# Strategies for enhancing lead–acid battery production and performance

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## Abstract

This paper is a record of the replies given by an expert panel to questions asked by delegates to the Eighth Asian Battery Conference. The subjects are as follows. *Analysis of lead and lead compounds*: accuracy; critical aspects of sampling. *Grid alloys:* influence of tin on microstructure and grain size; optimum combination of grid-alloy technologies for automotive batteries. *Battery manufacture and design:* quality-assurance monitoring; acid-spray treatment of plates; efficiency of tank formation; control of $\alpha\text{-PbO}_2/\beta\text{-PbO}_2$ ratio; $PbO_2$ conversion level; positive/negative plate ratio; amount and type of separator for valve-regulated technology. *Battery performance:* use of cadmium reference electrode; influence of positive/negative plate ratio; local action; negative-plate expanders; gas-recombination catalysts; selective discharge of negative and positive plates. © 2000 Elsevier Science S.A. All rights reserved.

## 1. Analysis of lead and lead compounds

*1.1. Question: What is meant by 'limit of detection (LOD)', 'accuracy' and 'rounding rules' when applied to a set of analyses?*

**M. STEVENSON**

Metal analyses are an important tool in the operation and diagnostics of battery production. What is not often understood are the rules applied in obtaining and reporting analyses to produce a clear and accurate set of results. Limits of detection, accuracy and rounding rules should be understood before interpreting an analysis. Importantly, each analytical instrument will have its own limits of detection and accuracy, and these can vary over time for each element.

*1.1.1. Limit of detection*

The LOD is often considered to be the lowest obtainable measurement for a given element, but is actually derived from a series of samples tested on the required analytical instrument. The formula allows for the comparison of a known concentration of an element with a 'blank' sample, as follows:

$$LOD = 3s_{blank}m \tag{1}$$

where $s_{blank}$ is the standard deviation of $n$ blank determinations, $m = (c_{high} - c_{blank})/(I_{high} - I_{blank})$, $c$ is the concentration, $I$ is the intensity of the measurement.

Importantly, the LOD for an element should not be confused with the minimum reporting level for that element. The limit of quantitation (LOQ) is used for this purpose and its derivation is similar to that for the LOD, viz.,

$$LOQ = 10s_{blank}m \tag{2}$$

Actual measurements on an optical emission spectrophotometer (OES) over 10 readings at a concentration of 10 ppm are given in Table 1.

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Table 1
Actual LOD and LOQ for an operating optical emission spectrophotomer

| Analyte | Mean intensity ($\bar{x}$) | | Standard deviation ($s$) | | LOD (ppm) | LOQ (ppm) |
|---------|---------|-------|---------|-------|-----------|-----------|
|         | 10 ppm  | Blank | 10 ppm  | Blank |           |           |
| Ag | 590.1  | 152.9 | 12  | 32.2 | 2.2  | 7.4 |
| Ba | 42 927 | 124.3 | 176 | 39.9 | 0.03 | 0.1 |
| Cd | 1387   | 65.2  | 44  | 37.7 | 0.8  | 2.8 |
| Co | 688.9  | 42.8  | 20  | 17.4 | 0.8  | 2.7 |
| Cr | 582.3  | 31.1  | 26  | 23.6 | 1.3  | 4.3 |
| Cu | 1141   | 163.4 | 20  | 18.9 | 0.6  | 1.9 |
| Fe | 1463   | 208.6 | 67  | 43.6 | 1.0  | 3.5 |
| Mn | 6502   | 87.0  | 76  | 60.2 | 0.3  | 0.9 |
| Mo | 1452   | 30.1  | 24  | 32.0 | 0.7  | 2.2 |
| V  | 596.3  | 34.7  | 12  | 19.0 | 1.0  | 3.4 |
| Zn | 962.8  | 304.1 | 26  | 21.5 | 1.0  | 3.3 |

### 1.1.2. Accuracy

The accuracy of a set of analyses is determined by the reproducibility of a known set of data. This is done by analysing a known sample numerous times, as shown in Table 2. This determines the precision of the instrument on an element-by-element basis.

The variabilities found in accuracy (reproducibility) tests form part of what is termed the 'error of uncertainty' (EoA). The EoAs are sometimes quoted for elements with tight specifications, e.g., a selenium specification in a lead alloy of 0.020 to 0.025 wt.% usually has an EoA of $\pm 0.002$ wt.%. A result of 0.021 wt.% would be quoted as $0.021 \pm 0.002$ wt.%.

### 1.1.3. Rounding rules

An area that often causes confusion in the interpretation of results is the rounding of analyses. There are numerous International Standards that outline the method of round-ing. By way of example, the following extracts from the Australian Standard AS 2706-84 are given.

Example 12: 'rounding of numbers to two significant figures'.

7.2501 rounds to 7.3
7.3499 rounds to 7.3
7.3501 rounds to 7.4
7.4499 rounds to 7.4

Example 13: 'for numbers that fall exactly between two rounding values, choose the even round value'.

7.35 rounds to 7.4
7.3500 rounds to 7.4
7.45 rounds to 7.4
7.4500 rounds to 7.4
7.55 rounds to 7.6
7.5500 rounds to 7.6.

