

Towards improved manufacture of lead/acid batteries — panel discussion

K. Fuchida

Yuasa Battery Co., Ltd., 6-6 Josaicho, Takatsuki, Osaka 568 (Japan)

W. F. Gillian

Pasminco Metals, 114 William Street, Melbourne, Vic. 3000 (Australia)

L. E. Gardiner

T.B.S. Engineering, Longhill, Elmstone Hardwicke, Cheltenham, Glos. GL51 9TY (UK)

D. W. H. Lambert

Wirtz Manufacturing Co., Inc. Europe, 32 Clarendon Court, Winwick Quay Industrial Estate, Warrington WA2 8QP (UK)

J. E. Manders

Pasminco Metals, 114 William Street, Melbourne, Vic. 3000 (Australia)

D. A. J. Rand

CSIRO Institute of Minerals, Energy and Construction, Division of Mineral Products, P.O. Box 124, Port Melbourne, Vic. 3207 (Australia)

Abstract

During the Fourth Asian Battery conference panel session, topics under discussion were as follows. *Alloy and grid technology*: analysis of alloy composition; grain refiners; very-low antimony alloys; cracking of cast grids; strap alloys; cast-on strap process; inter-cell welds. *Separator technology*. *Plate processing*: oxide production; paste mixing; plate curing; dry-charging. *Battery performance*: JIS endurance test; overcharging; hydrogen sulfide generation; thermal runaway; grid corrosion; failure modes.

Alloy and grid technology

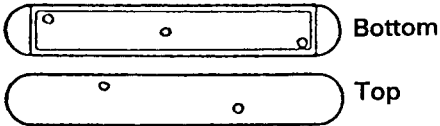
Question: What is the recommended technique for sampling alloy ingots in order to perform compositional analysis?

W. F. GILLIAN

The following ingot sampling technique is a recommended procedure.

(i) First, ensure that all surfaces to be drilled are cleaned of dirt and/or adhering foreign material prior to sampling. When cleaning the surfaces, metal brushes (such as iron or brass) should not be used as these may introduce spurious contamination.

(ii) The ingots are drilled according to the diagram given below. A 10 mm diameter bit is used and drilling is taken to at least three-quarters of the way through the sample. If necessary, the first 5 to 10 mm is discarded so that any oxide on the surface does not interfere with the chemical analysis.



(iii) All the samples are collected and inspected to ensure that they are all of approximately the same size (10 mm in length). If any long 'ribbon' pieces are present, they must be cut to size. If the iron content of the sample is to be determined, then the full sample should be treated with a strong magnet in order to remove any iron that may have been introduced by drilling.

(iv) The combined sample is mixed very carefully and then divided into four equal portions. Each portion is placed in a clean, sealed container to await analysis.

Question: Are grain refiners required in a Pb-3wt.%Sb alloy?

W. F. GILLIAN

The days of binary alloys of lead and antimony are virtually over. The demand for low-maintenance (i.e., low-gassing) battery designs has necessitated a reduction in antimony content. Alloys containing between 6 wt.% Sb and 11.1 wt.% Sb (the eutectic composition) do not generally require grain refiners, although Pb-6wt.%Sb alloys have been used with some copper and arsenic.

The problem with reducing the antimony content is that the amount of antimony-rich eutectic liquid is decreased. This means that fewer, but larger, dendritic grains are formed and these tend to orientate in a given direction. The development of these large grains causes the following difficulties.

(i) Because the alloys are very directional in their solidification progress (i.e., they grow from the mould face inward), the resulting large dendritic grains produce a resistance to metal feed within the mould cavity. This gives rise to incomplete castings, shrinkage cracks, and other minor structural weaknesses.

(ii) The presence of large dendritic grains can lead to severe intergranular corrosion problems. As the specific volume of PbO_2 is 21% greater than that of lead, penetration by the corrosion product along the grain boundaries induces further stress into the structure, thus accelerating the corrosion rate.

(iii) Gassing is also enhanced, as is the removal of antimony and its subsequent plating on the negative electrode.

To overcome these problems, particularly with the alloys containing < 4 wt.% Sb, grain refiners must be used.

Question: What are the advantages of multiple grain refiners, and can only one refiner be used for Pb-2wt.%Sb alloy?

W. F. GILLIAN

Having established the need for grain refiners, it is now necessary to know what to use. The common grain refiners are: (i) copper and arsenic; (ii) selenium; (iii) sulfur. Certainly, there are many companies that use only copper arsenide for Pb-3wt.%Sb

alloy. In the panellist's opinion, however, this denies the performance advantages that can be gained with the use of selenium or sulfur, or both.

The alloy mentioned in the question contains 2 wt.% Sb. For this alloy, more than one grain refiner is required. The choice is: (i) Pb-Cb-Cu₃As-PbSe; (ii) Pb-Sb-Cu₃As-PbS; (iii) Pb-Sb-Cu₃As-PbS-PbSe. The latter composition is preferred.

Grain refiners have been used individually, or in combination, and achieve their effect by coming out of solution prior to the solidification of lead. Their solid inter-metallic forms act as nuclei for the crystallization of primary-solid-solution material. Further, the solidification of these alloys does not proceed from the mould wall, as found for alloys with higher antimony contents, but occurs preferentially on the minute particles suspended in the liquid. At the final stages of solidification, instead of dendritic tearing there occurs both grain rotation and a more effective consumption of the remaining eutectic liquid. Ideally, the nucleation process should continue as the temperature decreases so that the advantage of the grain-control mechanism is maximized. In turn, this would overcome the problem of the wider freezing range that is common with low-antimony alloys. Therefore, a combination of grain refiners should be used, particularly with very-low antimony alloys. Selenium, which forms the inter-metallic compound lead selenide, has an overall advantage as a grain refiner when compared with sulfur; this is due to a higher solubility in lead and a tendency to be more stable on remelting.

Question: Is there any real advantage to be gained in the production of maintenance-free batteries by employing a grid alloy containing <1 wt.% Sb?

W. F. GILLIAN

In principle, very-low antimony alloys (i.e., <1 wt.% Sb) offer many benefits. Alloys of this type have demonstrated lower electrical resistance and lower gassing rates. In fact, such alloys have the capacity to perform as well as, or better than, calcium alloys. Nevertheless, there are a number of practical issues that need to be fully understood and resolved before very-low antimony alloys become widely used. Some of the difficulties are as follows.

(i) The inherent softness of the alloys. Appropriate material-handling techniques are required for optimum use.

(ii) The compositional stability of the alloys is important, especially for the grain-refining elements. This necessitates very good grid-casting housekeeping.

(iii) Attention should be paid to the plate-curing process. Controlled high-temperature/high-humidity is essential for such alloys.

(iv) Plates using alloys are prone to capacity loss via the 'antimony-free' effect.

(v) As with calcium alloys, the market niche for very-low antimony alloys needs to be identified correctly.

Question: Why does cracking of Pb-2 to 3wt.%Sb cast grids become evident sometimes within a period of days after casting?

W. F. GILLIAN

As mentioned above, low-antimony alloys without the benefits of grain refiners will suffer severe cracking problems. Likewise, if these grain refiners are lost in the casting process, cracking will inevitably occur. It is imperative that temperatures in

the melting pot are maintained in the range 460 to 500 °C. It is also important to ensure that the metal transfer system is not the cause of temperature loss. Feedlines can play a critical role in maintaining the composition and, as a general rule, should be set at least 10 to 15 °C above the melting-pot temperature.

When grain refiners such as selenium or sulfur are lost, shrinkage cracks and stress concentration points are produced in the structure. As the alloy ageing process develops and the grids become harder, stress cracks will begin to appear at these points. The danger period for such cracking is 24 h after casting until peak hardness is reached.

Question: Taking into account the strength of the inter-cell weld and the bus-bar to lug connection, what strap alloy is recommended for (i) low antimony, (ii) very-low antimony, and (iii) lead-calcium grids?

L. E. GARDINER

First, some comments about the cast-on strap (COS) process. The process is more akin to soldering than to the complete fusion of two components. This is particularly true where the grid-lug alloy is low antimony or lead-calcium. Figure 1 shows the type of connection that is preferred in batteries.

As regards the question, strap alloys must have two important attributes. First, the alloy, within the temperature and time constraints of the process, must transmit heat to the surface of the grid lug in order to partially melt the surface of the lug and create a bond. Of course, while the lug is gaining heat, the surrounding alloy is losing heat. Thus, unless the point at which the two reach the same temperature is above the solidification (or freezing) temperature of both alloys (assuming they are different), bonding will not occur.

The second attribute required of the alloy is that, after successful bonding with the plate lugs, the flag or tombstone produced in the cast-on mould should be capable of being successfully welded. In this respect, the hardness of the flag and its grain structure are both of great importance. Long delays between cast-on and inter-cell welding permit age hardening of the metal. Alloys with a high antimony content (>6 wt.%), combined with age hardening, could be almost impossible to weld on equipment that has insufficient power to extrude the alloy through the hole in the partition wall.

In summary, the requirement is for a fine-grained, ductile structure that is not prone to cracking during the welding process. Large-grain structures produce castings that are difficult to weld and frequently produce incomplete and brittle inter-cell connections.

Figure 2 shows the lead-antimony phase diagram, modified to represent the phases and temperatures that occur after pouring in a cast-on mould. The melting point of the eutectic corresponds to that for a typical lead-antimony-tin-arsenic COS alloy. Tests have demonstrated that the strap alloy, after pouring at between 480 and 500 °C, drops to between 440 and 460 °C by the time the lugs are immersed. Therefore, bonding between the strap alloy and lugs can take place until the temperature drops from the value at the time of dip to between 330 and 250 °C; the latter temperature depends on the type of alloy. Obviously, if there were no other considerations, a Pb-11wt.%Sb alloy would be the easiest to use. Nevertheless, after consideration of factors such as cost, tendency to dross in feedlines and, very importantly, hardness,

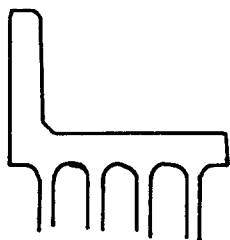


Fig. 1. Ideal grid/lug connection.

