechanically unstable, difficult to form, and have poor cycle life. If sulfuric acid and lead monoxide are blended together in the proportions calculated to produce the correct amount of tribasic lead sulfate and lead monoxide, the plate would again have poor mechanical strength and would have to be handled with care. Furthermore, the plate would be difficult to form. To ease the formation, red lead would have to be added to the mixture. One reason for this poor performance is that there is not much amorphous phase produced by these synthetic processes. The reactions of sulfuric acid and lead monoxide produce good crystalline lead sulfate and basic lead sulfates, but very little amorphous material. Leady oxide contains 20–30 wt.% metallic lead as small particles, and when this oxide is used, these small metallic particles start to oxidize at a high rate in the mixing process. It is this oxidation of metallic lead that produces most of the amorphous material in the paste. The oxidation process continues during the 'hydroset' (curing) process, in which the plates are also being dried. Thus, large crystals of tribasic or tetrabasic lead sulfate are formed in a drying plate (Fig. 2). These form an interlocking crystal network and the amorphous material acts as a glue in holding the crystals together. At the end of the curing process, the plates achieve some mechanical strength, and can be handled without losing pellets. The situation is very

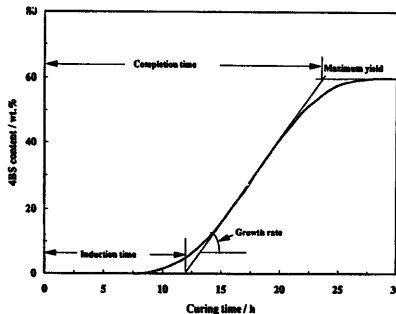


Fig. 1. Parametric description of the development of 4BS during plate curing at high temperature and high relative humidity.

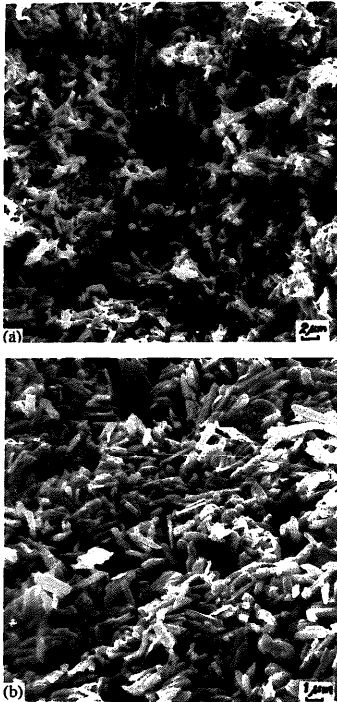


Fig. 2. Cured plates (40 °C, 72 h) prepared from Barton-pot leady oxide.

similar to the mixing, setting and drying of cement concrete. A plate with the sulfate crystals and oxide particles tightly glued together by the amorphous material is much easier to form and enjoys a longer service life.

#### 4. Plate formation

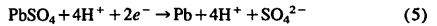
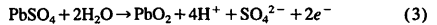
*4.1. Question: When applying 400 to 500% formation, the surface of positive plates becomes black and powdery. Why? If a low concentration of acid is used, the formation becomes faster and the formed plates become better. In this case, are there any possible problems?*

L.T. LAM

During formation, battery manufacturers commonly apply a charge of 280 to 500% of the  $C_{20}$  capacity of the battery. It is important to note here that the charge depends upon the type of cured plates, concentration of acid, temperature, and current profile, (i.e., the current levels and rest periods during

the different stages of formation). For 3BS-cured plates, the charge applied is usually in the range 280 to 350%. By contrast, 4BS-cured plates require a greater input of charge, namely, 400 to 500%, because this material is more difficult to form. If a 400–500% formation is used for 3BS-cured material then, obviously, the plates will be over-formed.

During formation, the conversion of  $PbSO_4$  to  $PbO_2$  at the positive, and to  $Pb$  at the negative, occurs together with the evolution of oxygen and hydrogen via the following reactions:



Gas evolution becomes more severe when the formation is nearly complete. If the process is continued, the positive material will start to disintegrate due to the vigorous gassing action. Under these conditions, the surface of the formed plates turns to a dark colour and becomes powdery in texture.