Table 2
Accuracy–reproducibility of a set of analyses

| Element | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | Average | SD[a] |
|---------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|---------|------|
| S  | 6.5 | 4.9 | 4.7 | 4.8 | 4.3 | 4.5 | 5.1 | 5.0 | 5.2 | 5.1 | 4.8 | 0.3 |
| Mn | 1.1 | 1.1 | 0.9 | 1.2 | 1.2 | 0.9 | 0.8 | 1.0 | 1.1 | 1.0 | 1.0 | 0.1 |
| Fe | 1.4 | 1.3 | 1.2 | 1.5 | 1.6 | 1.4 | 1.1 | 1.6 | 1.4 | 1.5 | 1.4 | 0.1 |
| Co | 0.4 | 0.4 | 0.4 | 0.4 | 0.5 | 0.4 | 0.4 | 0.4 | 0.5 | 0.4 | 0.4 | < 0.1 |
| Ni | 1.3 | 1.0 | 1.0 | 1.0 | 1.0 | 0.9 | 0.9 | 1.0 | 1.0 | 1.0 | 1.0 | 0.1 |
| Cu | 1.1 | 1.7 | 0.7 | 0.9 | 0.8 | 0.7 | 0.6 | 0.9 | 0.8 | 0.9 | 0.9 | 0.3 |
| Zn | 0.9 | 1.1 | 1.1 | 1.1 | 0.9 | 0.8 | 0.6 | 0.9 | 0.9 | 1.1 | 0.9 | 0.1 |
| As | 0.3 | 0.3 | 0.4 | 0.5 | 0.5 | 0.7 | 0.6 | 0.4 | 0.4 | 0.5 | 0.4 | 0.1 |
| Se | 0.7 | 0.8 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 | 0.2 | 0.3 | 0.3 | 0.1 |
| Ag | 3.4 | 3.2 | 3.0 | 3.4 | 3.4 | 3.4 | 3.3 | 3.1 | 3.3 | 3.1 | 3.2 | 0.1 |
| Cd | 0.1 | 0.1 | < 0.1 | < 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | < 0.1 |
| Sn | 0.1 | < 0.1 | 0.1 | 0.1 | 0.1 | < 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | < 0.1 |
| Sb | < 0.1 | 0.2 | < 0.1 | 0.2 | 0.3 | < 0.1 | < 0.1 | < 0.1 | 0.1 | < 0.1 | 0.1 | < 0.1 |
| Te | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | – |
| Bi | 240 | 235 | 229 | 242 | 245 | 250 | 227 | 232 | 235 | 237 | 237 | 7 |

[a] SD = standard deviation.

Table 3
Sample set of analyses (all values in wt.%)

| Element | As-received analysis | Correct analysis |
|---------|---------------------|------------------|
| Pb | 97.3382 | Remainder |
| Sb | 2.1906 | 2.20 |
| As | 0.1875 | 0.19 |
| Sn | 0.1877 | 0.19 |
| Cu | 0.0352 | 0.035 |
| Se | 0.0305 | 0.031 |
| S | 0.0021 | 0.002 |
| Ag | 0.0109 | 0.011 |
| Bi | 0.0167 | 0.017 |
| Zn | 0.0005 | 0.0005 |
| Fe | 0.0003 | < 0.001 |
| Cd | 0.0002 | < 0.0005 |

For lead specifications, it is general practice to quote the analytical value to the number of 'significant figures' according to the alloy specification. For example, a selenium specification of 0.020 to 0.025 wt.% would be quoted to two significant figures. Application of the criteria to a set of analysis results is given in Table 3.

*1.2. Question: In the sampling and analysis of lead and lead alloys, what are the critical areas which must be considered? Are these areas also applicable to the analysis of lead oxide?*

### M. STEVENSON

There are certain critical aspects in the sampling and analysis of lead and its alloys to obtain data that are accurate and can be useful in understanding the conditions of battery plants.

*1.2.1. Sampling*

The major aim in the sampling of a product is to obtain a homogeneous sample representative of that product. Many international standards are now available on the standard sampling of ingots and blocks, as shown in Fig. 1. In a battery-plant environment, however, these standards form only a small portion of assay/testing requirements. What these standards often do not cover is the preparation of other materials for analysis.

For materials such as turnings/swarf, grids and small parts, the sample should be melted in a graphite pot under reducing conditions, e.g., under a covering of charcoal. The temperature of the molten sample before casting should be between 450°C and 480°C, and, importantly, should only be held for a very short time before casting into a suitable sample mould. Holding the sample in a molten state for an extended period can result in the loss of volatile elements.

Samples from a molten metal bath are somewhat easier to take, but there are some guidelines that should be followed. The metal should be thoroughly mixed/stirred to homogenize the bath, and excess dross should be removed from the top of the melt. The metal should be held at temperature of around 450°C to 480°C. Upon sampling, the spoon/ladle should be immersed in the bath and the sample taken 5–10 cm below the surface. The sample taken should be free from dross and other inclusions. Samples should not be taken by skimming the surface of the lead.

The sample mould also plays an important role in producing a homogeneous sample. A copper sample mould that is suitable for lead alloy samples is shown in Fig. 2.

*1.2.2. Analysis*

Appropriate analytical equipment and settings are critical for the production of accurate, precise results. Generally, an OES is the standard operating equipment for metal analysis, often with back-up support from an atomic absorption (AA) instrument. Two important areas in the set-up of an analytical instrument are the correct emission lines (wavelengths) and minimization of the interfering emission lines.

Typically, an OES has up to 60 channels to cover varying concentrations from trace (< 1 ppm) to many percentage levels for various elements. To measure these concentrations, there is a choice of over 200 000 spectral lines of varying intensity. The selection of the correct wavelengths depends on the metal matrix and the desired ranges of analytical measurement. The major emission lines for OES analysis of lead alloys are listed in Table 4.