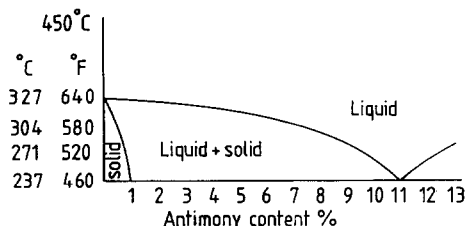


Fig. 2. Lead-antimony phase diagram for COS alloys.

the choice becomes an alloy with between 3.5 and 4 wt.% Sb. Even after the alloy enters the part-liquid/part-solid phase, at around 320 °C, bonding can still take place between the 25% of liquid metal that exists down to the eutectic temperature of 250 °C.

Following the identification of an alloy that gives a good bond with the lug, it must be ensured that the alloy is also suitable for inter-cell welding. This involves the addition of a grain refiner. It would appear that arsenic is favoured by most European companies. Tin is also added but there are differing opinions as to why. Some argue that it is to improve the cast-on connection, others claim that it reduces oxide formation in the feedlines, and particularly on the surface of the lead at the weir edges of the mould. Excessive amounts of tin create problems with tails or feathering at the weir edges. These, if not removed, will cause short circuits in the battery.

The alloy that has been used successfully by major European OEM supplier companies over many years, and that is suitable for the production of low-antimony and calcium grid alloys, is an alloy containing 3.5 to 3.6 wt.% Sb, 0.20 to 0.23 wt.% As, and with other elements in insignificant amounts. It should be noted that no tin is present and this appears to prevent the formation of frays or tails on the straps (a fact confirmed by the author when witnessing the production of OEM batteries for Volkswagen).

By very-low antimony grids, it is taken that the questioner must mean those containing ~1 wt.% Sb. Unfortunately, the panellist has no experience of working with such alloys.

Question: What is the recommended strap/grid-lug volume ratio, and does this vary with the type and make of equipment?

L. E. GARDINER

Let us deal with the second part of this question first, by saying "Yes, it can vary with different types and makes of equipment". Basically there are two moulding/casting methods for cast-on strap: one employs a fairly static mould temperature, while the other employs a cycling temperature. At the panellist's company, the static-temperature type is used with a high degree of control. The latter permits a rapid cycle time and long mould life.

Obviously, with a temperature-cycling mould with an upper temperature of ~420 °C, the huge mass of the mould, combined with the liquid lead, has sufficient heat energy to raise the lug surface temperature to a liquid state and thereby create

the necessary bond. A cooling medium (usually water) is then passed through the mould to lower the temperature to a point where the straps have solidified and are sufficiently hard for ejection to take place.

There are many problems with the temperature-cycling mould system and these are generally associated with mould life and cycle times. Huge amounts of energy are also used and when the energy is gas, the working environment can be very unpleasant and possibly dangerous. On the other hand, straps produced using this method can, in general, be smaller and lighter than those produced with the static-temperature type of mould.

It is difficult to specify a strap/grid-lug volume ratio as so many variables must be considered. Nevertheless, there is certainly a minimum strap volume below which, irrespective of lug volume, a consistent connection cannot be guaranteed. For automotive batteries, the ratio of strap to lug alloy is usually between 8.5:1 and 10:1.

Many factors must be taken into consideration when designing the top-lead layout. These include current-carrying capacity, mechanical strength, and grid height tolerance.

Figure 3 shows the preferred strap-to-lug relative dimensions for an average automotive battery when the following conditions apply.

- (i) Grid lug made from low antimony (1.7 wt.% Sb) or lead-calcium alloy.
- (ii) Grid lugs brushed to a bright metallic finish.
- (iii) Grid lugs of a thickness between 0.8 and 2.0 mm.
- (iv) Difference in grid-lug thickness between positive and negative not greater than 0.3 mm if groups are cast-on as they would be positioned in the battery, i.e., positive-negative, positive-negative. This difference can be increased if all positives are cast on the same side, and all negatives on the other, within the mould.
- (v) Strap alloy made from 3.5 to 4 wt.% Sb with 0.20 wt.% As, and up to 0.1 wt.% Sn if preferred.
- (vi) Appropriate flux is used for the grid alloy.
- (vii) The lead pour temperature is between 480 and 500 °C.
- (viii) The mould temperature is between 150 and 180 °C.
- (ix) The mould is dressed with the appropriate insulating material.
- (x) The lug immersion time is precisely controlled.

Figure 4 shows the method for lead pouring in the TBS system; the lead feedline holds a constant charge of lead at the appropriate set temperature, ready for pouring.

The mould in the filled state, after the lead pump has completed its cycle, is illustrated in Fig. 5. The mould cavities are overfilled to ensure even strap thicknesses after run back. The mould in its filled state, ready to accept lugs after run back, is shown in Fig. 6. An actual group held prior to immersion, within a few millimetres of the molten lead, is represented in Fig. 7. If the previously mentioned conditions apply and the mould is of the static-temperature type, then a satisfactory connection should be achieved.

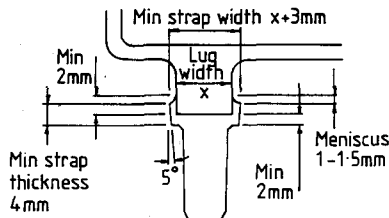


Fig. 3. Preferred strap-to-lug dimensions.

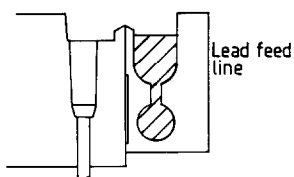


Fig. 4. Mould in prepared state.

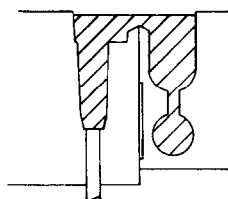


Fig. 5. Mould in lead-filling state.

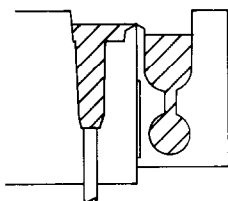


Fig. 6. Mould ready to accept plate lugs.

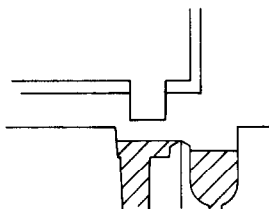


Fig. 7. Lugs prior to immersion.

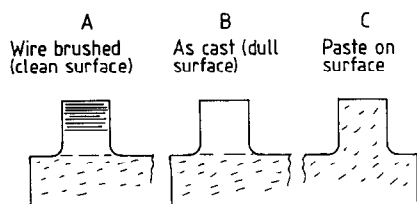


Fig. 8. Plate lugs in different conditions.

Question: How should lugs be prepared prior to the cast-on process? Does this vary with different alloys and varying thickness of lugs?

L. E. GARDINER

Clearly, the joining of any two materials by welding, soldering or brazing is made easier, and the resultant joint stronger, if the abutting faces have all oxides and contaminants removed prior to the process. Therefore, cleaning plate lugs to a bright metallic finish immediately prior to cast-on will produce the best lug-to-strap connection. By presenting components of a consistent standard to the cast-on strap (COS) machine, a consistent connection can be achieved.

By careful pasting, many manufacturers avoid the need to carry out a separate lug-cleaning process. Most COS machines are fitted with lug brushing but, in truth, these will only give a final abrading. For effective cleaning, the plate lugs should be prepared individually so that the sides of the lug are exposed and can be brushed or milled to give a cleaned length of approximately 5 mm. This is vital where either formed positive plates or calcium grid lugs are being processed.

Figure 8 presents a selection of plate lugs and it is obvious which one will give the quality of connection shown in Fig. 1. Lug B will produce a satisfactory connection

providing the lug brush and fluxing system on the cast-on machine are in good working order. Lug C will result in dropped plates and returned batteries and should not be contemplated for cast-on processing. In summary, the cleaner the lugs, the better the quality of the cast-on product.

Question: What type and concentration of flux is required for various strap alloys, lug alloys, etc.? What volume and dipping time is required?

L. E. GARDINER

The panellist's company has tried numerous fluxes over the years; manufacturers tend never to divulge their constituents for fear of their product being copied. These studies have shown that when a grid-lug alloy of down to 1.7 wt.% Sb and a strap alloy of 3.5 wt.% Sb are used, and the lugs have been brushed to a bright metallic finish, then a fairly inexpensive oil-based flux can be used. For grid lugs made from a calcium alloy, a more expensive water-based flux has to be used. The oil-based flux is preferable to the machine manufacturer as, unlike the water-based equivalent, it does not corrode the COS equipment.

As to the volume and dipping time, it is recommended that the lug is very lightly fluxed to a depth of 4 to 5 mm by a brushing system. The aim is to coat the lug without soaking it and leaving any drips. When the lugs are immersed in the lead, the flux gases off and the minimum gassing that occurs maximizes the possibility of cavities developing around the lug within the strap.

Question: Is there any critical temperature range for pouring of alloys?

L. E. GARDINER

Certainly, pour temperatures need to be varied for different alloys, for variations in lug thickness and cleanliness, and for the type of flux being used. When casting-on pure-lead grid lugs to pure-lead straps, the pour temperature is of the order of 530 to 550 °C. Similar high temperatures are also required for the alloys used in valve-regulated batteries and cause the problem of excessive drossing in the lead feedlines. It is therefore recommended that particular attention be paid to lug cleanliness, lug fluxing, mould temperature and mould dressing in order to run the pour temperature such that it is not excessively high to compensate for these other conditions.

