



Lead/acid battery design and operation

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Abstract

In keeping with the tradition of previous meetings, the Seventh Asian Battery Conference closed with the delegates putting questions to an expert panel of battery scientists and technologies. The proceedings were lively and the subjects were as follows. *Grid alloys*: gassing characteristics; influence of minor constituents on metallurgical and electrochemical characteristics; latest trends in composition; alloys for cast-on straps. *Battery manufacture and operation*: plate formation (α -PbO₂: β -PbO₂ ratio); dendritic shorts. *Separators*: contribution to battery internal resistance; influence of negative-plate enveloping; reduced backweb. *Valve-regulated lead/acid batteries*: positive active-material: negative active-material ratio; hydrogen evolution and dry-out; negative-plate self-discharge; tank vs. box formation. © 1998 Elsevier Science S.A. All rights reserved.

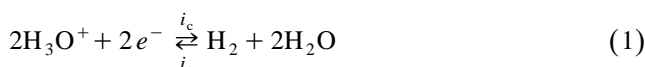
Keywords: Gassing; Grid alloy; Lead/acid battery; Plate formation; Separators; Valve-regulated

1. Grid alloys

1.1. Question: what is meant by ‘overvoltage’ in relation to gassing rates?

1.1.1. Definition of ‘overvoltage’

N. Bui: ‘Overvoltage’ or ‘overpotential’ (η) is the potential difference between the non-equilibrium (E) and the equilibrium potential (E_{eq}) of a redox reaction, i.e., $E - E_{\text{eq}}$. This potential difference produces a net current density (i). Consider, for example, the hydrogen redox reaction in acid solution:



The classical plot of the potential, E , vs. the net current density (log scale) shows the exchange current density,

$i_o = (i_o = i_a = |i_c|)$, at the equilibrium potential where the net current density, i ($i = i_a - |i_c|$), is zero, refer Fig. 1.

Since, for reaction (1), the potential, E , of the electrode is lower than the equilibrium potential, E_{eq} , hydrogen evolution occurs at a rate proportional to i_c under an overpotential of $\eta_c = E - E_{\text{eq}}$.

1.1.2. High and low ‘overvoltage’

Consider, for example, hydrogen evolution on two lead-alloy electrodes, alloy 1 and alloy 2, that have two E vs. $\log(i)$ relationships as follows, Fig. 2.

For the same rate of hydrogen evolution, i , alloy 1 requires a high overvoltage, η_1 , while alloy 2 requires a low overvoltage, η_2^1 . If the same low overvoltage η_2 is applied to the alloy 1 electrode, the rate of hydrogen evolution is decreased to i_1 . Therefore, alloy 1 is said to have a high hydrogen overvoltage, and alloy 2 a low hydrogen overvoltage. If an element in the alloy 2 is responsible for this behaviour, then this element is said to lower the hydrogen overvoltage (e.g., antimony), while an

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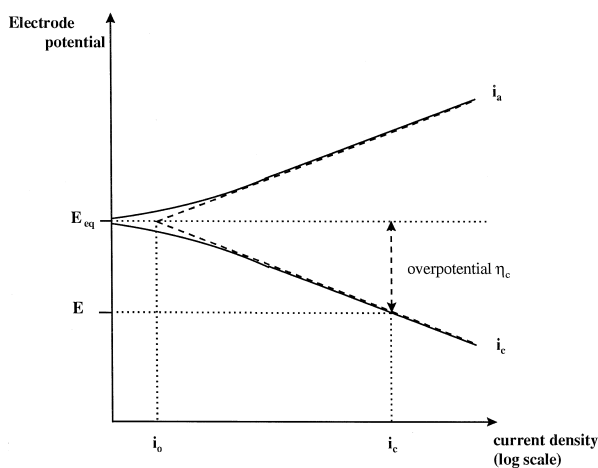


Fig. 1. Schematic of the potential vs. current plot for an electrode reaction.

element in alloy 1 would increase the hydrogen overvoltage (e.g., tin).

1.1.3. Gassing rate

The gassing rate, for example the volume of hydrogen evolved during a definite time, is proportional to the current density.

Since, in the above example (Fig. 2) the gassing rate is higher on alloy 2 (low overvoltage) than on alloy 1 (high overvoltage), it follows that a low overvoltage promotes a high gassing rate.

1.2. Question: Could you give some examples where elements affect overvoltage and hence gassing?

N. Bui: The following elements exert a marked influence on overvoltage and gassing rate:

tin: increasing oxygen overvoltage (low oxygen gassing).
silver, arsenic: decreasing oxygen overvoltage (high oxygen gassing).

tin, bismuth: increasing hydrogen overvoltage (low hydrogen gassing).

antimony, arsenic, nickel: decreasing hydrogen overvoltage (high hydrogen gassing).

1.3. Question: Silver is included in positive-grid alloys to provide resistance to corrosion at high-temperatures. Are there any detrimental effects associated with the use of silver?

N. Bui: Alloying silver has the effect of increasing both the corrosion resistance and the creep resistance of grid alloys, as well as of preventing the shedding of active material. The main detrimental effect is the lowering of the oxygen overvoltage (high oxygen gassing). Silver is also known to retard the oxidation of PbO to PbO_2 .

1.4. Question: Is there very much difference between the conductivities, impedances, etc., of the various alloys which are being used in, or considered for, the latest battery technology?