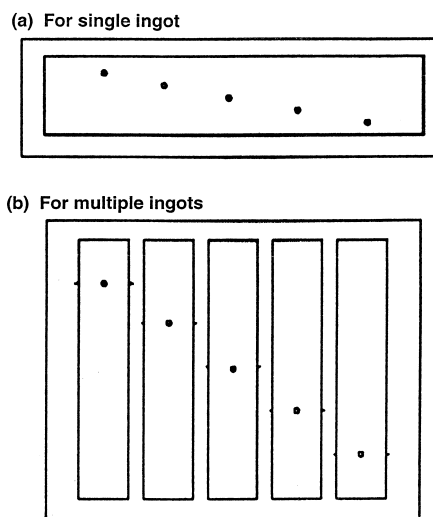(a) **For single ingot**



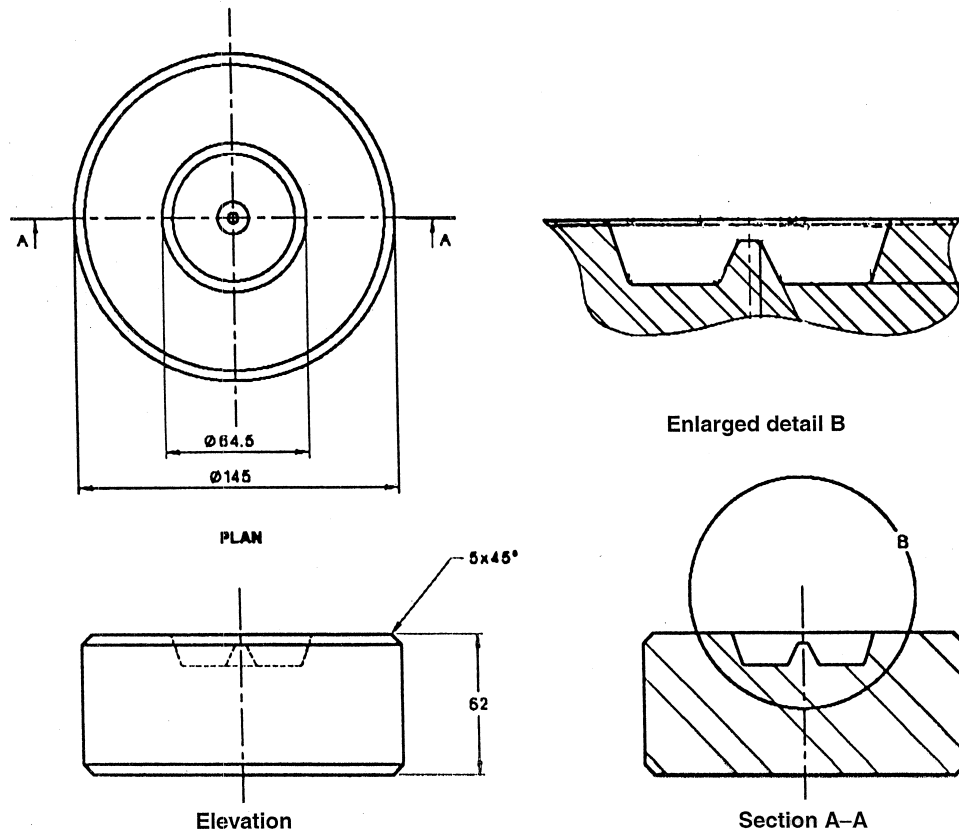(b) **For multiple ingots**



Fig. 1. Sampling of ingots.

Fig. 2. Sample mould design.

Once the analytical equipment has been set up with the correct settings, it is important to conduct day-to-day monitoring of equipment, such as 'drift' and an ongoing maintenance programme.

The criteria outlined above are certainly valid for all oxide materials. It is important, however, to obtain a homogeneous sample that is representative of the batch, and to use the correct analytical instrument and setting for the analysis.

Table 4
Major emission lines for OES analysis of lead alloys

| Element[a] | Emission line (nm) | Order |
|---|---|---|
| Ag (I) | 328.068 | 1 |
| Ba (II) | 455.403 | 1 |
| Cd (II) | 226.502 | 3 |
| Co (II) | 228.616 | 3 |
| Cr (II) | 276.716 | 2 |
| Cu (I) | 324.754 | 2 |
| Fe (II) | 259.940 | 2 |
| Mn (II) | 257.610 | 2 |
| Mo (I) | 379.825 | 1 |
| V (II) | 311.071 | 2 |
| Zn (II) | 213.856 | 3 |
| Al (I) | 396.152 | 1 |
| As (I) | 193.696 | 1 |
| Bi (I) | 223.061 | 3 |
| Ca (I) | 422.673 | 1 |
| Sb (I) | 217.581 | 3 |
| Se (I) | 196.026 | 1 |
| Sn (II) | 189.926 | 1 |

[a]Emission line state: (I) = atomic; (II) = ionic.

## 2. Grid alloys

*2.1. Question: In calcium − tin alloys, what effect does the level of tin have on the microstructure / grain-size of the alloy?*

### M. STEVENSON

With calcium − tin alloys, the addition of tin will cause an increase in the grain size of the alloy, as shown in Fig. 3. This is the opposite effect to calcium, which produces a smaller grain structure. The grain boundaries are also noticeably different: low tin levels produce a serrated boundary, while higher levels give a smooth boundary.
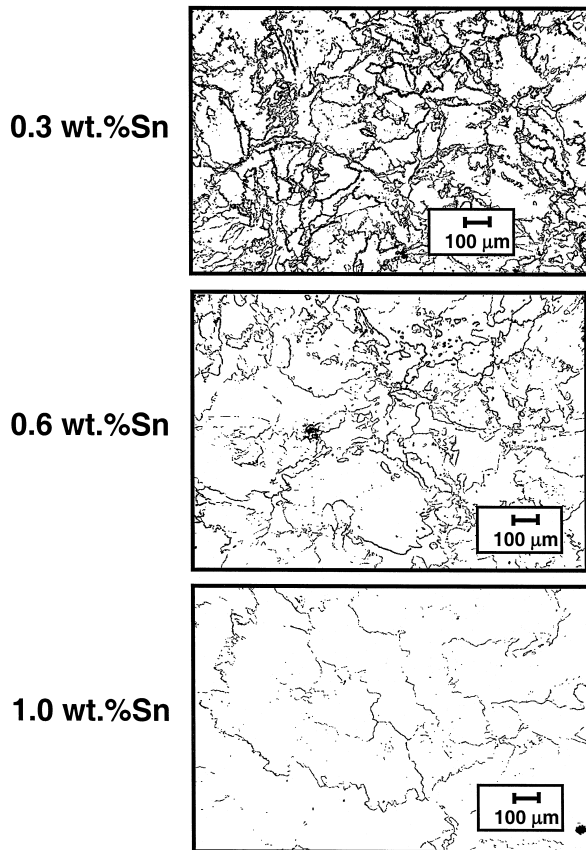
Fig. 3. Metallographs of Pb–0.11 wt.% Ca–Sn alloy grids.