Question: What is the best way to check the quality of the cast-on strap weld? Can non-destructive inspection or testing be employed?

L. E. GARDINER

At present, there appears to be no complete method for checking the integrity of the cast-on strap (COS) product. Most companies conduct visual inspections on a random basis and combine these with pulling the odd plate to ascertain if it is loose. Clearly, this is not very satisfactory and is a problem that must be tackled jointly by equipment manufacturers and battery manufacturers. In the meantime, all the conditions

that apply to the COS process should be monitored and maintained within parameters that have been proven by destructive testing to give satisfactory results.

As a result of pressure by a Japanese car manufacturer on one of the leading battery manufacturers in the UK, a system that will go a long way to evaluating the quality of COS welds will be fitted to TBS machines in the next two months.

Question: What are the relative economics of using the cast-on strap technique compared with other methods such as turnover burn?

L. E. GARDINER

This is a very difficult question because there are many variables involved. As a result of labour costs, volumes and mix, Asian battery factories cannot, in general, justify the purchase of expensive automated machinery. More sophisticated equipment requires more technically able maintenance personnel and better support; the first is not always available and the latter is not always given.

With regard to converting from hand-burn to cast-on strap (COS), each case must be considered on its own merits. In the long term, society will doubtless insist on workers being removed from lead-in-air environments. This is already occurring in the richer countries of the world and it will, in time, spread throughout the whole world.

There are of course other considerations for converting to the COS process, of which the most important is the quality aspect. Providing the conditions outlined earlier are met, the quality and repeatability that can be achieved with cast-on is superior to hand burning. This is not to say that hand-burnt batteries are unsatisfactory, or that inferior quality cannot be produced by the cast-on method. It is well known that millions of excellent hand-burnt batteries have been made, and that quite a few sub-standard batteries have been produced by the COS method. In general, it is likely that there will always be hand burning for oddball types of batteries and for low-volume specials, but the way forward is automation with total process control.

Question: Shear testing of inter-cell welds tends to be destructive. Therefore, 100% testing by this means alone appears to be undesirable. What is the best way to test inter-cell welds? Is resistance testing effective?

D. W. H. LAMBERT

The electrical resistance of lead-antimony alloys is quite low. For example, a typical inter-cell connector alloy containing 3 wt.% Sb has a resistance of only $0.0000234 \Omega \text{ cm}^{-1}$ (Fig. 9). Consequently, if a through-the-partition (TTP) weld has a defect and is not completely fused, then the increase in the resistance of the weld is so small that the results of an electrical resistance test, at a typical value of $\sim 100 \text{ A}$, will be inconclusive. By contrast, shear testing is a very effective method for characterizing the integrity of the TTP weld but, by virtue of its destructive nature, is not recommended as a routine Quality Assurance test procedure.

To overcome these problems, it is possible with equipment manufactured by LEKO, for example, to subject each weld to a combined electrical current and shear test, or any desired combination of these two methods. It appears that the best way to evaluate the quality of a TTP weld is to apply, simultaneously, a high current (500

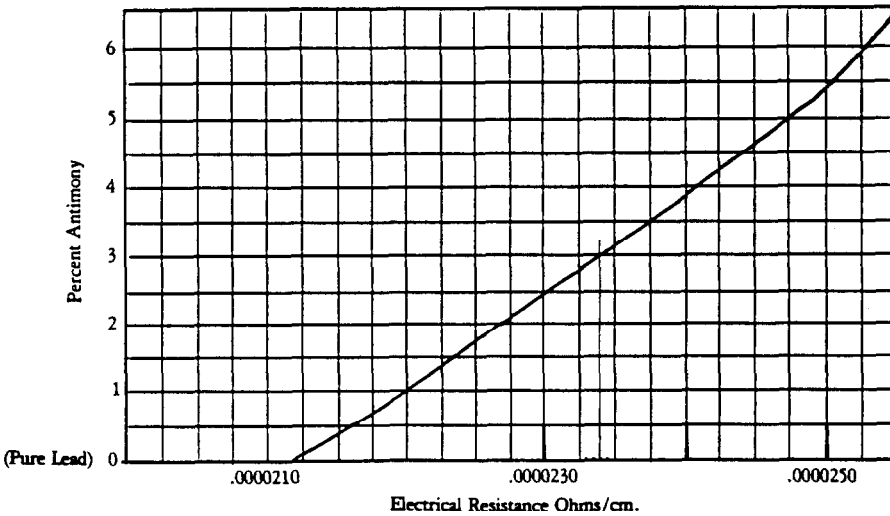


Fig. 9. Electrical resistance of grid as a function of antimony content in alloy.

to 1000 A) and a low shear (~50% of the failure pressure). The destructive shear, torque and peel tests are used as a Quality Control method to establish the correct parameters for the welding process.

Question: Some battery manufacturers determine the correctness of welding conditions via metallographic examination of a sectioned weld. What types of weld structure are commonly encountered?

D. W. H. LAMBERT

Metallographic examination involves cutting a section through the sample under study, mounting this section in acrylic resin, and then polishing and etching to reveal the crystal structure. Optical and electron microscopic analysis is used to determine the effects of variations in the welding parameters (e.g., squeeze time, weld current magnitude (heat control), weld time (current flow time), weld force, hold (cool) time) on the crystallographic structure of the through-the-partition (TTP) inter-cell weld.

Figures 10 to 14 show characteristic failure patterns for 15 mm diameter TTP welds. The latter were taken from a 150 A h commercial vehicle battery, and were subjected to destructive shear tests. The shear test is suitable as an in-the-plant check on the weld quality.

The voids observed in Fig. 10 may result from: (i) porosity in the casting; (ii) oxidized or dirty connectors; (iii) insufficient volume of the electrode projection, e.g., partition hole diameter too large, partition too thick, use of incorrect electrodes. In general, an acceptable quality standard for automotive batteries is: void 1: <3.0 mm diameter; void 2: 3.0 to 4.0 mm diameter. Voids 3 to 5, with diameters >4.0 mm, are unacceptable.

The partial welds and cold spots (ring welds) shown in Figs. 11 and 12, respectively, are caused by insufficient weld time and/or current. Examples 1 and 2 in both Figs. 11 and 12 have a partial weld of >80% and are generally acceptable.

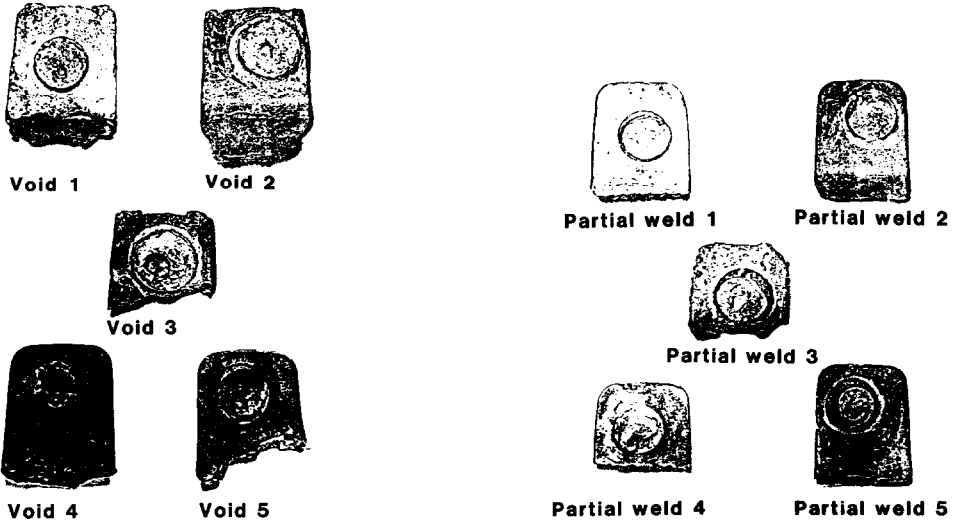


Fig. 10. Ratings for welds with voids: (1) from $\frac{1}{16}$ " to $\frac{1}{8}$ "; (2) $>\frac{1}{8}$ " to $\frac{3}{32}$ "; (3) $>\frac{3}{32}$ " to $\frac{3}{16}$ "; (4) $>\frac{3}{16}$ " to $\frac{1}{2}$ "; (5) $>\frac{1}{2}$ ".

Fig. 11. Partial weld ratings: (1) $\frac{3}{32}$ " weld circle up to, but not including, $\frac{1}{16}$ " weld circle; (2) $\frac{1}{16}$ " weld circle up to, but not including, $\frac{3}{16}$ " weld circle; (3) $\frac{3}{16}$ " weld circle up to, but not including, $\frac{1}{8}$ " weld circle; (4) $\frac{1}{8}$ " weld circle up to, but not including, any part of weld circle post of $\frac{1}{4}$ "; (5) $>\frac{1}{4}$ ".