From the above reactions, it can be seen that the conversion of  $PbSO_4$  to  $PbO_2$  at the positive plates requires water. In another words, the positive plates will be formed faster in dilute acid solution. By contrast, the conversion of  $PbSO_4$  to  $Pb$  at the negative plates requires acid. Thus, the negative plates will be formed faster in concentrated acid solution. Although lowering the specific gravity of acid will promote the oxidation of positive plates, if the acid concentration is too low (<1.01 sp. gr.), the negative plates will not be formed. Therefore, the optimum specific gravity of formation acid is between 1.03 and 1.06. (Note, this is the concentration of acid after soaking and before the application of current.) Consequently, the concentration of acid before soaking should be higher than the upper limit (1.06 sp. gr.) of the recommended range.

Positive plates formed in dilute sulfuric acid will contain high levels of  $\alpha$ - $PbO_2$  because this material only develops in neutral or alkaline solution. It is well known that the capacity of pure  $\alpha$ - $PbO_2$  is lower than that of pure  $\beta$ - $PbO_2$  [6–8]. Thus, the capacity of formed plates prepared in dilute sulfuric acid will be low initially, but will increase with cycling as the  $\alpha$ - $PbO_2$  converts to  $\beta$ - $PbO_2$ .

*4.2. Question: Dr Lam has stated that for cured plates with tribasic lead sulfate, the formation usually requires a charge of about 280 to 350% of the  $C_{20}$  capacity, but for plates with tetrabasic lead sulfate 400 to 500%  $C_{20}$  is required. Are these amounts of charge for positive plates, negative plates, or both?*

L.T. LAM

If the positives and negatives are formed in the same sulfuric acid solution (1.03 to 1.06 sp. gr. after plate soaking), the same amount of charge is applied to both plate polarities,

namely, 280–350%  $C_{20}$  for 3BS-cured positives and 400–500%  $C_{20}$  for 4BS-cured positives. If, however, the positives and negatives are to be formed separately by using dummy plates of the appropriate opposite polarity, then the overcharge factor for 3BS-cured and 4BS-cured positives will be 280–350 and 400–500%  $C_{20}$ , respectively, but only 280–350%  $C_{20}$  for the negatives. This is because negative plates are always prepared via the 3BS-curing route. Nevertheless, a higher concentration of sulfuric acid solution (1.15–1.20 sp. gr. after plate soaking) is recommended for negative-plate formation because the reduction process requires acid.

## 5. Valve-regulated batteries

### 5.1. Question: What are the preferred mass balances in VRLA batteries?

K. PETERS

The preferred ratios of positive and negative active-materials, and of electrolyte, depend essentially upon the nature of the application. For example, deep-cycling batteries are invariably designed with a good reserve of positive active-material, and most manufacturers design with positive:negative ratios that vary between 1.3 to 1.75. The value of the ratio depends on the approach that is taken by the design engineer. The requirement for excess positive material is due to the relatively poor charge acceptance of the positive plate which results in progressive capacity decrease, particularly in cases where overcharge is minimized.

There are exceptions to the above, such as in designs that contain negative-plate depolarizers, either as a component in the grid alloy or as a contaminant. In such situations, the charge efficiency of the negative plate will decrease quickly, unless the depolarizers are removed, and some allowances in the weight and composition of the negative plate may be necessary to take account of the changes. This is particularly relevant in stationary applications where batteries are float-charged for 10 or 20 years with the likelihood of very few cycles. It is necessary to meet standards of very high purity in order to prevent these effects and, possibly, it may be necessary to increase the negative-plate weight.

With VRLA batteries, however, there is a general misconception with respect to the need for excess negative weights and surface area to achieve good gas recombination. The early patents relating to oxygen recombination specified this as a requirement. Since then, several workers have pointed out that the limiting reaction is the rate of transfer of oxygen from the positive to negative, and that this is controlled essentially by the separator/acid ratio. As a result, in most applications where this aspect of the design is properly controlled, there is no need to have excess negative active-material to achieve good gas recombination.