The serrated feature has been explained [1] as the cellular precipitation of $Pb_3Ca$ behind moving grain boundaries during solidification. At higher tin levels, the precipitation reactions change to a continuous precipitation to form the more stable $(Pb,Sn)_3Ca$ phase. As Manders et al. [2] has previously outlined, an optimum grain size is produced at a Sn/Ca ratio of 9:1, with the calcium content restricted to 0.08 wt.% or below.

*2.2. Question: Which combination of grid technologies — calcium–calcium, calcium–antimony, or antimony–antimony — gives the most cost-effective and most reliable performance in automotive applications?*

### D.W.H. LAMBERT

The reliability of automotive battery performance can be measured in various ways, and is very much related to the requirements of the vehicle manufacturer. Increasingly, the major (global) manufacturers are demanding still higher battery performance against even more stringent test standards. In summary, the following characteristics are critical: high discharge 'cranking' current; good cycle-life at high temperature; and low overcharge/water loss.

In attempting to meet the above targets, the battery designer should be aware that the grid alloy should not be

taken in isolation. More realistically, it is the plate-group technology that is more important, namely: the material and design of the grid; the method of grid fabrication; the ratio, composition and structure of the active material; and the separator. Thus, it is this 'total system' that should be considered when optimizing the design of an automotive battery. The above question, however, concerns the grid alloy only. The effects of alloy composition on battery performance are as follows.

#### 2.2.1. Cranking current

Battery performance at high discharge currents, and particularly at low temperatures, follows the trend:

$$Pb–Ca/Pb–Ca > Pb–Ca/Pb–Sb > Pb–Sb/Pb–Sb. \quad (3)$$

#### 2.2.2. Cycle-life

The performance trend in (3) is reversed and is exacerbated by high temperatures, where grid corrosion and grid growth are the predominant causes of failure.

#### 2.2.3. Water loss

Volkswagen, for example, have recently introduced a new test for water loss, namely: $< 2$ g/A h water loss after 21 days at 40°C and 21 days at 60°C, at a constant charge potential of 14.4 V. Typical rates of water loss for the three alloy combinations are given in Table 5.

#### 2.2.4. Cost-effectiveness

There is a move towards continuous grid and plate production, in order to maximize both productivity and material utilization (i.e., to reduce cost). A variety of techniques are used, e.g., continuous casting, with/without subsequent rolling (Wirtz); strip–metal expansion (Cominco, Comac, Sovema). These high-speed production techniques favour the use of Pb–Ca alloys for both the negative and the positive grids.

In conclusion, there is an overwhelming move towards Pb–Ca/Pb–a batteries by high volume, state-of-the-art producers who are making original equipment (OEM) products. For the smaller automotive battery producer, however, the simplicity of casting both positive and negative grids from one alloy, combined with the need to produce a safe and reliable 'basic technology' battery that can withstand the rigours of use and abuse, render Pb–Sb alloys the favoured choice.

Table 5
Water-loss data

| Positive grid | Negative grid | Water loss (g/A h) |
| --- | --- | --- |
| Pb–1.8 wt.% Sb | Pb–1.8 wt.% Sb | 5.0–7.0 |
| Pb–1.8 wt.% Sb | Pb–Ca | 3.0–5.0 |
| Pb–Ca | Pb–Ca | 1.5–2.5 |

## 3. Battery manufacture and design

*3.1. Question: For quality assurance (QA) monitoring in a battery plant, which parameters should be measured routinely during lead oxide manufacture, paste mixing, pasting, skin drying, curing, formation, etc.? Can appropriate specifications be recommended, and are they different for Ball-mill and Barton-pot oxide technology?*

### D.W.H. LAMBERT

Ideally, the QA department in a battery plant should monitor and control each parameter at every stage of the manufacturing process that may ultimately affect the final performance of the battery. The complexity of the measures will vary with the type of plant, e.g., automotive, valve-regulated, industrial. In reality, this QA either does not happen, or may be minimized by ensuring that each critical process is under proper control. Alternatively, there can be an almost paranoiac approach in which everything is measured! In situations where adequate process control is not achievable, the following key characteristics must be checked, both routinely and regularly.

Oxide manufacture:

- lead impurity levels (to suit battery application)
- mill or pot 'load'
- process air-flow rate
- ambient air temperature and humidity
- reaction temperature
- free-lead content (Barton 18–28 wt.%, Ball mill 25–35 wt.%)
- acid absorption (Barton-pot oxide: $160 - 180$ mg $H_2SO_4$/g oxide, which may be increased up to 240 by 'hammer milling'; Ball-mill oxide: $220 - 240$ mg $H_2SO_4$/g oxide)
- baghouse lead emissions (in accordance with local environmental requirements)
- storage time before use (typically 3 to 7 days, and 10 days maximum)
- temperature and atmosphere of oxide storage (nitrogen content for fire safety reasons).

Paste mixing, pasting and flash-drying:

- paste time/temperature profile control during mixing and discharge (mixing: 65°C maximum; discharge: usually 40–50°C)
- plasticity 'penetration' (affected by oxide type and paste formulation, and adjusted to suite the type of pasting machine, as well as the composition, strength and design of the grid alloy)
- density to suite battery application ($\pm 3$ sigma variation $< 0.2$ g cm$^{-3}$)
- contamination levels of barium sulfate in positive paste (none)
- paste storage time to completion of use (typically, 1 h maximum)
- pasted plate weight and thickness (left-hand and right-hand grid/plate)
- paste moisture in pasted plate prior to flash drying ($10.5 - 13.0$ wt.%)
- paste moisture after flash drying ($8.5 - 10.0$ wt.% for positives; $7.5 - 9.5$ wt.% for negatives).

Curing ('hydrosetting'):

- temperature ($50 - 55$°C for tribasic lead sulfate; $75 - 85$°C for tetrabasic lead sulfate)
- humidity ($90 - 95$% relative humidity)
- curing and drying process times
- free-lead content after curing/drying (typically $< 2$ wt.%)
- residual moisture content after curing/drying (typically $< 1$ wt.%).

Battery formation:

- acid relative density and impurity levels (in particular, limits for iron, manganese and chlorine)
- filling acid temperature (typically, 10°C)
- current − voltage schedule
- maximum battery temperature (generally, $40 - 60$°C)
- high-rate discharge performance after formation.