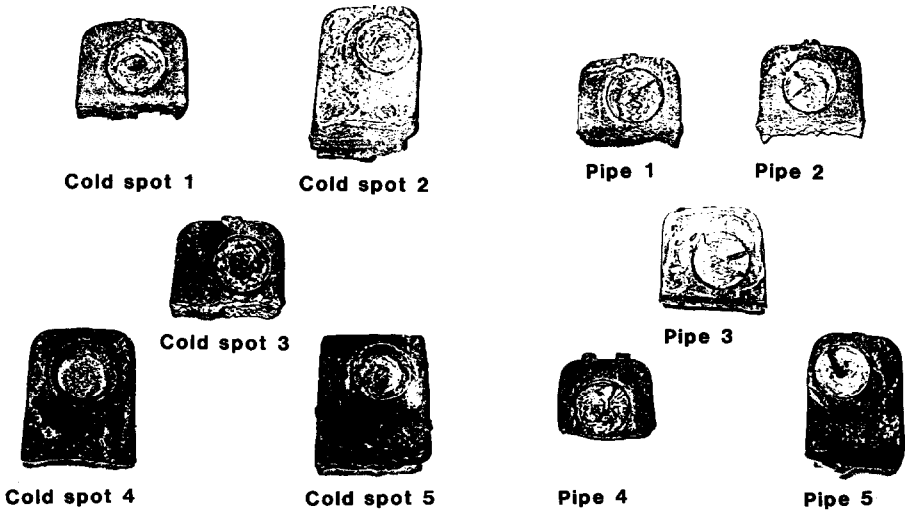


Fig. 12. Cold spot weld ratings: (1) from $\frac{1}{16}$ " to $\frac{1}{8}$ "; (2) $>\frac{1}{8}$ " to $\frac{3}{32}$ "; (3) $>\frac{3}{32}$ " to $\frac{1}{16}$ "; (4) $>\frac{1}{16}$ " to $\frac{1}{4}$ "; (5) $>\frac{1}{4}$ ".

Fig. 13. Ratings for welds with pipes: (1) faint pipe indication, or void, or no more than two not to edge; (2) few small pipes not to edge; (3) one noticeable pipe to edge, or two small pipes to edge; (4) more than one noticeable pipe to edge; (5) large distinct pipes to edge.

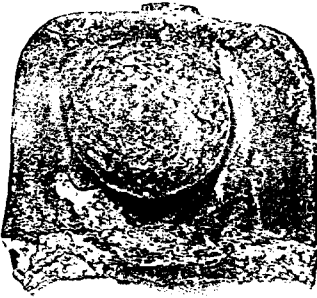


Fig. 14. The perfect weld.

Figure 13 illustrates the effects of a plastic intrusion on the weld quality. Bad hole punching (which leaves flashes or burrs of plastic around the hole), in conjunction with an excessively long weld time, causes the plastic to 'gas' into the weld. This produces 'pipe' defects. Examples 3 to 5 in Fig. 13 are not acceptable.

In order to achieve uniform, high-quality welds (see Fig. 14), it is important that all the following parameters are carefully controlled:

- weld setting variables
- connector alloy composition
- connector age

Note: the above standards for welds must be increased for standby-power and remote-area power-supply (RAPS) multi-cell batteries because of the importance of inter-cell connection resistance.

Separator technology

Question: We are using polyethylene envelope separators in all of our batteries. Upon filling with electrolyte of 1.250 sp.gr. at 25 °C, heavy bubbling is noticeable in all the cells. This bubbling lasts for about a minute and then subsides. What is the cause(s) of this phenomenon and how can it be eliminated? Will such bubbling affect battery quality, e.g., shelf life, life span, initial dry-charge activation?

D. W. H. LAMBERT

The vigorous bubbling is caused by the displacement of air from the pores of the plates and separators. In addition, small quantities of hydrogen and oxygen gas may be evolved as self-discharge reactions commence, i.e.,



All separator materials, (i.e., polyethylene, polyvinyl chloride, paper or glass), by virtue of their microporous structure, will absorb moisture from the local environment. Any moisture present in the separators and/or plates will result in the oxidation of the negative plates during storage. This, in turn, affects adversely the state-of-charge of dry-charged batteries at the time of commissioning.

If a quality product is to be achieved, then all the following manufacturing processes must be carefully controlled. Furthermore, the plate characteristics must be preserved during storage both prior to, and after, assembly:

- plate formation conditions (temperature, acid specific gravity and current density)
- plate washing and drying ($O_2 < 1.0$ wt.% in the negative plate drying oven)
- battery assembly (water-based flux for the COS process evaporates during casting)

Plate processing

Question: Some battery manufacturers have problems in producing battery oxide with a consistent free-lead content. How should a company deal with oxide batches containing excessively high or low free-lead contents (e.g., 40 or 15 wt.%, respectively)?

K. FUCHIDA

The content of free lead in mill oxide is dependent upon the mill operating conditions, e.g., quantity of lead pig in the mill, rotating speed of the mill or reactor, amount of air supply, mill temperature, etc. These operating parameters must be adjusted and maintained within a close range. In particular, a temperature sensor and a device for controlling the air supply should be fitted. Ideally, mill operation should be computerized. Use of a Quality Control chart is very helpful. The mill temperature should be adjusted according to the ambient temperature.

When irregular oxide compositions are obtained, it is essential to examine first the operating conditions of the plant. If these are normal (i.e., mill temperature, pig quantity and air supply are normal), oxide that exceeds specification can be mixed with normal product to achieve the required composition. If, however, the operating conditions are found to be abnormal (e.g., as experienced when a mill is started up after a long shutdown, or operated on an irregular basis), it is advisable to discard oxide that has either a high or a low content of free lead.

Question: What are the conditions in plate processing that give rise to large quantities of monobasic lead sulfate? What ill effects occur with monobasic lead sulfate and what is a safe maximum level?

D. A. J. RAND

Under well-controlled mixing conditions, the level of monobasic lead sulfate ($PbO \cdot PbSO_4 = 1BS$) is controlled by the acid-to-oxide ratio specified by the paste formulation: the level increases when large amounts of acid are used. If the acid is not added slowly and with good dispersion, then localized decreases in the pH of the paste will promote abnormal amounts of 1BS. This influences the consistency of the paste [1] (thus introducing problems during pasting) and lowers the eventual performance of the plates in battery operations.

It is generally considered that 1BS is harmful to plate performance [2, 3]. The material consists of fine, needle-shaped particles that have a poor cohesive strength. Thus, the presence of 1BS will promote shedding of active material during both plate formation and charge/discharge cycling. For this reason, it is advisable to keep the level of 1BS below ~ 10 wt.%.

Question: How does the quantity of sulfuric acid used in the mixing process affect: (i) efficiency of formation; (ii) quality of plates and in-house scrap; (iii) life cycle of the active material?

K. FUCHIDA

Generally, before introducing sulfuric acid to the paste mixture, about 80% of the necessary amount of water should be added in order to prevent the production of lumps and to attain a homogeneous paste.

The quantity of sulfuric acid is defined in terms of concentration and volume. The concentration is usually 1.400 sp.gr., because acid is supplied at this strength. The volume is specified according to plate performance and productivity in the pasting process. The quantity of acid is generally determined by the requirements of process workers and design engineers. When the quantity is too large, the paste mixture becomes 'sticky' and productivity falls. When the quantity is too small, the paste mixture becomes softer and, again, there is a decrease in productivity.

In general, the quantity of sulfuric acid has no significant effect on the electrical performance of the plates. More specifically, the following observations can be made.

(i) It would appear that variations in the amount of sulfuric acid cause little change in the efficiency of plate formation.

(ii) If too much sulfuric acid is used, there is a tendency for the resulting plates to exhibit active-material shedding; naturally, this results in a higher rate of plate rejection. In addition, the paste will become stickier during the processing time and a greater level of in-house scrap will eventuate. Alternatively, if small amounts of sulfuric acid are employed during mixing, then mechanically weak plates will be produced after curing; this, again, creates a high rejection in the parting and assembly processes.

(iii) Sticky paste, caused by the use of excessive amounts of sulfuric acid, does not affect battery cycle life. By contrast, plates prepared from soft paste are susceptible to ready shedding of active material and this will shorten battery life.

Question: How does paste density vary with acid and water additions during paste mixing?

J. E. MANDERS

This is a complex subject that requires a considerable amount of time to explain in detail.

The amount of water and acid required in a paste mix depends on the mixer type, the oxide characteristics (i.e., water absorption, acid absorption, free-lead content, etc.), and the consistency of the paste required for the particular grid-pasting machine. In the case of acid addition, the desired sulfation level is also important. Nevertheless, regardless of these constraints, there are some fundamental 'bulking' factors that apply, although the absolute values may vary.

The cube weight, or 'paste density', is almost a direct function of the total fluids added. Water is a much better bulking agent than dilute acid. For example, at a cube weight of 80 g in^{-3} , 65 cm^3 of acid per kg is required to reduce the density to 4.1 g cm^{-3} (67 g in^{-3}) whereas only 40 cm^3 of water are required. The more water added prior to acid addition, the larger the decrease in cube weight. Hence, almost

TABLE 1
Effect of the quantity of initial water on paste mixing

	Initial water (ml per kg oxide)				
	45	65	85	110	130
Acid (ml per kg oxide)	72	72	72	72	72
Final water (ml per kg oxide)	44	35	24	12	0
Total water	89	100	109	122	130
Total fluids (ml per kg oxide)	161	171	181	194	202
Cube weight (g in ⁻³)	77	75	72	69	67
(g cm ⁻³)	4.7	4.57	4.39	4.2	4.1
Globe penetration	24	24	24	24	24

all water required by the mix should be added initially and prior to acid addition. Water added after acid addition has little effect on paste density. The required cube weight can also be achieved by increased acid addition, but this can be at the expense of over-sulfation of the mix.

Table 1 shows the effect of increasing the amount of initial water added prior to acid of fixed volume to give a paste with a given degree of sulfation (approximately 15%). Final water is added to give a constant consistency, as determined by a Globe penetrometer.

Question: Does the length of time used for kneading the paste affect the quality or performance of the battery? If it does, then what is the chemical mechanism?