N. Bui: Lead–calcium–tin–silver alloys are preferred for advanced batteries. Calcium and silver have no effect on the conductivity. Tin has a strong effect on the conductivity, when present in the range 1.5 to 2.0 wt.%. The conductivity of the passivation layer increases with the tin level.

1.5. Question: What alloys should be used for Cast-on straps for book-mould, cast grids for: low-maintenance batteries (i.e., antimony grids); maintenance-free batteries (i.e., Pb–Ca grids, flooded electrolyte); valve-regulated batteries (i.e., Pb–Ca grids, immobilized electrolyte); valve-regulated batteries (i.e., Pb–Sn grids, immobilized electrolyte)? Are the alloys also suitable for expanded-metal grids and continuous-cast grids?

E.M. Valeriotte: Both low-maintenance grids (Pb–1.2 to 3 wt.% Sb) and maintenance-free or valve-regulated head/and (VRLA) grids (Pb–Ca–Sn) pose problems for cast-on strap (COS)/lug joining because neither of these grid alloys melts easily enough to form a good metallurgical bond with the strap alloy. Preferred strap alloys contain 2.75–4.5 wt.% Sb with moderate levels of grain refiners such as 0.07 wt.% Cu, 0.003 wt.% S or 0.02 wt.% Se (somewhat lower than their levels in Pb–low Sb grid alloys). The COS alloys may also contain As (hardening and strength characteristics) and Sn (to prevent As and Sb oxidation and improve joining). These COS compositions are chosen because of their ductility and wide freezing range that makes them attractive for through-the-partition welds and ease of joining materials even with wide differences in melting points. Thus, while the COS temperature may be 415–450°C, the lug alloy begins to melt at 280–285°C and is slushy up to the liquidus temperature of 315–325°C. Typical process parameters are melting pot and feedline temperatures of 450°C and a mould tempera-

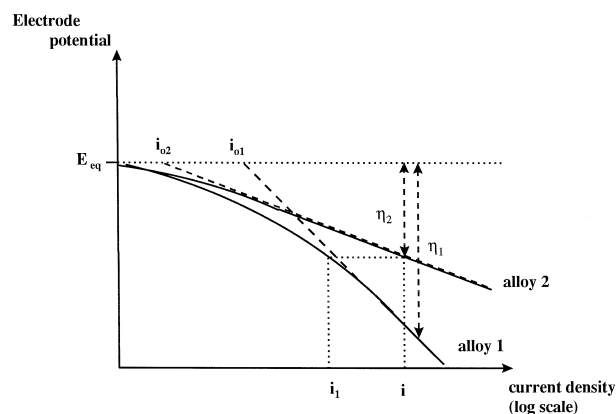


Fig. 2. Schematic of potential vs. current plots for hydrogen evolution on two different lead alloys.

Table 1
Typical alloy compositions (wt.%) for cast-on straps

	Typical Cu/S–Sb COS alloy	Typical Se–Sb COS alloy	Typical Pb–Sn COS alloy
Sb	2.9–3.3	2.7–3.5	< 0.002
As	0.15–0.3	0.1–0.25	< 0.002
Sn	0.15–0.3	0.1–0.3	2.0–2.25
Cu	0.05–0.07	< 0.04	< 0.002
S	0.002–0.004	< 0.002	< 0.001
Se	NS ^a	0.015–0.025	0.015–0.025
Ni	< 0.001	< 0.001	< 0.0002
Fe	< 0.001	< 0.001	< 0.001
Te	NS	< 0.005	< 0.0002
Bi	< 0.05	< 0.05	< 0.05

^aNS = not specified.

ture of 110°C. For COS joining, the mould temperature is critical since the surface of the lug must be only partially melted.

When non-antimonial straps, such as Pb-2 wt.% Sn (with 0.015–0.025 wt.% Se for grain refining) are used to minimize gassing, the narrow freezing range makes joining especially difficult and temperature control critical; usually pre-tinning is necessary. (For gelled batteries where the gel covers the straps and posts, 0.03 wt.% As is sometimes added for strength). Since the joining of the grid lug to the strap is more like a soldering operation than welding, fluxes and pre-tinning have been introduced for such difficult alloys.

In the case of the Pb–Ca–Sn alloys, their melting point is relatively high (322–327°C) and solidification of the strap may take place around the lug without any bond forming. With low-Sb alloys, the difficulty is that insufficient eutectic liquid is available to flow and react in the contact areas. The COS alloy must remain liquid long enough for gases and surface oxides disturbed in the melting process to float away from the lug/strap interface.

For Pb-2 wt.% Sn, there is virtually no eutectic to flow and the melting temperature is so high that little of the lug melts and soldering of much of the lug is needed.

Soldering is primarily a surface process, so pretreatment of the surface is important. Grid lugs are often brushed,

prefluxed, or pre-tinned. The flux removes surface oxides and pre-tinning proves a low-melting eutectic at the interface to permit good bonding. Again the tin level is critical since too much may make the lug susceptible to corrosion. The flux may release gas bubbles as it reacts with the oxide surface and these need to escape through a sufficiently fluid interface before solidification of the eutectic.

For AGM types of VRLA batteries, impurities in the Pb–Sn alloy must be controlled to much lower levels than in flooded batteries. In general, for these, Sb and As are specified at below 0.002 wt.% and Ni and Te are specified at less than 5 ppm to reduce the chance of negative-lug corrosion.