*3.2. Question: Some manufacturers subject pasted plates to an acid-spray treatment immediately after the pasting stage. How is this done? What benefits does this treatment impart to plate processing and subsequent battery performance?*

### D.A.J. RAND

Acid-spray treatment provides several advantages and is applied to battery plates (positives and negatives) immediately after the pasting stage. The following are two common procedures (refer to Fig. 4).
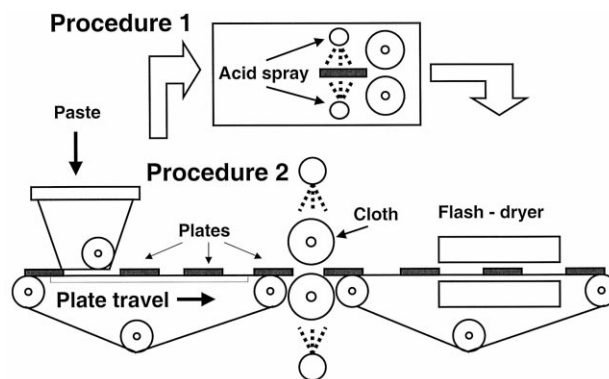


Fig. 4. Procedures for treating pasted battery plates with acid spray.

*Procedure 1*: Plates are fed between a pair of pipes. In each pipe, rows of small holes are drilled through that section of the wall that faces the plates. Dilute sulfuric acid (about 1.1 rel. dens.) is pumped through the pipes and is emitted through the holes as a fine spray on to, respectively, the upper and lower surfaces of the plates.

*Procedure 2*: Plates are fed through a pair of rollers. Each roller is wrapped with cotton cloth, which is kept permanently saturated with dilute sulfuric acid (1.1 rel. dens.) from an external spray.

Procedure 2 is preferred because it applies acid more evenly to the plate surfaces.

Acid-spray treatment produces at least three improvements in plate processing, namely: (i) fewer or no cracks during flash drying; (ii) better plate curing, i.e., through more efficient oxidation of free-lead and enhanced cohesion; and (iii) less dust generation during plate handling. A detailed examination of these improvements is presented in Sections 3.2.1–3.2.3.

### 3.2.1. Crack formation in plates

In a battery plate, the grid alloy has a much better heat conductivity than the paste. Thus, when a plate is passed through the flash-drying oven, the grid members will become hotter than the surrounding paste material. This differential heating will cause preferential evaporation of water at the grid/material interface. In the worst situation, cracks will develop at this interface, especially if the oven is set at too high a temperature and/or the speed of plate travel is too slow. Plates produced via the standard belt-pasting technique are particularly susceptible to crack formation because the grid members are exposed on the under-side (or belt-side) of the plates. Although, cracking obviously weakens the mechanical integrity of the plate and increases the electrical resistance (and, hence, hinders plate formation), it may also cause preferential discharge of the grid itself during subsequent battery operation. Such discharge results in the formation of highly resistive corrosion layers.

With acid-spray treatment, a thin ($\sim 40$ $\mu$m) crust of lead sulfate (and, possibly, some basic lead sulfates) is produced on both surfaces of the plate, which become grey in colour. This coating prevents the rapid evaporation of water during flash drying, particularly at the grid/material interface, and, thus, lowers the incidence and severity of crack formation. Equally important is that the coating also allows the internal moisture to be retained at the optimum level ($\sim 10$ wt.%) for the first stage of plate curing, which is the next step in the plate-processing sequence.

### 3.2.2. Plate curing

To achieve good plate quality, curing should proceed via three consecutive stages: (i) growth of basic lead sulfates, which provide the linkages (or 'glue') by which the material develops its mechanical strength; (ii) oxida-

tion of the free-lead; and (iii) bonding and drying of plate material. Control of plate moisture is critical to the success of each stage.

The water entrapped in the paste is distributed in three distinct forms (Fig. 5): (i) interstitial water, which is drawn by capillary forces into the pore system; (ii) wedge water, which accumulates at the contact points of the paste particles, and at the contact points of the paste with the grid members; and (iii) adsorbed water, which covers the exposed surfaces of the paste components [3].

Crystals of basic lead sulfate, which are formed during paste mixing, continue to grow during the first stage of the curing process. This growth proceeds via a dissolution–precipitation mechanism, which requires the presence of adequate and well-dispersed interstitial and wedge water to deploy a saturated solution of basic lead sulfate uniformly throughout the plate. To achieve this condition, the plate moisture should be maintained at around 10 wt.% for sufficient time at the elevated temperature of the process. This emphasizes the value of the acid-spray treatment, which by coating plates with crusts of lead sulfate, delivers plates from the flash-drying oven with a well-controlled and sufficient amount of internal moisture. As will be seen later, the basic lead sulfates provide the essential particle-to-particle cohesion ('bridges'), which enables the plate material to withstand the expansion − contraction forces encountered during battery discharge − charge service. Thus, control of plate moisture is the key objective of the first stage of curing.

During the second stage of curing, the oxidation of free-lead proceeds via an electrochemical mechanism and, therefore, the presence of moisture is again required. Once enclosed in a sheath of water, each lead particle can develop anodic and cathodic sites. The lead surface is corroded at the anodic site, while oxygen is reduced at the cathodic site. Overall, the lead is converted to lead hydroxide which, in turn, probably loses some water and precipitates as partially hydrated lead monoxide. The oxidation reaction proceeds at its maximum rate over a relatively narrow band of moisture levels, viz., 7 to 8.5 wt.%. Too little moisture would be insufficient to sustain water films around all the lead particles, while too much moisture
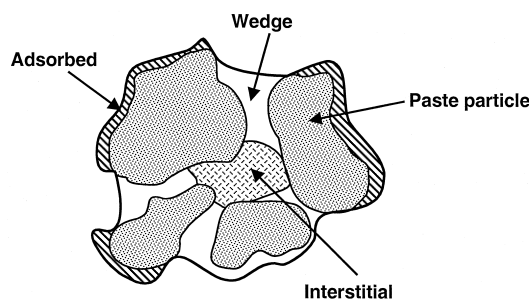
Fig. 5. Forms of water entrapped in battery paste.

would diminish the rate of oxygen diffusion to the cathodic sites. Unfortunately, lead oxidation generates heat, and this will tend to dry out the plate. Acid-spray treatment reduces this problem by helping to maintain the moisture within the required band-width, particularly during the initial stages of free-lead oxidation when water is supplied from within the paste material itself. As the reaction proceeds, however, the water content of the plate should be sustained by careful regulation of the ambient humidity conditions. The overall residual content of free-lead should be kept below 5 wt.%. Under-curing, that is, a higher level of residual free-lead, generally results in the swelling/warping of plates, the shedding/spalling of material, and the development of short-circuits — both during the subsequent formation stage and during battery operation.