K. FUCHIDA

If paste is kneaded for excessive periods, then the contained water will vaporize. As a result, the past becomes stickier and the productivity of the mixing process will be lowered. Conversely, if the time for paste kneading is shortened, the mixture will not be homogeneous and the resulting batteries will exhibit wide variations in performance. In each plant, the mixing time has been determined according to many trials and experiences that have identified the optimum conditions in terms of plate performance and productivity.

In addition to the kneading time, the storage time prior to pasting is important. In the simplest terms, the chemical mechanism of mixing is:



but the compounds $\text{PbO} \cdot \text{PbSO}_4$, $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$ and $4\text{PbO} \cdot \text{PbSO}_4$ may also be produced. For further details of the phase composition and morphology, readers are referred to the published literature, e.g., ref. 4.

Question: Is there any problem associated with re-using waste paste from the pasting machine by mixing a proportion back through the mixer? If it is acceptable, what is the recommended maximum proportion?

K. FUCHIDA

If it is desired to re-use waste paste, it is recommended that an experiment be conducted in which the waste paste is mixed with normal product and processed into finished plates and then the plates tested for mechanical strength, discharge capacity, life, etc. It is further advisable that waste paste is put into negative plates at 10 wt.% or less, and that the waste paste is used immediately it is produced. Waste paste from mixture washing at the end of a work shift is not usable.

Question: What are the recommended tests and required specifications for cured plates? In particular, what is an accurate method for determining the free-lead content?

D. A. J. RAND

The curing process is that stage in the production of flat plates during which a paste of lead particles ('free lead'), lead oxides, sulfuric acid and water is converted to a cohesive, porous mass that becomes strongly bonded to the supporting grid [4].

Prior to curing, and directly after pasting, the plates are passed rapidly, at high temperature, through a tunnel oven in order to reduce the water content of the paste to the optimum range for efficient curing, and to dry the surfaces so that the plates will not stick together during subsequent handling. This process is called 'flash drying' and after this stage the plates should contain 8 to 9 wt.% water and 8 to 10 wt.% free lead.

The second important effect of curing is to bond the plate material to the grid. Apparently, mild corrosion of the grid establishes a firm contact between the grid surface atoms and the oxides or basic lead sulfates in the paste. This process generally requires periods of the order of 24 to 48 h to become effective.

Finally, the plates are dried and, at this stage, should contain ~3 wt.% water and ~2 wt.% free lead.

Given the importance of moisture content, temperature and time, plates should be cured in well-regulated environments. This requires the use of purpose-built ovens (or chambers) that provide temperature control, forced air flow, and humidification [5]. The latter is particularly important when plates containing high contents of tetrabasic lead sulfate ($4\text{PbO} \cdot \text{PbSO}_4 = 4\text{BS}$) are required, otherwise the higher temperatures that must be employed may cause premature drying and, therefore, will lower the conversion of basic lead sulfate.

The oxidation of free lead and the loss of water are two major, inter-related, processes that take place during curing. Moisture is required to catalyse the lead oxidation process which, in turn, produces heat and thereby tends to dry out the plate. The rate at which water leaves the plates can be controlled by the ambient humidity conditions. The third major change during curing is the progressive growth (and inter-conversion) of basic lead sulfates. At temperatures below ~70 °C, the predominant species is tribasic lead sulfate ($3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O} = 3\text{BS}$) and unreacted lead monoxide (usually $\alpha\text{-PbO}$). At higher temperatures, and in the presence of sufficient water, 3BS recrystallizes to 4BS. It is also possible for basic lead carbonates (e.g., hydrocerussite, $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2 = \text{HC}$) to be formed, especially on the surface of the plate material.

Water content, free-lead content and plate strength are the most common tests for monitoring quality control during the curing process. The water content is determined by the simple procedure of periodically removing a plate from the curing chamber, weighing it, and then drying at 70 °C until the weight becomes constant. The difference between the initial and final weights gives the water content. The plate strength can be evaluated by conducting vibration tests. These, however, require fairly sophisticated (and expensive) equipment. Therefore, many manufacturers apply the simple, but effective, 'drop test'. The plate is allowed to fall from a height of ~150 cm so that it lands on its face. The amount of dislodged active material is taken as a measure of plate strength; judgement on the plate's acceptability is empirical.

Free lead can be measured by either physical or chemical methods. Good accuracy is essential as excessive amounts of free lead can result in the swelling and warping of plates, extensive shedding of material, short circuits, etc — both during the subsequent formation stage and during actual battery operation. Differential scanning calorimetry (DSC) is the most reliable method for determining free lead [6], but has the disadvantages of requiring expensive and sophisticated equipment, a high level of skill for operation, and a long running time. For these reasons, chemical methods are generally preferred. Several chemical formulations are in frequent use. All operate on the same principal: the mixtures dissolve the lead oxide and lead sulfate from a given amount of plate material to leave the uncombined lead which is then determined by weighing. Studies at CSIRO have shown, however, that there are difficulties in obtaining good accuracy in the presence of red lead (with leady oxides) and/or basic lead sulfates (with cured materials). As a consequence of these investigations, a specific procedure has been developed. This is based on the use of ammonium acetate and dihydrochloride hydrazine ($N_2H_4 \cdot 2HCl$): a mixture that converts red lead to soluble divalent lead monoxide. The suitability of this method has been confirmed by comparing measurements of the free-lead content in a range of leady oxides and cured materials with those obtained by DSC, X-ray diffraction (XRD), and alternative chemical procedures.

Finally, it is also important to monitor the levels of the basic lead sulfates in the cured material since these compounds exert a strong influence on plate performance (i.e., 3BS-rich material promotes capacity, while 4BS-rich material imparts cycling capability). This is most readily achieved by application of XRD phase-analysis techniques. In this respect, the PEAKS[®] procedure developed in the CSIRO laboratories [7] is now widely used by battery companies throughout the world for quality control, trouble shooting, and research and development.

Question: What are the recommended curing procedures for positive plates with grids made from very-low antimonial alloys (i.e., ≤ 1.7 wt.% Sb)? Do positive plates with different antimonial alloys require different curing conditions?

D. A. J. RAND

Flooded-electrolyte batteries

Positive plates with very-low antimonial alloy grids are subject to the antimony-free effect during discharge [8]. The suggestion [9] that the problem can be ameliorated by promoting a high level of α -PbO₂ in the grid corrosion product, together with the popular belief that tetrabasic lead sulfate ($4PbO \cdot PbSO_4 = 4BS$) favours the formation

of α -PbO₂ [10], has encouraged some manufacturers to adopt a high-temperature curing process for plates with grids fabricated from very-low antimonial alloys. The 4BS/ α -PbO₂ relationship has, however, been questioned by Culpin [11] and experimental evidence has now shown [12] that the phase composition of the cured material exerts little influence on the crystal modification of the PbO₂ produced during plate formation. Thus, there is no reason to suppose that a 4BS-curing route offers any benefits to plates with very-low antimony alloys. Indeed, such processing may in fact be detrimental. For example, Chang [13, 14] has found that the premature failure is due to the preferential discharge of the grid corrosion product and, consequently, has suggested that the problem may be ameliorated by restricting the access of acid to the grid surface. The open structure formed by the large 4BS crystals (compared with the tribasic lead sulfate counterpart) is not conducive to such a requirement. Furthermore, the high-temperature conditions necessary for the production of 4BS may invoke thermo-passivation problems (i.e., the development of α -PbO). On the other hand, it is well known that 4BS improves the grid/active-material adhesion and extends the deep-discharge cycle life of batteries with plates fabricated from high antimonial alloys (> 3 wt.% Sb). It may be possible to pass these advantages on to very-low antimonial plates if other parameters (e.g., active-material composition and density, plate thickness) can be controlled to minimize the acid concentration in the vicinity of the grid. Since 4BS-rich plates exhibit a reduced initial capacity during cycling, they are not generally used in high-rate designs of batteries (e.g., automotive types).

Valve-regulated batteries

Batteries using very-low antimonial alloys suffer charge-acceptance (passivation) problems after prolonged discharge or self-discharge. This is due to the formation of a lead-monoxide (α -PbO) layer directly on the grid surface when the acid concentration is low. The problem is particularly acute under the acid-starved conditions of valve-regulated batteries. Thus, any feature that increases the acid concentration near the grid should be beneficial to plate performance. For this reason, the more porous structure emanating from 4BS-cured plates is considered by some manufacturers to be the best approach to plate processing.

Question: Are there any technical problems in making dry-charged plates from lead-calcium grids?

J. E. MANDERS

There have always been problems associated with producing quality dry-charged batteries. The degree of charge retention is limited to a certain period of storage that is dependent upon the quality-control techniques employed during both production and storage prior to activation.

There are no further problems associated with using calcium alloy for the negative plates. More emphasis should, however, be placed on positive-plate washing and drying in order to avoid lead sulfate formation at the grid/paste interface (Fig. 15) and to prevent thermal passivation [15]. Ideally, all positive plates should be dried at the lowest temperature possible. Dry-charged calcium positives should not be subjected to temperatures above 60 °C and antimonial positives should be kept below 80 °C.

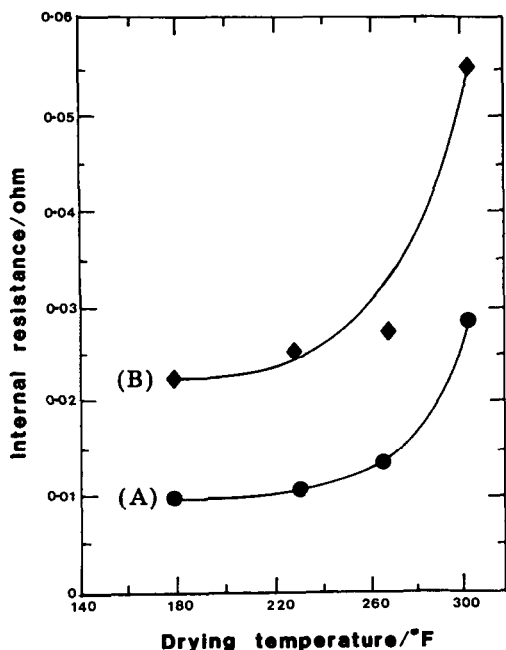


Fig. 15. Effect of drying temperature on positive-plate resistance (at 15% relative humidity): (A) well-washed plates; (B) rinsed plates [15].