For hybrid flooded batteries, the same COS alloys are used as for Pb–Ca batteries. These alloys are suitable for Pb–Ca in the form of conventionally cast, rolled-expanded, or continuously cast-expanded grids. In fact, for hybrid batteries, Cominco's Multi-Alloy Caster continuously cast-expanded negatives may be superior because the thin sections obtainable in this process produce less heat extraction from the COS and may more closely match the melting characteristics of the Pb–Sb positives.

Typical COS alloy compositions are listed in Table 1. These data have been provided by Prengaman who has produced two excellent reviews of alloys for cast-on straps [1,2].

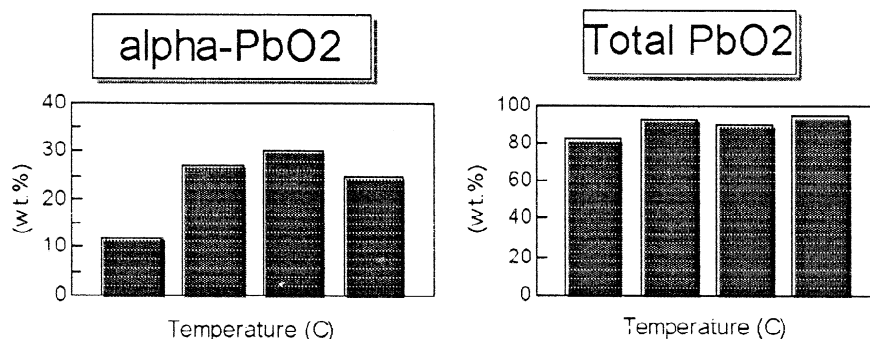


Fig. 3. Effect of increasing formation temperature (20, 40, 55 and 70°C) on the composition of positive active-material.

2. Battery manufacture and operation

2.1. *Question: Under what conditions of formation is there an increase in the ratio of α -PbO₂ to β -PbO₂ in the positive plate?*

D.W.H. Lambert: Temperature, acid density, and current density all exert a pronounced effect on the phase chemistry of the formed positive plate. For a given formation regime (current density, time, and acid density), the amount of α -PbO₂ increases with increasing temperature, up to a maximum of $\sim 30\%$ at 55°C (Fig. 3). Any further temperature increase results in a reduction in the amount of α -PbO₂. In addition, the highest levels of α -PbO₂ are obtained at the lowest formation acid densities (Fig. 4) and lowest current densities (Fig. 5).

It should also be noted, that as the sulfate content of the paste increases, the portion of α -PbO₂ decreases. Conversely, lack of acid low porosity, diluted formation acid, mill oxide with a high PbO content, or a dense lead sulfate layer) induces the formation of α -PbO₂ [3].

In summary, lower temperature, increasing acid density, and current density result in a decrease in the proportion of α -PbO₂,

2.2. *Question: What are the principal conditions that give rise to dendritic shorts ('leading-through')? What steps can be taken to minimize this problem?*

D.W.H. Lambert: 'Leading through' is the term applied to the development of dendritic short-circuits through the separator. The problem can occur for a variety of reasons.

All lead acid cells and batteries, in particular those for automotive SLI (starting lighting and ignition) systems and for solar (photovoltaic) applications, are vulnerable if deeply-discharged and then left in a fully discharged condition. In addition, VRLA batteries which use AGM (absorptive glass mat) separators are (by design) acid-starved, and inherently prone to this failure mechanism during formation. The phenomenon is pH-related, and only occurs when the acid strength has fallen to around 1.030 (~ 0.5 M).

A model for the development of dendritic shorts (leading-through) in VRLA batteries during initial plate formation, has been proposed and involves five stages, namely; (i) neutralisation of the electrolyte (pH = 9.0–9.5); (ii) generation of a low activity (sulfate ion strength) solution; (iii) lead removal (dissolution) from the positive grid; (iv) migration (movement) of the lead ions through the separator; (v) lead deposition, and dendrite formation.

Consequently, the stand time between acid filling and commencement of formation, the acid filling-density and the temperature all influence the likelihood of leading-through. The incidence of dendritic shorts can, therefore, be reduced by; shortened stand times (~ 30 min); maximized filling-acid densities; lower filling-acid temperatures (to reduce the rate of reaction); where possible, even distribution of the acid throughout the plates and the separators; if the battery design and cost permits, increased electrolyte volumes and the use of dry-charged plates.

In addition, since it is the dissolution of lead from the positive grid that produces leading-through. Protecting the positive grid by overpasting, preferably on both sides, by applying the paste with a fixed orifice pasting, machine will reduce the problem significantly.

Lastly, the addition of 'common ion effect' salts (for example, sodium sulfate) to the electrolyte will raise and 'buffer' the ionic strength of the electrolyte in the cell and, thereby, will slow the rate of the lead dissolution reaction and prevent, the formation of dendritic shorts.