### 5.2. Question: What grid thickness should be used for positive plates in VRLA batteries in order to obtain a minimum of 1300 cycles at 80% depth-of-discharge at 30 °C?

K. PETERS

In general, VRLA batteries will fail much earlier than 1300 cycles for reasons other than grid corrosion. Therefore, even if a 6 mm or an 8 mm thick grid is used, the battery will probably fail due to a variety of non-corrosion reasons. Only when some of the major failure modes (such as lack of compression, grid growth or stratification problems) have been resolved, will grid corrosion become the limiting factor of battery performance. Under such conditions, the battery can be designed for life.

For a life of 1300 cycles (which is a good endurance based on current alloy technology and the use of chargers that are not too sophisticated), it is advisable to use a grid thickness of not less than 3.5 to 4 mm. It is to be hoped, of course — especially with the imminent prospect of electric-vehicle applications where specific energy is so important — that much lighter and thinner grids can be successfully employed. Certainly, many of the electric-vehicle batteries that are currently being developed have positive grids in the thickness range of 1.8 to 2.4 mm. It is expected that these thin-grid batteries will sustain 1300 deep-cycles once the correct alloy specifications and method of fabrication have been resolved.

### 5.3. Question: What is the permissible wet shelf life of valve-regulated lead/acid batteries?

K. PETERS

At ambient temperatures, automotive valve-regulated batteries suffer a self-discharge rate of about 4 to 5% per month at 25 °C. The rate increases at higher storage temperatures. Thus, at the end of a year, the battery would probably be only half-charged. (Note, the self-discharge rate is not constant, it does tend to taper a little.) In order to keep the battery healthy, it is necessary to give it a freshening charge before that time, preferably after about six months.

## 6. Battery charging

### 6.1. Question: During constant-current/constant-voltage charging of VRLA batteries, the level of current after the constant-voltage segment varies between batteries. Why does this happen? Does this overcharge factor impact adversely on battery cycle life? Are there any accurate methods for monitoring low taper currents (i.e. 50 mA) following constant-current levels of 20 A?

K. PETERS

In any system, if overcharge is limited to prevent water loss or corrosion, then there is always the likelihood that finishing currents will vary greatly from one battery to

another. Only when adequate overcharge is provided will the end-of-charge current be stable and uniform. This is more effectively demonstrated by monitoring individual cell voltages when, due to variety of factors, the end-of-charge voltages may differ to a considerable extent.

The factors that affect this variability could be minor differences in cell make-up (e.g., variable active-material weights), possibly differences in formation efficiencies, and differences in cell temperatures. Two further factors may affect VRLA designs, namely, separator compression and acid volume. With the latter factor, not only can variable amounts of acid affect the material balance, but they can also influence the degree of recombination which, in turn, will affect the depolarization of the negative plate and the overall cell and battery voltage. Consequently, it is very difficult to maintain uniformity across batteries, and unless there is some means of cell equalization, the variability will cause a reduction in cycle life. Obviously, the problem intensifies under deep and frequent cycling duties.

Equipment to monitor wide variations in current is used regularly and is available commercially.

**6.2. Question:** *Fast charging is being promoted for electric-vehicle batteries. To what extent do the following technologies resist the adverse effects of high temperature that results from fast charging: flooded low-antimony; flooded lead-calcium; VRLA, AGM immobilized; VRLA, gel immobilized?*