Question: What are the advantages and disadvantages of producing a dry-charged valve-regulated lead/acid battery prior to filling with electrolyte?

J. E. MANDERS

The state-of-the-art for valve-regulated lead/acid batteries (VRBs) with absorptive glass mat separators is to tank form and charge the plates prior to cell assembly and electrolyte filling. There are, however, some definite advantages and cost savings (see Table 2) to be gained by substituting this procedure with container formation. At present, a number of manufacturers produce batteries — particularly small sizes — by this method. Meanwhile, others are endeavouring to develop the technology. Nevertheless, unless a radical change is made to the separator material and certain technical problems are overcome (Table 3), tank formation will remain the favoured practice for dry-charged VRBs.

Question: Some dry-charged batteries exhibit full charge very soon (or immediately) after acid filling. What are the main factors or considerations that give rise to this capability?

J. E. MANDERS

The ability of a dry-charged battery to provide a high percentage of its full charge on activation with electrolyte depends on the level of oxidation of the negative active material and/or the internal resistance of the positive plate. The high resistance of

TABLE 2

Advantages of container formation for absorptive-glass-mat VRBs

Cost savings	removes washing process, i.e., less:	power water effluent treatment labour space and equipment
	removes dry-charging process, i.e., less:	power labour doubling handling space and equipment
Flexibility	removes many of the problems of tank formation of very thin grids and small grids	

TABLE 3

Disadvantages of container formation for absorptive-glass-mat VRBs

If a single fill, form and dump operation is to be employed, then the specific gravity of the electrolyte will need to be of the order of 1.210 to 1.240 to give a final service gravity, after dumping, of 1.270 to 1.290. If formation electrolyte of a lower specific gravity is used, then a series of fill and dump operations must be undertaken to arrive at a consistent final service specific gravity. This would remove most of the advantages listed in Table 2.

Effect of 1.210 to 1.240 sp.gr. acid

- | | |
|---|---|
| (i) less efficient formation | time longer/more power
quality/incomplete processing
higher temperature |
| (ii) antimony-free effect more pronounced | predominantly β -PbO ₂ , i.e.,
poor cycling
PbSO ₄ at grid interface, i.e.,
poor performance |

Effect of separator compression

- (i) formation difficult
- (ii) hydrogen gas entrapment
- (iii) dendritic growth — offset by Na₂SO₄ addition

Additional problem

pore-volume/void-volume difficult to achieve because system is fully saturated with electrolyte

the positive plate can be controlled by attention to the plate-washing process and by ensuring that thermo-passivation does not occur during plate drying [16]. The temperature should be kept below 80 °C.

With negative plates, oxidation of the active material must be minimized as far as possible during: (i) the dry-charging process itself; (ii) plate storage; (iii) battery storage [16].

Battery performance

Question: Some manufacturers outside Japan find confusion with the JIS D 5301 procedure and endurance test. This confusion relates to interpretation of the cycle termination, i.e., Clause 8.3.6-(4) which states: "The test is terminated when it is verified that the capacity, obtained as the product of the discharge time and the discharge current measured in the test, decreases to 50% or less of the capacity (5-h rate) given in Table 1." Should the product of time and current, in ampere-hours, be used to find the percentage of the 5-h capacity, or should the measured ampere-hours be adjusted to the capacity at the 5-h rate before the percentage of the 5-h capacity is assessed?*

K. FUCHIDA

First, the JIS D 5301 procedure was revised in May 1991. It is expected that an English version of the new JIS D 5301 test will be published around December 1991. The main feature of the revision is the addition of a light-load endurance test. This is intended to cover calcium-alloy maintenance-free batteries. The latter technology is becoming widely used in Japan but does not meet the deep-discharge requirements of the previous schedule.

The revised JIS standard now includes a 10% depth-of-discharge test (i.e., similar to the SAE cycle test) as the light-load test; the previous test has been renamed the 'heavy-load test'. A battery is regarded as acceptable if its endurance meets that specified by either of the two tests. The heavy-load test has been retained in the JIS standard because of the strong trend towards an increase in the power requirements of automobiles. The procedure for each test is as follows.

(i) *Heavy-load test.* Discharge the battery at a specified discharge current, according to the battery size, and repeat charge and discharge until the value of the discharge time during one cycle multiplied by the discharge current reaches 50%, or less, of the designated 5-h capacity, at which time the number of discharge cycles is counted.

(ii) *Light-load test.* Discharge the battery at 25 ± 0.05 A for 5 min at 40 to 50 °C, and then charge at 14.8 ± 0.03 V for 10 min. Repeat the treatment for 480 cycles, and let the battery stand for 16 h after the last charge. Then, discharge the battery at a separately specified discharged current and measure the battery voltage after 30 s. When the latter reaches 7.2 V, or lower, terminate the test. Count or calculate the number of cycles.

There is no need to convert the capacity to the 5-h value. Simply, the multiplied value of the discharge current and discharge duration for every 25 cycles is counted and compared with 50% of the designated 5-h capacity value. When the test is finished, the number of the discharge cycles can be counted. When the final discharge capacity falls below 50% of the designated value, it can be adjusted to the correct 'endurance value' by using both the previous discharge and the last values.

The JIS standard specifies discharge currents in only three categories and, therefore, some batteries (e.g., 36B20) may be discharged at a higher current than that equivalent

*Note, the reason for the confusion is the inconsistency in the rates of discharge. For example, the NS40 type of battery is discharged at 10 A at approximately the 2-h rate. This also holds for N70 (at 20 A) and N120 (at 40 A) batteries. By contrast, the NS40ZA design is discharged at the 1-h rate and the N200 at the 4-h rate. If all the measured capacities are factored back to the 5-h capacity, then the inconsistencies will be removed.

to the 5-h rate. Theoretically, a battery should be discharged at the actual 5-h discharge current, depending on its size and designated capacity. Computer-assisted and easily adjustable test equipment is now becoming available to allow this practice. Therefore, it is possible that the heavy endurance test may be further modified and improved at the time of the next revision of the JIS standard; this is expected in 1994.

Question: There are some arguments between the end-users and the manufacturers with regard to the 'overcharged battery' claim. (i) What is the definition of an overcharged battery? (ii) What are the signs/symptoms of an overcharged battery without conducting a post-mortem on the battery? (iii) Are there any signs/symptoms of an overcharged battery due to faulty car alternators?

D. W. H. LAMBERT

An overcharged battery is one in a fully charged condition that is then subjected to an additional charging current. Overcharge accelerates the corrosion of the positive

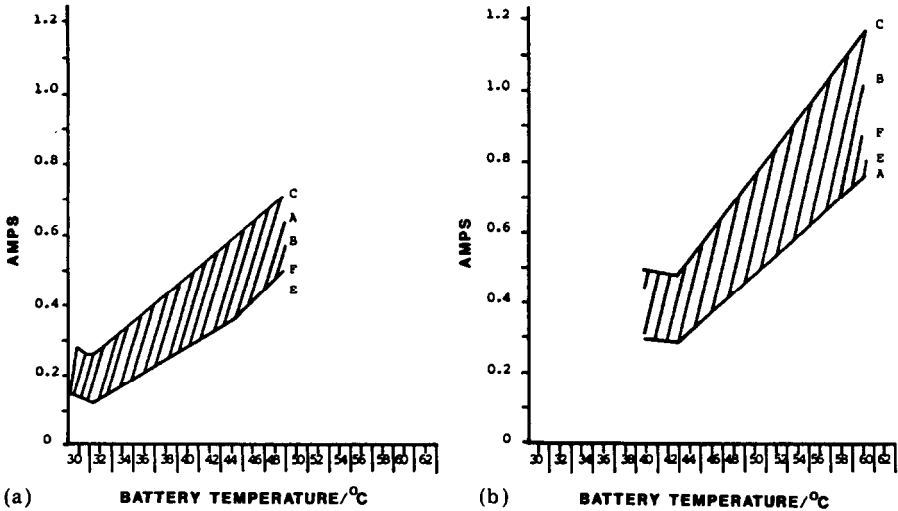
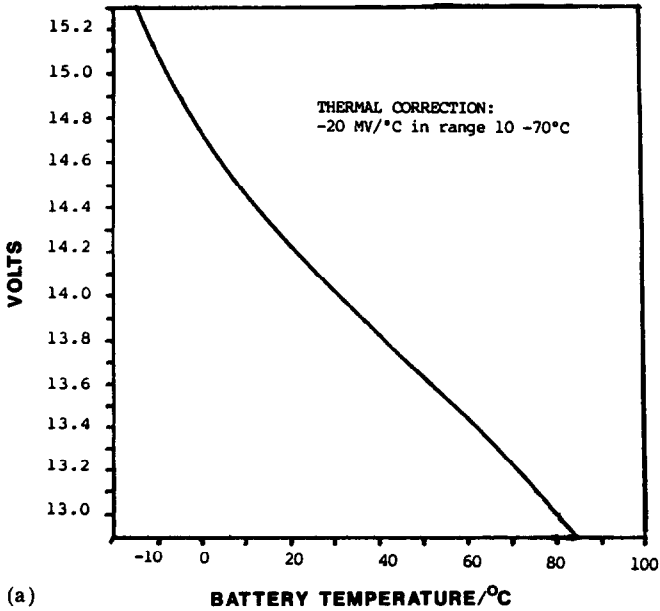


Fig. 16. Range of charging currents arising at ambient temperatures of (a) 30 °C and (b) 40 °C with different regulators A–F [17].