3. Separators

3.1. *Question: What contribution do the separators make to a battery's internal resistance? Does thinner backweb and/or higher porosity change this contribution dramatically? What is the effect of the trend to underhood temperatures of 80 to 90°C?*

J. Navarette: The contribution of the separator resistance is only a small, but additive, contribution to the total

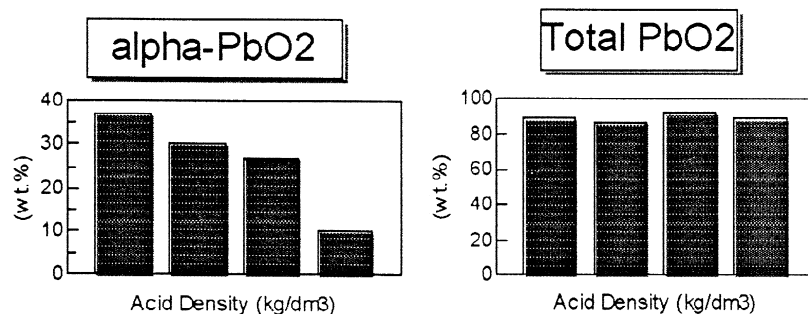


Fig. 4. Effect of increasing formation acid density (1.005, 1.030, 1.060 and 1.120) on the composition of positive active-material.

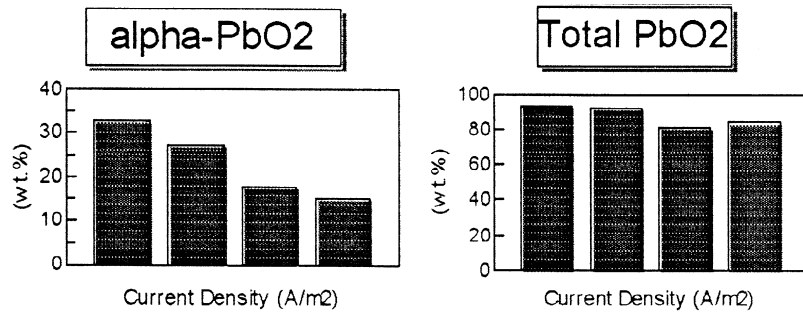


Fig. 5. Effect of increasing formation current density (37, 74, 175 and 370) on the composition of positive active-material.

battery electrical resistance that derives from the connectors, lugs, grids, active material, transition resistance at the active material–electrolyte interface, etc. However small the contribution to total battery electrical resistance, it is generally accepted that even the slightest shifts in the separator electrical resistance, either up or down, has more of an impact on cold-cranking performance than on reserve-capacity. Thus, in cold-cranking tests the electrical resistance of the separator can contribute about 5–6% to the total battery resistance.

Going to a thinner backweb provides only a slight decrease in separator electrical resistance. A decrease in the backweb thickness of 0.05 mm can result in a reduction of total internal battery resistance by approximately 1.0%, corresponding to an improvement in cold-cranking performance of about 0.4% [4]. Fig. 6 shows an improvement in cold-cranking voltage of about 35 mV with a 0.05 mm drop in backweb thickness. This is a slight improvement, but an improvement nonetheless.

Increasing the porosity can also have the same effect of reducing separator electrical resistance as thinner backwebs. In order for higher porosity separators to have an advantage, however, the internal pore surfaces must be fully wet. Fig. 7 compares the cold-cranking performance (-18°C) of a separator with excellent wettability and lower porosity with a separator having higher porosity and a slower wet-out. The more porous separator has a larger initial voltage drop which corresponds to higher electrical resistance. Higher porosity does not necessarily relate to

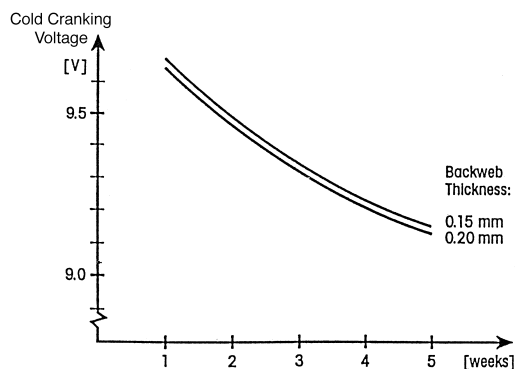


Fig. 6. Effect of separator backweb thickness on cold-cranking voltage.

better performance. Similar differences are noticed in separator resistance measurements using a Palico.

There is the concern that lowering the backweb thickness will also reduce the resistance of the separator to oxidation. A drop in separator oxidation would correspond to reduced battery life at elevated temperatures ($80\text{--}90^{\circ}\text{C}$). Fig. 8 demonstrates an increase in separator oxidation with a decrease in backweb thickness. An alternative to the standard separator is the Daramic HP type, developed to improve oxidation and puncture resistance even as backweb thickness is lowered (Fig. 9). In hot climates where oxidation resistance is more important than cold-cranking performance, Daramic HP and/or thicker backweb (0.25 mm) separators should be considered.

3.2. Question: If negatives are enveloped is the cold-cranking performance affected?

J. Navarette: Studies conducted in the Daramic laboratories indicate there is no significant effect on the cold-cranking performance when enveloping either positives or negative plates (Table 2). The decision to envelope the negative or positive is probably due more to the battery design and/or the goals of the battery manufacturer. For

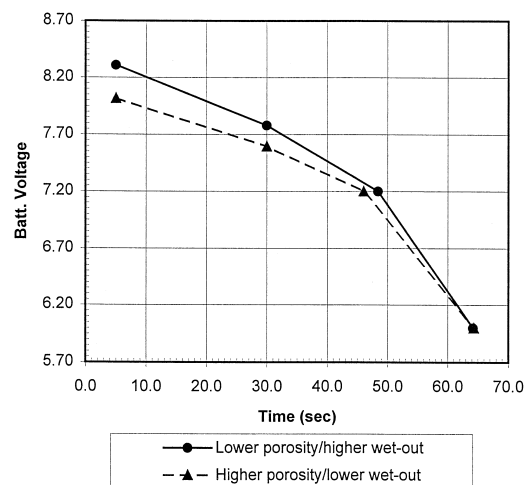


Fig. 7. Cold-cranking performance of separators with different characteristics. (Pb–Ca Group 24; cold-cranking rating = 550 A at -18°C).