The final stage of curing — plate drying — must also be performed carefully. The water is removed in the order: interstitial → wedge → adsorbed. During evaporation of the interstitial and wedge water, the dissolved basic lead sulfates (which can be either tribasic lead sulfate or tetrabasic lead sulfate) precipitate at the contact points of the particles and form a network, which serves to consolidate the matrix into a sturdy and continuous structure. For successful drying, there must be a balance between the rate of surface evaporation and the rate of capillary movement of water from the interior of the plate material. If surface evaporation is the faster, then shrinkage will be greater at the surface of the plate than in the bulk, and differential stresses will promote the formation of cracks. Thus, to avoid cracking, it is essential to decrease the rate of evaporation from the plate surface. The lead sulfate layer produced by acid-spray treatment provides an effective means for now controlling the *removal* of water from the plate.

It should also be noted that there can be a considerable interval between the pasting and curing steps, particularly if large batches of plates are being produced and/or curing ovens are not available at the time. In such situations, it is usually difficult to maintain the plates under controlled conditions of temperature and humidity. Accordingly, water can evaporate quickly from the plates and the oxidation of free-lead can occur before development of basic sulfates. This degrades the bonding of the material and, hence, the mechanical integrity of the plate. Again, the application of acid-spray treatment will moderate the rate of evaporation and thus preserve the cohesion and strength of the cured material. It should be noted that, prior to curing, it is common practice to store plates under sheets of plastic in order to prevent excessive 'dry-out'. Initially, water evaporates quickly from the plates, but this slows down as the humidity beneath the plastic covers increases. Although this procedure is more prudent than storage in the open air, it is still advisable to use acid-spray treatment as a safeguard against the premature oxidation of free-lead and its accompanying adverse effect on plate quality.
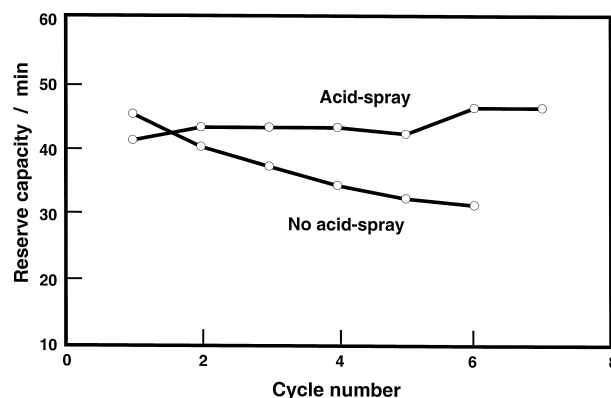


Fig. 6. Influence of acid-spray treatment on reserve capacity of automotive batteries.

### 3.2.3. Dust generation

As mentioned above, acid-treatment causes the plates to be covered with a thin, but dense, layer of lead sulfate crystals. These crystals bond strongly with each other and with the underlying paste material. Thus, acid-treated plates are less prone to dust generation during handling. Consequently, the plates present less of a health risk to factory workers.

### 3.2.4. Improved battery performance

In addition to assisting plate manufacture, acid-spray treatment can also enhance battery performance. For example, the technique can cause a remarkable improvement in the reserve capacity of automotive batteries, as shown in Fig. 6.

It should be noted that acid-spray treatment does have several disadvantages. For example, it can be a messy process, it can cause corrosion of plate equipment and, importantly, it can provide an avenue for the introduction of pernicious impurities into the plate material.

The acid-spray technique has been in use for many years and was introduced at a time when flash-drying and curing ovens were relatively simple in design. Present equipment is much more advanced. For example, curing chambers are now fitted with computer control to allow precise regulation of temperature and humidity conditions. In modern battery plants, therefore, the benefits of acid-spray treatment have less impact and application of the technique has been largely discontinued.

### 3.3. Question: In tank formation, how can the $PbO_2$ conversion rate be increased, how can the $\alpha\text{-}PbO_2$ / $\beta\text{-}PbO_2$ ratio be controlled, and what is the best $PbO_2$ conversion level?

**R.F. NELSON**

In tank formation, the important parameters are acid concentration, temperature, time and the formation programme itself (especially the current densities and the use of rest periods or discharges). The theoretical ampere-hour

input is 241 A h/kg of PbO; $150 - 250\%$ of this value must be put into the plates for complete formation ($> 90$ wt.% $PbO_2$). Longer formation procedures at lower current densities require lower ampere-hour inputs for complete formation. For the positive plate, acid of 1.05 to 1.15 rel. dens. is recommended, with a period of 0.45 to 2 h for immersion of the plates prior to formation (pickling). Use of red lead in the positive paste (10 wt.% or more) gives more efficient formation due to an enhancement in conductivity (note: $Pb_3O_4 = 2PbO \cdot PbO_2$) and the 'seed crystal' function of the $PbO_2$ in the red lead. The presence of high levels of $\beta$-PbO (yellow lead oxide) in the positive paste can, however, make formation more difficult. Formation of the positive plate is favoured by higher temperatures, in the range of 35°C to 45°C or more. Longer formation at lower current densities, or with long periods of rest and/or discharge, gives higher $PbO_2$ levels and a better-formed corrosion layer between the positive active-material and the grid. On the other hand, high current densities early in formation (reportedly for as little as 10 to 15 min) may form a finer crystal structure due to high initial nucleation rates, but this may not yield higher levels of $PbO_2$. Early and later in formation, high current densities may drive plate voltages high, which will produce more gassing. Excessive gassing can hinder the penetration of acid into the plates, and, thus, slow down the conversion rate of PbO to $PbO_2$ in the plate interior.