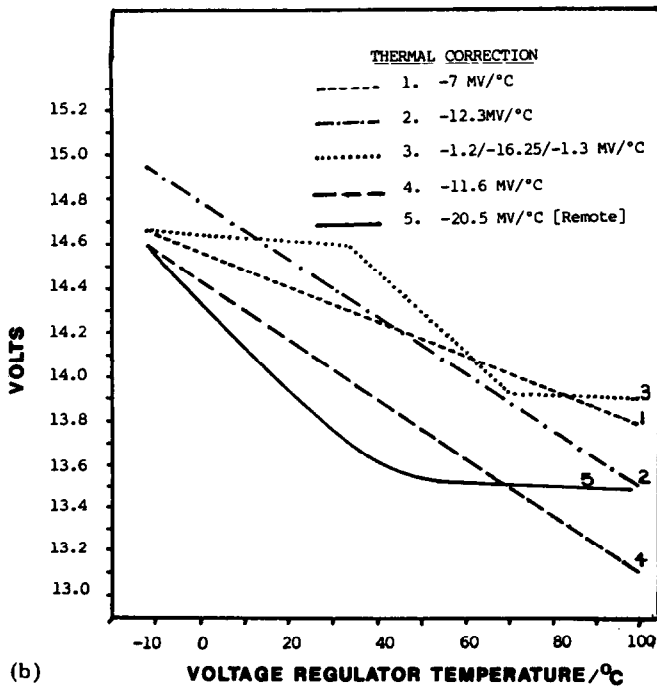
TABLE 4

Main factors affecting charging voltage

1. Availability of current from the alternator
2. The ability of the charge system to stay out of nett discharge conditions
3. Ambient temperature
4. Age of battery
5. State of original charge
6. Electrolyte level
7. Impurity content of electrolyte
8. Grid alloy specification



(a)



(b)

Fig. 17. (a) Voltage required to maintain full charge effectively for a low-maintenance battery at varying temperatures. (b) Comparison of present-day voltage regulators with varying thermal correction [17].

grids and promotes excessive gassing during charging. The latter loosens the active material (particularly in the positives) and thereby reduces the useful service life of the battery. The active material from the positive plates is deposited as a fine brown sediment. This may be observed, quite clearly, after agitating the electrolyte in the cells, e.g., by syringing the acid into and out of a hydrometer bulb several times.

In addition, overcharging increases the temperature of the battery; 40–50 °C is not uncommon and, in some cases, temperatures in the range 60 to 90 °C have been observed. These conditions will bring about the destruction of both separators and plates.

Rapid loss of water also accompanies the overcharge reaction, i.e., approximately 33 cm³ water loss/100 A h overcharge. This problem is readily identified by the constant need for water replenishment in order to maintain the correct electrolyte level in 'low-maintenance' batteries, and by the drying-out of the non-maintainable automotive battery types that are fitted with irremovable vent plugs.

All automotive batteries, particularly in tropical climates (> 30 °C ambient), are subjected to varying amounts of overcharge, Fig. 16 [17]. This is the result of a mismatch in the voltage/temperature characteristics of the battery and alternator, Fig. 17 [17]. The charge voltage is affected by eight main factors, see Table 4. Without careful attention to these parameters, during both the specification and the subsequent use of the power system in the vehicle, the battery will be subjected to overcharge and its operational life will be reduced.

Question: When full with electrolyte, normal batteries will produce a faint smell. In some instances, a strong pungent smell develops. This is attributed to hydrogen sulfide. What are the conditions that cause this compound to be formed and how can the problem be rectified?

D. W. H. LAMBERT

A search of the literature has failed to reveal a definitive explanation for the development of this phenomenon. Consequently, the following mechanism is proposed.

During the drying of negative plates, particularly in (inert) gas ovens, any residues of sulfuric acid left over from the plate-washing stage will be decomposed to lead and antimony sulfide on the surface of the negative active material. When the plates are subsequently activated, the antimony sulfide reacts with the sulfuric acid, forming hydrogen sulfide, i.e.,



This gas is responsible for the pungent odour that sometimes accompanies the activation of dry-charged plates and batteries as discussed by Manders [16]. Careful and complete washing of the negative plates, prior to drying, is therefore critical.

Other dry-charge processes, such as vacuum oven, hot plate, solvent displacement (e.g., 'TUDOR' paraffin) or superheated steam oven, seem less prone to the generation of hydrogen sulfide.

Question: Certain telecommunications users of valve-regulated lead/acid batteries state that such batteries are more prone to thermal runaway than flooded cells. If this is correct, what is the reason and what precautions should be taken to avoid such behaviour?

K. FUCHIDA

It is indeed true that valve-regulated lead/acid batteries (VRBs) will suffer thermal runaway if not maintained correctly. VRBs have less volume of electrolyte than conventional flooded cells, and if the electrolyte in the former evaporates and decreases, then the negative plates become exposed more quickly. This exposure reduces the active area of the negative plate and thereby accelerates the gas-recombination process so that heat is produced continuously and begins to accumulate. In turn, the heat promotes the gas-recombination reaction. If these processes are repeated, they accelerate the generation of heat so that it becomes discernible even on outer faces of the battery. Simultaneously, heat causes water evaporation and an increase in the electrical resistivity. Both these effects also stimulate heat generation.

In addition to water evaporation, concentration of electrolyte occurs, and this promotes the growth of the so-called 'barrier layer' and brings about an increase in plate resistivity. The heat generated by these processes accumulates and is finally released to the outside of the battery.

Under severe conditions, grid corrosion causes the growth of plates (especially the positive plates), the development of shorts between both plates, or cell breakage. In the worst case, these effects result in fire or explosion in the battery.

In order to prevent thermal runaway, the following counter-measures should be taken; they are based on avoiding water evaporation due to external and/or internal heat generation.

(i) The operating temperature should be kept below 30 °C.

(ii) When batteries are assembled in a close-packed configuration, they should be so arranged that heat can be readily released to the outside. One measure is to provide good clearances between the batteries. When a VRB is used with a battery charger or an inverter, it should be positioned so that the heat generated from the equipment is not conducted to the battery.

(iii) When a VRB is used on a float charge, the voltage should be adjusted to lower than instructed.

(iv) The temperature of the battery should be monitored during the summer months.

Question: Grids made from Pb-2wt.%Sb alloy are allowed to stand for up to 7 days prior to pasting so that they may harden sufficiently. Does this pose any problems as far as corrosion of the grid surface is concerned?

W. F. GILLIAN

The storing/ageing of grids for periods beyond a day, in order to achieve hardness, is basically a waste of space, money and effort, and is also counter-productive to quality. In the panellist's opinion, the only legitimate reason for storing grids (and this is still doubtful) is in the need to meet production/planning shortfalls or to introduce some level of flexibility in product type.

If storing is to be carried out, it should be conducted in a controlled manner. The stocks should be: (i) covered/protected from the atmosphere; (ii) stored in a secure location away from fork-lifts, wash-down water, etc.; (iii) rotated on a regular basis.

In regard to surface corrosion, a surface layer of oxide is quite normal and by itself does not present a quality problem. If, however, a more complex corrosion product (such as $\text{PbO} + \text{PbSO}_4$ and/or some hydrate or carbonate) is developed, this may lead to local passivation problems that, in turn, will have an influence on the general corrosion behaviour.

Of similar concern should be the risk of contamination from other products used throughout the plant, e.g., barium, iron, copper. There have been many examples of external contamination causing serious batch-failure of batteries. These remarks are equally applicable to lead-calcium alloys.

Question: How can the capacity loss during cycling of positive plates using lead-calcium alloys be minimized?

J. E. MANDERS

The capacity loss during cycling of calcium positive plates cannot, at present, be totally prevented. Nevertheless, the degree of impact of the antimony-free effect can be minimized by using certain processing and design techniques. All of the adjustments involve some cost in terms of equipment and material utilization. Therefore, a balance must be made between these disadvantages and the performance required for the product.

There are two distinct effects when antimony in the positive grid is replaced with calcium. For the purpose of this discussion, these effects are denoted the Sb^1 and Sb^2 effects, i.e.,

(i) *Sb^1 effect.* Early and random failure of a varying proportion of electrodes due to the development of a high-resistance barrier layer at the grid/active-material interface.

(ii) *Sb^2 effect.* This appears later in a service life and causes a gradual decay in the performance of the active material; the latter becomes inactive, though not necessarily through shedding.

The Sb^1 effect can result in cells exhibiting very low (or no) voltage and an inability to accept charge. Clearly, the effect must be nullified. Under the influence of the Sb^2 effect, cells fail to provide satisfactory life under cycling conditions; the deeper the discharge required, the more pronounced the effect. It is obvious, therefore, that when cycling is required, this second effect should be minimized.

To nullify the Sb^1 effect, it has been found that the grid alloy should contain at least 0.25 wt.% Sn, and that plate curing should be conducted at higher temperature and humidity conditions than standard (e.g., $> 64^\circ\text{C}$, 100% humidity). Similarly, the Sb^2 effect can be minimized by using: (i) higher curing temperatures, viz., 85 to 95°C , 100% humidity; (ii) high density paste, viz., 4.5 g cm^{-3} (74 g in^{-3}).