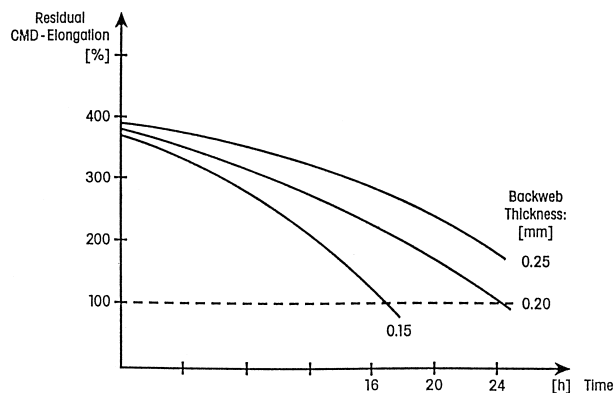


Fig. 8. Increase in separator oxidation with a decrease in backweb thickness for standard separators.

instance, the negatives will not grow and cause tears in the separator much like the positives are prone to do. This positive-plate growth may be more of an issue with expanded grids where sharp edges may cut into the separator as the plate grows. Also, in enveloped positive plates, the separator sides and bottom are in intimate contact with the plate and these areas tend to show the highest levels of oxidation. There may also be economic reasons. If the total plate count is odd, the lower plate, usually the negative, will be enveloped. Less material is used and the cost per battery is lowered. The savings can be significant for the larger battery manufacturers.

3.3. Question: Is there an increase in dendritic shorts with a reduction in backweb thickness?

J. Navarette: A polyethylene separator possesses pores with a range of tortuosities. This characteristic is one of the reasons why at even flow backweb thickness (~ 0.150 mm) there should not be a significant increase in failures due to dendritic shorts. Of course, this statement is also dependent on the application and construction of the battery itself. What is likely to have a more significant impact

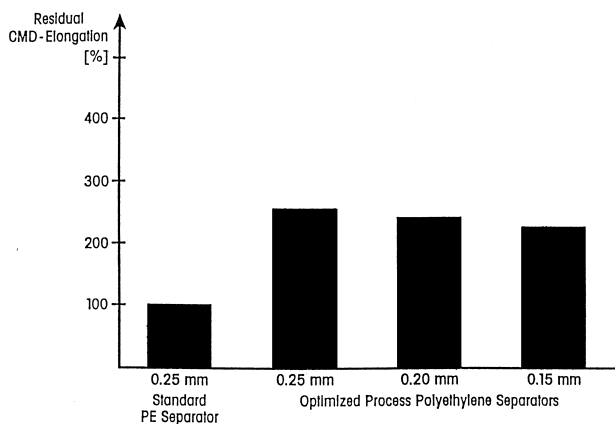


Fig. 9. Process optimized separators with improved oxidation resistance over standard separators.

Table 2

Effect of positive/negative enveloping on cold-cranking (CCA) performance (175 A at -18°C) of a hybrid battery (Pb-1.6 wt.% Sb positive, 36-Ah cells)

Parameter	Negative envelope	Positive envelope
30-s voltage		
1st CCA	1.66	1.66
2nd CCA	1.66	1.66
Time (s) to 1.0 V/cell		
1st CCA	211	204
2nd CCA	196	186

on dendritic shorts is the reduction of the overall thickness together with a reduction in the backweb—especially in high-performance batteries where acid and separator volume is displaced by plate volume, to satisfy increasing electrical load requirements in the same dimensional footprint. In these instances, there can be a more severe drop in acid specific gravity and thus more opportunities are provided for dendritic shorts to develop.

Previous reports on warranty returns indicate that shorts due to deep discharge and recharging accounted for about 11% of the total failures [5]. Because the trend towards thinner backwebs is relatively new (within the past 2 years), however, a new study on battery failure modes may need to be considered to verify that the thinner backweb separator has not become the weak link.

4. Negative-plate expanders

4.1. Question: What is the impact of the quantity of expander on voltage characteristics?

E.M. Valeriotte: Although they have been the subject of considerable study, expanders have not been developed much since the 1950s, after it had been found that removal of wood separators caused loss of cold-cranking capacity, which could be restored by adding sulfonated lignin, a wood extract. Since then, battery design and applications have greatly changed, and the conventional expanders may not be the best any longer. They are generally made up of a mixture of carbon (lampblack), barium sulfate (blanc fixe) and an organic component, usually lignosulfonate, a natural tree extract. It is widely accepted that the effects of barium sulfate and lignosulfonate appear to be synergistic.

Vinal [6] says that the carbon has little effect on capacity (slight effect at low temperatures), but that it clears the plates on formation. He also said that it counteracted the tendency to high final charge voltages caused by the other expander ingredients. Although carbon may help to control impurities, or provide conductivity during formation or at the end of a deep discharge, it is hard to find anyone prepared to state unequivocally that the benefits of carbon

go beyond colouring the negative plate and making it identifiable.