#### E.M. VALERIOTE

The question seems to imply that a rating of batteries for their fast-charging performance would be based on their internal grid alloy and electrolyte resistance. Cominco's experience, however, suggests that the most important factor is the structural design of the batteries, rather than the generic battery technology. For example, if the number of plates in each cell is higher, the resistance will be lower. The resistances of pure-lead, Pb-Ca, Pb-Ca-Sn and low-antimony-lead differ only slightly. Thus, the alloy composition is not an important factor except, perhaps, for high-antimony-lead alloys. The 50 Ah, 12 V batteries tested by Cominco all had a fully-charged resistance of 3.0–3.5 m $\Omega$  regardless of battery type, with few exceptions. The pseudo-bipolar design had a very low resistance of 1.8 m $\Omega$ . This was a flooded, pure-lead battery. The Optima prototype (the battery currently used in Cominco's rapid-charge tests) has a spirally-wound, cylindrical configuration. It is a VRLA battery (AGM type with Pb-Sn grids) and has an internal resistance as low as 2.6 m $\Omega$ . In general, batteries with gelled electrolyte appeared to have higher resistances, viz., 5–6 m $\Omega$ . Nevertheless, these values could certainly be lowered through design modification.

It should be noted that ohmic resistance is not the only polarization that limits rapid charging. Non-ohmic polarizations are also important, particularly as the state-of-charge increases.

**6.3. Question:** *What is the maximum temperature inside the cell during charging of a valve-regulated lead/acid battery? How will the ambient temperature effect this maximum temperature?*

#### E.M. VALERIOTE

In fast-charging studies conducted by Cominco, the temperature inside valve-regulated batteries could typically get up to 70 °C with no apparent damage, and may be even somewhat higher. Nevertheless, the temperature at the outside of the case, where it is more normally measured, will be appreciably lower (~55 °C). There is a temperature limit with which battery manufacturers feel comfortable. Of course, the length of time at the high temperature is important. There are internal sources of heat that raise the battery temperature and, unless special probes are placed inside the battery, it is not possible to know from the outside world the extent to which the cell gets hot. The higher the ambient temperature at the start of charge, the higher the temperature at full charge. Nevertheless, the temperature rise at higher ambient temperatures is not quite as much as it would have been at a lower temperature. For example, Cominco tests showed that the rise was 25 °C starting at 25 °C, but only 20 °C starting at 35 °C. This is easily understood in terms of the heat dissipation that occurs from a higher temperature to a lower ambient temperature.

**6.4. Question:** *Some manufacturers are paralleling VRLA cells of different capacities in order to obtain higher higher capacities. Is this approach permitted for only particular rates and depths-of-discharge, or is it applicable to all rates of discharge? How do these cells behave in a normal 10 h discharge? What are the precautions to be taken? Please highlight the principles under which these paralleling systems are set up and what would be the approximate life of the batteries?*

#### K. PETERS

It is very, very unusual to parallel cells of different capacities, especially in stand-by (float) applications such as telecommunications or UPS systems. Telecommunications companies would never adopt this strategy. In Europe, for example, three parallel strings of cells are used—all the cells would be from the same manufacturer, all would have the same number of plates and, invariably, all would be of the same age. In addition, great care is taken to ensure that there is uniformity of current down each string. (Note, a relatively low voltage is applied across these parallel strings and the float current in a stable system might be only a few milliamperes.) If there is cell variability down one string to another, then it is impossible to control the total system. It is very surprising, therefore, that some manufacturers are even considering such an approach.



6.5. *Question: What is the purpose of adding sodium sulfate to the acid solution in some types of lead/acid batteries?*

K. PETERS

The use of sodium sulfate started some years ago when there was grave concern about over-discharging batteries that contained limited amounts of electrolyte, in particular, valve-regulated designs. If a battery is allowed to stand in a discharged state for a reasonably short period, there can be great difficulty in achieving recharge. This is especially true when recharging from a relatively low voltage, such as in a car alternator system where the regulator may be set at 14.5 or 14.6 V. In this case, the battery normally will not recharge and it will be necessary to remove the battery and place it on a charger that has some sort of boost-charging facility. Sodium sulfate tends to act as a buffering agent and to maintain a degree of conductivity that helps to recharge a deeply-discharged battery from a low-voltage source. Obviously, there is a limit to the effect of sodium sulfate, but it does indeed have some benefit and this is the major reason why it has been used.

J.E. MANDERS

If a VRLA battery with AGM separators is tank-formed, then there will be some development of dendritic growth and shorts. By adding sodium sulfate to the electrolyte, an appreciable soluble sulfate level is maintained and this tends to arrest such dendritic growth.

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