When using calcium positives, most manufacturers apply the above conditions as a minimum specification. Other design/process features include:

- heavier grid structure, including thickness and number of wires
- greater loading of positive active material
- tight assemblies

- burying of grid wires in paste
- limiting of acid and excessive PbSO_4 by using low acid sp.gr.
- limiting depth-of-discharge by addition of phosphoric acid
- favouring $\alpha\text{-PbO}_2$ formation by using formation acid of low sp.gr. and at low temperature

Question: What are the major causes of failure of: (i) flooded-electrolyte batteries in both automotive and deep-discharge cycling applications; (ii) valve-regulated batteries?

D. A. J. RAND

In order to classify the failure modes of lead/acid batteries, it is necessary to distinguish between catastrophic battery failure, as characterized by a sudden inability of the battery to function, and progressive failure, as demonstrated by a gradual decline in capacity [18].

In general, *catastrophic failure* is easily diagnosed and characterized. The following problems are commonly encountered:

- incorrect cell design and component selection
- poor quality control during battery manufacture
- incorrect operation of batteries ('abuse')
- external and/or internal damage

Clearly, there is a certain degree of overlap between some of these categories, and battery failure may have indeed resulted from some combination of effects.

Progressive failure is more difficult to predict and explain. Often, it represents a subtle deviation from optimum performance that originates from microscale changes in plate characteristics brought about by the influence of manufacturing variables and service conditions. Parameters that depend upon the materials, processing and design of the battery are known as 'inner parameters'. While those determined by the conditions of battery use are referred to as 'outer parameters'. The parameters are:

Inner parameters

- the chemical composition and physical properties of leady oxide
- the composition (including additives), density, method of application, loading and pellet size of the paste
- chemical composition and structure of cured plates (flat type) or pickled plates (tubular type)
- chemical composition and structure of formed plates
- plate thickness
- composition and processing conditions of grids
- composition (including additives) of electrolyte
- choice of separator
- cell design

Outer parameters

- storage time before use
- frequency and current density of discharge
- depth-of-discharge
- stand time in a state of partial or complete discharge
- current and voltage of recharge
- degree of overcharge
- temperature
- uniformity of concentration and maintenance of electrolyte

Both sets of parameters will act (to varying degrees) to cause the eventual failure of the battery.

Failure modes of flooded batteries

Negative plate. Over the years, developments in lead/acid 'technology' have resulted in significant improvements in the performance of negative plates. In particular, the use of 'expanders' has given a very long-life negative plate that is rarely the cause of battery failure. The expander reduces the tendency for the spongy lead to coalesce and densify. Thus, expanders impart favourable low-temperature and high-rate capabilities to the negative plate, in addition to inhibiting capacity-loss processes. Nevertheless, degradation of the lignin fraction of the expander, and hence failure of the negative plate, may occur via:

- solubility in the electrolyte (and thus transport to the positive plate and destructive oxidation thereupon)
- thermal decomposition during battery manufacture or service
- chemical reaction with sulfuric acid

Of these, thermal stability has emerged as the most important criterion for expanders as certain applications (e.g., automotive and RAPS duties) are requiring batteries to operate under increasingly aggressive conditions of elevated temperature.

Separator. Apart from obvious faults associated with mechanical defects, construction errors and damage during battery manufacture, common problems arising with separators include:

- degradation under conditions of persistently high temperature
- attack from contaminants (introduced, for example, via top-up water)
- failure to resist penetration by lead dendrites growing from the negative plate, i.e., 'leading-through'

Nevertheless, advances in polymer science now allow the use of thin, low-cost, high porosity, small pore-size materials so that the separator is no longer a major determinant of battery life.

Positive plate. The positive plate is the major life-limiting factor. It should be remembered that the positive plate has to be sufficiently robust to withstand the mechanical stresses caused by the differences in the molar volumes of the active material (PbO_2) and the discharge product (PbSO_4). Under such forces, however, the structure of the active material tends to change with repeated charge/discharge cycling; the agglomerate structure is gradually and irreversibly broken down into individual crystallites. This process causes softening and shedding of the active material. The latter, in turn, promotes the secondary problems of 'mossing' and 'leading through'. The loosening of the inter-particle contact, together with the fact that not all of the PbSO_4 is necessarily converted back to PbO_2 during charging, also causes a reduction in electrical performance.

The corrosion and growth of positive grids are also life-determining degradation phenomena. These processes have been the subject of a vast number of studies. In summary, the results show that the rate of grid corrosion is influenced by the:

- grid composition and microstructure
- plate potential
- electrolyte composition
- temperature

These parameters, together with the geometry of the grid and the creep properties of the alloy, also determine the growth (or elongation) of grid members during battery service.

During the discharge and recharge of batteries, sulfuric acid is, respectively, consumed and produced. These processes can result in the development of a vertical concentration gradient of acid. This gives rise to non-uniformity in both current distribution and active-material utilization — factors that shorten service life through the irreversible formation of PbSO_4 — as well as to irregular grid corrosion and growth. Acid stratification is a particular problem in tall cells and can be avoided by agitating the electrolyte, e.g., by ‘gassing’ during extended overcharge, air bubblers, or circulation with pumps.

A particular problem arises with grids made from lead–calcium alloys, namely, batteries can exhibit a rapid walkdown in deep-discharge capacity with cycling. This degradation in performance is more severe than that observed for batteries with lead–antimony alloys containing $> 1 \text{ wt.}\%$ Sb and, accordingly, has come to be called the ‘antimony-free effect’. In other words, there is a general consensus of opinion that the premature loss of capacity is due to the absence of antimony, rather than to the presence of calcium. Nevertheless, an unequivocal understanding of the effect has still to be found.

Major failure modes of valve-regulated batteries

Grid corrosion. Grid corrosion is an important life-limiting process for valve-regulated batteries (VRBs) that are used in float, cycling and remote-area power-supply (RAPS) duties. This is not unexpected as the polarization characteristics of electrodes in VRBs are different to those of electrodes in flooded-electrolyte designs. In particular, the float current is higher because of the depolarizing effect of the recombination reaction on the negative electrode [19]. Furthermore, for the same applied cell voltage, the positive in a VRB will experience a higher potential. These characteristics will influence the rate of grid corrosion.

During overcharge, water is lost at the positive, and this gives rise to an increase in acidity ($2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$) and, hence, in corrosion rate. This effect is compounded by the gradual loss of water during service life as the recombination efficiency is $< 100\%$. Finally, the partial saturation of the system and the oxygen environment around the positive also serve to enhance grid corrosion, particularly later on in life when the saturation falls below the initial level.

These effects are mitigated to a certain degree by the cell design of VRBs. In this, the plates are held under compression so that mechanical support of the grid is less of a problem than in flooded batteries.

Grid growth. The incidence and severity of grid growth is determined by the creep resistance and tensile strength of the alloy used, the extent of the corrosion, and the morphology of the corrosion product. VRBs can be designed to accommodate some grid growth. Excessive corrosion can, however, be accompanied by appreciable grid growth. This promotes loss of contact between the grid and the active material and, in severe cases, gives rise to the development of short circuits.

Water loss. Water is lost from VRBs via:

- recombination inefficiencies (particularly under cycling duty)
- permeation through the container material (the driving force is the difference in water vapour pressure between inside/outside)
- grid corrosion ($\text{Pb} + 2\text{H}_2\text{O} \rightarrow \text{PbO}_2 + 4\text{H}^+ + 4\text{e}^-$)

Water loss will reduce the degree of saturation of the system and, consequently, will increase the resistance of the separator. This is particularly important in automotive

applications where the batteries are required to deliver high currents for engine starting. For low-rate applications, a much greater water loss can be tolerated before the deterioration in battery performance becomes significant. At this stage, the problem will be compounded by an increase in the rate of grid corrosion that is brought about by the development of a higher acid concentration. In this situation, failure of the battery will result from a combination of both effects.

Acid stratification. With VRBs, it is obviously not possible to equalize the acid concentration by mixing the electrolyte. As with other designs, the severity of acid stratification in VRBs depends on both the cycling regime and the cell design. Nevertheless, it is generally found not to be a serious problem, especially in VRBs using gelled-electrolyte. In tall designs, the problem can be alleviated by operating the cells in a horizontal position.

Thermal runaway. Thermal runaway is a possible problem with many battery systems and is caused by the heat, produced during charge and overcharge, depressing the cell potential and causing an increase in current. In VRBs, the recombination reaction results in an increase in heat generation and this enhances the possibility of thermal runaway. In addition, VRBs tend to be smaller and lighter than flooded types and have reduced gassing levels — features that encourage heat build-up and hinder heat dissipation. Nevertheless, as long as the battery layout is correctly arranged, failure via thermal runaway should not be a common occurrence.

Cell imbalance. Oxygen recombination can result in an irregular distribution of voltage between cells, especially in new batteries. This is because there are two possible reactions at the negative (hydrogen evolution and oxygen reduction) plate and, therefore, the potential of the plate can lie between the two reaction voltages, depending on the level of oxygen recombination. This gives rise to cell-to-cell imbalances that, in large banks, can result in premature system failure due to some cells being persistently undercharged and then deep discharged so that, as time goes on, the weak cells become progressively weaker.

Summary

The design of a lead/acid battery, or indeed any battery, is a compromise between cost, performance and life. Life is the most difficult parameter to estimate, particularly with the introduction of new concepts such as the VRB. In summary, there are problems with the:

- positive plate
 - morphology changes
 - shedding
 - grid corrosion/growth
 - sulfation
- negative plate
 - mousing
 - expander degradation
 - sulfation
- separator
 - degradation
 - penetration by lead dendrites

Of these problems, the performance of the positive plate gives the most cause for concern. This is true for all types of battery designs and applications. Nor is this a

new problem. As long ago as 1893, the Birmingham Electric Tramway attributed battery failure principally to the degradation of positive plates [20]. Thus, despite many decades of intensive research, finding a way to increase the resilience of the positive plate, without impairing its other performance characteristics, is still a prime target of research.

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