As far as barium sulfate is concerned, its main role is believed to be to provide nuclei for the precipitation of lead sulfate. Thus, its effect on discharge voltages would be most evident in reducing the early discharge spike of a fully-charged plate, the ‘coup-de-fouet’ or ‘spannungsack’). By providing a more finely distributed lead sulfate, it might also have some effect on polarizations related to true vs. apparent surface area (roughness).

The organic component of the expander affects plate morphology and reaction kinetics. Organic expanders now most used are based on wood or cellulosic materials, most notably extracted lignosulfonic acids, such as Vanisperse/Maracell, Lignosol, Totanin or Indulin. Other commercial expanders are humic-acid salts, tanning agents, such as BNF, and so on. They are known to improve capacity, particularly at high rates and low temperatures. These are not very effective above 50°C). The organic is adsorbed on the lead and lead sulfate. Thus, during discharge, it inhibits lead sulfate growth and passivation of the lead surface. During charge, however, it adsorbs on the lead and maintains porosity but results in an increase in the final charging voltage, by increasing the hydrogen overpotential. These effects would be expected to increase with expander level because of increased adsorption. Too much expander will cause a decrease in charge-acceptance. Insufficient quantities or effectiveness of expander may also result in a decrease in plate surface-area or loss of electrical continuity caused by densification, which would also increase plate polarization due to higher real current densities, so an optimum level must be established for each expander type and application.

For VRLA, cells, where the negative plates stay very close to the Pb/PbSO₄ potential, the charging voltage may not be affected. Nevertheless, instabilities of the negative-plate potentials in battery strings, reflected by a bi-modal voltage distribution, have led some manufacturers to put only barium sulfate in their negatives.

A higher level of expander might be better when plates are compressed, because the compression would prevent over-expansion and any additional expander would allow maintaining a reservoir to make up losses. Typical expander formulations contain 0.15–0.2 wt.% C, 0.3–0.5 wt.% BaSO₄ and about 0.3 wt.% lignin per unit of oxide weight, but whose levels vary according to the particular organic and application.

4.2. Question: Does expander degradation occur during formation process or only during cycling? If the latter, what are the critical conditions?

E.M. Valeriotte: A special, closed session on negative-plate issues was held before the Fifth European Lead Battery Conference in Spain in 1996. The Chairman of this Meeting, H. Geiss, summarized the consensus reached on

expander degradation. The key parameters affecting expander degradation are hydrogen, oxygen, temperature, and pH. During formation, all of these parameters may reach extreme values, so some degradation of the expander is to be expected. At this stage in the battery’s life, however, there should be an excess of expander available. The degradation will be like smoking cigarettes. One cigarette or pack may not cause any measurable decrease in life, but the cumulative effect over the life of the smoker or the battery is significant.

Cycling should also cumulatively cause expander degradation but primarily during the times when the negative plate is exposed to high temperatures and highly reactive oxygen and hydrogen. In VRLA batteries, the exposure is greatly exacerbated because oxygen is deliberately allowed to reach the negative plates and because such batteries reach higher internal battery temperatures, both due to the internal release of the heats of the recombination reactions and to the lower heat capacities of the limited electrolyte quantities. Fast charging, of course, adds additional heat due to high i^2R heating and so can be expected to add to the stresses on the expander.

During the meeting in Spain, Pavlov discussed work that he had done looking at synthetic formaldehyde expanders and he recommended a combination of organic and synthetic expanders, with one type giving beneficial capacity maintenance at the beginning of cycle life, with the other providing long-term performance as the first degrades. Both Nelson and Pavlov pointed out the necessity of protecting the hydroxyl groups in the organic expander to prevent the degradation, which probably occurs through polarization reactions. Boden said that expanders with a low ash content in the Hammond ashing test apparently perform better and this may be because they contain less polymeric materials. Boden’s paper [7] at this conference may provide more details.

4.3. Question: Under what conditions / circumstances, if any, is expander failure the mode of failure for the battery?

E.M. Valeriotte: About twenty years ago, negative-plate densification was a failure mode in automotive batteries, particularly under some test conditions or in some applications. This appeared to become solved by reformulating expander compositions/quantities. At any rate, perception of the problem disappeared. As under-the-hood temperatures have increased and new stresses, such as fast charging and the aggressive conditions in VRLA batteries, have appeared, there is the expectation that we should be seeing more negative-plate failures than in the past. At the Spanish meeting mentioned above, one large manufacturer reported premature negative-plate failures in an application with 15-min-rate cycling. Another large manufacturer said that negative-plate failures were seen under conditions of 20–25%DDs and that this was a problem. In our own

laboratory, we have witnessed negative-plate degradation under fast-charge cycling and this is related to changes in negative-plate morphology and surface area.

4.4. Question: What is the present state-of-the-art for expanders? For example, is there a problem with high under-the-hood temperatures? Is there room for improvement?

E.M. Valeriotte: We do not yet know how widespread is the problem of high temperature and whether it is becoming much worse. We need to be exchanging information to find out. The ALABC Research Management Team, at another meeting in Spain (just before the Fifth European Lead Battery Conference) followed up on the consensus of the negative plate meeting by deciding to issue requests for proposals on the following topics:

- a review of the state-of-the-art of the negative plate;
- an assessment of the origins of performance degradation of the negative plate that can arise from high-rate discharge;
- search for synthetic negative-plate expanders.

Contracts for some of this work have already been issued. It is hoped that these studies will identify any problems more clearly and, if there is need for improvement, will encourage further work to overcome any deficiencies in expander performance.