### 3.4. Question: In formed plates, how can the $\alpha$-$PbO_2$ / $\beta$-$PbO_2$ ratio be controlled?

**R.F. NELSON**

The formation of $\alpha$-$PbO_2$ is favoured by the use of dilute acid, or even basic conditions, and by the use of higher-density pastes. Low-to-moderate current densities also favour the $\alpha$ polymorph, as do high formation temperatures (40°C to 60°C) and the use of yellow PbO in the positive paste. Most of the $\alpha$-$PbO_2$ is converted to the more electrochemically active $\beta$-$PbO_2$ form during initial cycling or during float charging. Bode [4] has given an excellent account of this subject.

In valve-regulated lead-acid (VRLA) batteries, the $\alpha$-$PbO_2/\beta$-$PbO_2$ ratio is also affected greatly by the acid-filling process. This is because poor filling can create areas of low acidity or, in extreme cases, basic conditions. The lead dioxide formed in these areas can be of the $\alpha$ form, which would reduce the initial discharge capacity somewhat. With cycling, however, the capacity should rise to normal levels.

### 3.5. Question: What is the best $PbO_2$ conversion level during formation?

**R.F. NELSON**

From the standpoint of manufacturing throughput, the best level of $PbO_2$ depends upon the application. Forma-

tion time and, thus, throughput, is often balanced against the minimum level of $PbO_2$ that can be tolerated in a product. For automotive batteries with a short distribution time, $PbO_2$ levels of 75% to 85% can be allowed, on the expectation that with use in the vehicle this level will rise. For longer distribution/sales pipelines, higher $PbO_2$ levels may be required. For VRLA batteries in general, a $PbO_2$ level of 90 wt.% or more is considered to be the fully formed state. In stationary, industrial and portable-device batteries, the danger of a lower formation level is that the unformed oxide, due to its reaction with the sulfuric acid electrolyte, will significantly reduce the normal shelf-life. Hard sulfate, which may be difficult to convert back to $PbO_2$, can then form. In order to prevent this in long distribution chains, battery manufacturers may recommend a periodic 'boost charge', perhaps every 3 to 6 months (depending upon the $PbO_2$ level after formation).

### 3.6. Question: Are there any advantages or disadvantages in changing the positive/negative plate ratio (p:n) in VRLA batteries from, for example, 6p:7n to 7p:6n, 7p:7n or 6p:6n? Are the effects similar for thick-plate and thin-plate batteries (i.e., low-rate and high-rate product, respectively)?

**R.F. NELSON**

Most batteries, including VRLA types, are positive-limited at medium- and low-rate discharges. Also, many have relatively thick plates. Both of these facts have dictated a standard design where an 'extra' negative is in the plate stack so that all faces of the positive plates have an opposite negative for optimum active-material utilization. Some automotive batteries (not VRLA) now have even-numbered plate counts, based upon the premise that for high-rate discharges with thin plates, little is to be gained from the 'extra' outside negative. In addition, the plate counts tend to be high (85 to 90 per 12-V battery) and with thin plates there is some 'through-plate' utilization.

Many VRLA batteries still utilize the 6p:7n configuration, but there are some (most notably the Delphi EV battery) that have a 7p:6n design. This is a relatively thick-plate battery, which may have a less-efficient negative plate, so that with positive surfaces opposite all the negative ones, there is high utilization of the negative. Alternatively, the greater mass of the positive active-material may not only yield higher discharge capacities, but may also extend cycle-life due to an effectively lower degree of working of this material.

In non-automotive applications, an even-plate design for VRLA products is, in fact, viable if the plates are thin, i.e., $< \sim 1$ mm. With thin plates, the 'through-plate' utilization is sufficiently high for extra plates to be necessary. In the Gates spiral-wound design, the plate lengths are the same so it is, effectively, an even-plate design. Studies using a 'wrap-around negative' (an extra negative

plate in flat-plate cells) show no improvement in discharge capacity or cycle-life at high rates of discharge. What has been found to be necessary is to have some separator on the outside of the plate stack so that there is electrolyte access to all plate surfaces. In flat-plate cells, this should always be done, regardless of the number of positive and negative plates. Electrolyte access from the 'outside' surfaces effectively reduces by half the diffusion path for electrolyte to the plate pores.

### 3.7. Question: What is the correct amount of glass-mat separator to use in a VRLA battery and what is the typical cost?

#### R.F. NELSON

This is an area of VRLA battery design that has not been researched (or at least reported on), although it is very important. The designs vary significantly and the range of separator usage is probably between $\sim 1$ and $2$ g/A h of rated capacity. The uncompressed separator thickness is roughly equal to the plate thicknesses. After compression, the separator thickness is reduced to $\sim 70\%$ to 80% of the initial value. For a given amount of electrolyte, the less separator used, the more saturated the design. This can cause problems in the form of excessive gassing, acid spray or leakage, and/or rapid stratification. On the other hand, if too much separator is used (for a fixed amount of electrolyte), the design is relatively unsaturated and more efficient oxygen-recombination may make it difficult to recharge the negative plate. An acceptable or, possibly, superior approach may be to use a relatively large amount of separator (2 g/A h or more) and an increased amount of electrolyte. This would aid recovery from deep discharge and may improve low-rate discharge capacities, as well as cycle-life.