5. Valve-regulated lead / acid batteries

5.1. Question: What is the recommended positive to negative (P:N) active-material ratio for VRLA batteries for the following applications: (i) float service; (ii) deep cycling; (iii) shallow cycling?

R.F. Nelson: The classic condition for gas recombinant technologies, both nickel/cadmium (Ni/Cd) and VRLA, is to have an overbuilt negative plate so that excess negative material is always present to participate in the oxygen-recombination cycle. This is an excerpt from the basic VRLA Gates patent (US 3,862,861): “The ampere-hour capacity of the negative plate is greater than that of the positive plate thereby allowing the positive plate to overcharge before the negative plate. Thus, oxygen which may be evolved during overcharge is thereby allowed to diffuse and recombine with the exposed portion of the negative plate”. This is similar to the conceptual view of the sealed Ni/Cd cell.

If the P:N ratio is defined in terms of paste weights (which is what is usually done), there will be an automatic bias toward the negative, as its percent utilization is about 20% greater than that of the positive. So even if we just have balanced paste weights we have a $P:N < 1.0$. An overbuilt negative is useful in high-rate applications, where many lead/acid batteries are negative limited. It is also

perceived to be important in float applications so that there is always excess negative to deal with the continuous generation of oxygen and its subsequent recombination. On the other hand, for deep cycling an overbuilt positive has been favoured, because of the traditional relationship between plate thickness and cycle life (thicker is better). These are probably the right choices, but not for the traditional reasons given. Recently, Berndt and Feder have stressed that when VRLA batteries are floated at low voltages, discharge of the negative on float can actually occur; clearly, having more negative active material (NAM) will ameliorate this situation. Separately, Atlung has shown that, in cycling applications, it can be difficult or impossible to completely recharge the NAM if there is a high level of oxygen recombination; this implies that an overbuilt positive would be beneficial in cycling use because it would generate less oxygen than in a balanced plate situation. Moreover, Rand and co-workers have shown that compression can have a significant beneficial effect on the improvement of cycle life due to the pressure keeping good contact between the grid and positive active-material (PAM) and within the PAM itself. Because the density of the PAM is less than that of the NAM, higher compression levels will be realized with overbuilt positives.

Given the above, I would make the following recommendations for the three cases:

- (i) float service: overbuilt negative;
- (ii) deep cycling: overbuilt positive;
- (iii) shallow cycling: balanced or slightly overbuilt positive;

In practice, factors such as the charging method and the electrolyte amount (as it affects the recombination balance in the cell) will probably have more to do with improving life than the P:N ratio.

5.2. Question: Does the P:N ratio need to be altered according to acid concentration?

R.F. Nelson: Large changes in acid concentration would usually mean that a battery was being designed for different applications. For example, a 1.280 acid might go with an automotive thin-plate design, with a low P:N for high-rate/low-temperature performance and good alternator charging. For 1.300–1.320, you might have a thicker-plate design for telecommunications or UPS standby ($P:N \sim 1$) or a deep-cycling application ($P:N > 1$). In a given battery, an increase or decrease in acid concentration would primarily have an impact on charge voltage and, to a lesser extent, as discharge capacity. With a lower acid concentration, a significant amount of excess negative or positive material is not wanted because it would tie up sulfate in the plates as inactive material. Thus, a balanced condition is required (unless an application-specific design such as automotive or deep cycling is intended) in order to have the maximum amount of sulfate available for discharge. With a high specific gravity, it is not advisable to have a

P:N ratio, cell design and/or charging method that would promote loss of hydrogen and oxygen gases, as this would raise the specific gravity even higher and create other problems such as undercharging and, in the extreme, softening of the PAM.

Having said all of this, for a given VRLA product, variations of the acid specific gravity within reasonable bounds (plus or minus ~ 100 basis points) should not require any alteration of the P:N ratio.

5.3. Question: If there are good reasons for using a P:N value greater than unity, does the negative then become charged first, giving rise to hydrogen evolution and dry-out?

R.F. Nelson: Keeping in mind the difference between P:N based upon paste weights (for equal weights the negative is about 20% overbuilt due to a higher utilization level) and utilization levels (for equal utilization levels—hence, both plates going out together on discharge—the P:N based upon paste masses is actually ~ 1.2), it is generally the case that, if there is excess positive the negative will, in fact, go into gassing before the positive can generate sufficient oxygen to bring down the negative voltage out of the gassing region. In this design, however, advantage can be taken of this process by using the rapid rise in negative-plate (and, hence, the cell) voltage to terminate charge. This will keep oxygen evolution to a minimum and the small amount of hydrogen evolution (which may not be vented) will not be sufficient over time to result in dry-out.

A P:N greater than unity will usually be employed in VRLA designs for deep cycling, rather than a float-charge duty cycle. Dry-out is usually associated with float applications involving continuous charge at relatively high currents and voltages. Moreover, water loss due to overcharge is not necessarily the primary mechanism, particularly in cyclic applications. Loss of water through the case walls, case/lid/terminal leaks and defective vent valves are also important contributors to dry-out.

Between using the appropriate charging and termination strategies and the limited amount of time that VRLA batteries with high P:N ratios are in overcharge, it is not likely that failure will occur due to dry-out. If, for some reason, a battery with a high P:N ratio is used in a float application, or is subjected to heavy overcharge in a cyclic application, then there may be significant hydrogen evolution and, possibly, venting. On float, it is not really certain that a battery with a high P:N would experience significant hydrogen evolution, except early on. If the battery is nominally brought to full charge and then put on float, the positive will continue to charge and the negative will go into gassing. If the float voltage and current are quite low, as noted by Berndt, this condition can go on indefinitely, as the positive plate could actually discharge on float and all of the current would go into maintaining the positive at

some partial state-of-charge without fully charging it so that it could go into oxygen evolution. A better scenario would be that the positive would eventually become fully charged and go into oxygen evolution. The evolved oxygen would diffuse to the negative and create a mixed potential situation, thus lowering its voltage and decreasing the amount of hydrogen evolution. Once balance is achieved, the battery could float in this condition for long periods of time.

Clearly, this is a question that depends largely upon the battery design and the intended application, primarily the charging condition. It may or may not be a serious problem.

5.4. Question: At INTELEC '96, Jones and Feder intimated that if positive-grid corrosion did not occur in a VRLA battery then negative discharge and unbalanced release of hydrogen will occur. How can this condition be avoided?

R.F. Nelson: The paper referred to is on pages 184–192 of the INTELEC '96 Proceedings, there is also a companion paper on pages 358–366 of the same Proceedings. Supporting information can be obtained from Berndt's book, *Maintenance-Free Batteries*, on pages 97–101. In the first INTELEC paper (pp. 184–192), it is pointed out that if, in a VRLA cell, the oxygen-recombination efficiency (ORE) is 100%, then the sum total of overcharge would be decomposition of water at the positive and its reformulation at the negative via the oxygen cycle. In this case, neither grid corrosion nor negative discharge would take place. Jones and Feder then go on to state that on float, grid corrosion cannot be avoided; and when it occurs, there must be a balancing level of hydrogen evolution at the negative. These reactions will occur when the ORE is $< 100\%$, which is most of the time. This reduction in ORE results in the consumption of water and is accompanied by hydrogen evolution. The major point in these papers was to focus on dry-out as a failure mode, but it was concluded that failure is most likely to occur by discharge of the negative plate on float. Therefore, it is possible that the failure of VRLA batteries on float is due to negative-plate sulfation rather than dry-out. According to Jones Feder, the best way to counter this is to provide a boost charge periodically or use some other device such as a catalyst to allow the negative plate to polarize so that it will not discharge.

The same authors observed that many VRLA cells on float ride at, or below, their open-circuit value—i.e., they discharge. This is clearly due to the oxygen-recombination process that tends to 'drag' the negative plate down, but if it gets to a point where the float current is not sufficient to keep the negative fully charged then there is a problem. It is a well-known fact that, when overcharged at relatively high currents, the negative plate goes to a high voltage and gassing occurs by the direct reduction of

hydrogen ions to hydrogen gas. Even on open circuit, however, the self-discharge of the negative plate will produce hydrogen gas and under float conditions, where the negative plate is at or near its open-circuit value, hydrogen will also be evolved due to the ‘mixed potential’ nature of the lead/acid cell negative (and positive) plate. It is likely that this negative-plate discharge will not continue indefinitely, but will proceed to a point where this process is balanced by the applied float current. Anything in the design or operation of the VRLA cell that increases the polarization of the negative plate will diminish the influence of this unusual process. Conversely, anything that significantly decreases the hydrogen overpotential on the negative (such as heavy-metal impurities, organics, etc.) will lead to higher levels of hydrogen evolution. In long strings such as in telecommunications applications, it is virtually impossible to avoid this condition in some of the cells.

5.5. Question: Is tank formation will preferred for VRLA batteries of the AGM type and are there quality risks associated with box formation?

R.F. Nelson: A critical aspect of VRLA technology is the filling process. Because of the nature of the battery design and the materials, it is extremely difficult to achieve uniform distribution of the fill acid in VRLA batteries that are processed with unformed plates. Whatever the fill process (‘dunk’, vacuum, gravity, pressurized), as soon as the electrolyte enters the plate stack it begins to react with the lead oxides in the plates. As this is an acid-base reaction, it is very exothermic; management of the heat generated is a significant consideration. As the acid penetrates into the plate stack, it becomes more dilute and hotter. The ingress of the acid is hindered by the nature of the AGM separator, which is crushed to some extent to achieve a moderate or high degree of compression. In the uncompressed state, the separator is a tangled mat of fibres

that wicks acid primarily by capillary action. In the compressed state, liquid transport is even slower and so it can be some time before the acid can penetrate to the last areas of the plate stack that are not wetted. The last acid to enter the plate stack during fill will wet areas of the plates that have largely reacted with the previous acid to form lead sulfates. At the end of fill, there will be areas where the acid has undergone little or no reaction and other areas where it is completely reacted, or almost so. In addition, in the areas where it has completely reacted the liquid will be quite hot for some period of time. This promotes the dissolution of lead sulfate, which will then diffuse into the separator. If this process occurs to a significant extent, dendrites can be created during formation or early in service life.

None of this will occur with tank-formed plates; therefore, this is, in fact, the preferred method of manufacture for VRLA cells and batteries. From the above scenario, it is clear that there are, indeed, quality risks associated with box filling and formation, but for many designs (thin-plate prismatic, spiral-wound) tank formation of plates is difficult or impossible. The major quality risks are dendrite formation and/or severe grid corrosion in the areas that are poorly filled. Moreover, due to the large differences in specific gravity throughout a cell, formation of the plates will not be uniform and possibly will give rise to erratic charge–discharge performance in some applications.

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