It appears that many VRLA designers are unduly influenced by the 'myth of separator cost'. The cost of materials for a typical 6-V, 100-A h Telecom VRLA battery is presented in Table 6. In this case, the separator accounts for only 13% of the total materials' cost. In fact, for this product, it is just about the cheapest major component in the battery. Perhaps, it is viewed as unnecessarily expensive because its critical functions in the VRLA design are

Table 6
Typical costs for materials in a 6-V, 100-A h VRLA battery

| Material | Cost (US$/kg) | Amount (kg) | Material cost (US$) | % Total cost |
|---|---|---|---|---|
| Lead grid, top lead | 0.88 | 7.26 | 6.39 | 21 |
| Oxides, additives | 1.43 | 5.90 | 8.44 | 27 |
| Separator | 8.82 | 0.45 | 3.97 | 13 |
| Electrolyte | 1.10 | 4.54 | 4.99 | 16 |
| Box, lid | – | $\sim 1.36$ | $\sim 7.00$ | 23 |
| Total cost | | | 30.79 | |

not well understood. It can have a large influence on acid-filling uniformity, formation efficiency, discharge capacity, and life (both cyclic and float). It is not only the amount that is important, but also the nature of the glass mat used. The use of fine or coarse fibres, organic binder fibres and/or inorganic fillers will have a large impact on cost, manufacturability and, most importantly, battery performance. The use of such a key material (or, worse, a switch to a cheaper form) should never be driven by economics, but rather should be dictated by purely technical issues. As shown by the data in Table 6, even doubling the cost of the separator does not drive up the total materials' cost excessively. If this results in longer life and better performance, then it is a bargain in the long run!

In terms of the materials' cost alone, the separator is one of the cheapest major components in a VRLA battery. If labour and capital costs are taken into account, areas such as grid preparation and paste mixing are considerably more expensive; one only needs to cut separator to length in the VRLA process. Therefore, the use of a little more separator does not contribute significantly to the cost of a VRLA battery, but it can have a large effect on discharge capacity and other performance parameters. The separator is the most expensive material in a VRLA battery on a *per weight basis*, but in terms of actual cost it is not that great. Given the critical nature of its role in VRLA technology, the separator should be chosen with regard to higher quality and, possibly, greater quantity.

### 3.8. Question: Should different types of separator be used in VRLA batteries designed for deep-cycling, float or high-rate (e.g., automotive) applications? If so, what are the recommended types for each service?

#### R.F. NELSON

The type of separator used, whether glass mat or gel, or newer variations of these, can have a tremendous influence on battery manufacturability, performance and even life. In fact, for a VRLA product, the choice of separator material is probably the single most important factor to consider. Key parameters are fibre/filler composition, purity, surface area ($m^2 \ g^{-1}$), tensile strength/percentage elongation/toughness, compressibility, and nominal thickness. Even the number of layers between the plates can have an influence on processing and performance. This is a complex issue that requires considerably more analysis than is possible here, but the following are a few comments on the material to be used for each application.

#### 3.8.1. Deep-cycle use

Key issues are cycle-life, discharge capacity and electrolyte stratification. Cycle-life and stratification will be aided by using a high-surface-area glass, but this may be detrimental to discharge capacity at high rates (see below). Purity will be important in order to minimize any influence

to hydrogen and oxygen overpotentials. For thin-plate products, the use of gel may be prohibited. For thick-plate designs, gel or newer variants may be preferable to glass mat in terms of pore structure and its effect on oxygen-re-combination efficiency. It is recommended that glass mat is subjected to high compression.

### 3.8.2. Float or stand-by use

Issues such as compression and stratification are not as important here. Purity is essential, as even low levels of gassing over a number of years can limit life. The surface area of the selected glass mat is dependent upon the discharge application. Probably, the most important factor is the performance on float. For this, use of gel or a fine-pore glass mat is preferred. This, combined with a high saturation level, will reduce the impact of the oxygen cycle and lead to improved cell-to-cell uniformity.

### 3.8.3. High-rate (e.g., automotive) use

Again, compression and stratification are not as significant as in deep-cycle service. The single most important characteristic is the surface area of the glass fibre. This is because coarse fibre mats will release more electrolyte to the negative plate, and will thus enhance high-rate performance (which is often negative-plate limited). This would apply, for example, to automotive, uninterruptible power supply (UPS) and pulse-power applications. Gel or variants would not be useful because of their higher impedances and plate-thickness limitations.

## 4. Battery performance

### 4.1. Question: How and why is the cadmium electrode used to monitor the performance of individual positive and negative plates during charging and discharging?

#### D.W.H. LAMBERT

In fundamental terms, a lead − acid cell is formed from two porous electrodes — a positive $(PbO_2)$ and a negative (Pb) — immersed in an electrolyte ($\sim$ 5M, $H_2SO_4$). A potential difference of 2 V, nominal, develops between these two electrode polarities. During discharge, the voltage of the cell decreases and is a function of the performance of the individual electrodes. The cell voltage increases during the subsequent recharge. Without a reference point, it is not possible to measure the individual electrode potentials, and therefore ascertain the relative performance of the positive and negative plates. Hence, the use of a cadmium electrode (or 'stick' as it is commonly called), which enables the battery technologist to measure the 'half-cell' voltage. It should be noted, however, that the cadmium/cadmium sulfate reference electrode (although widely used for day-to-day measurement of battery-plate potentials) is unstable and may give spurious readings. Therefore, for 'serious' half-cell potential mea-
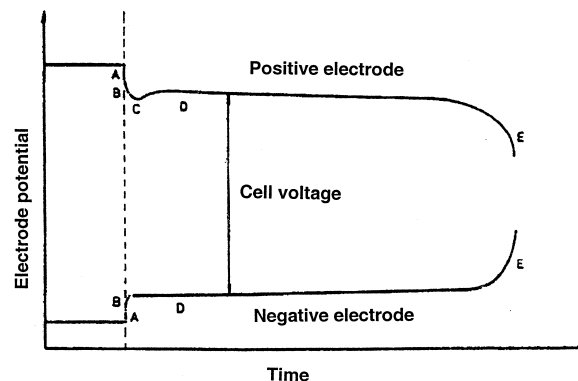


Fig. 7. Schematic of discharge curves for positive and negative electrodes in lead–acid cell.

surements, it is now common to use the mercury/mercurous sulfate $(Hg/Hg_2SO_4)$ reference electrode (0.6150 V vs. standard hydrogen electrode, or $\sim$ 1.02 V vs. cadmium).

The discharge curves for the positive and negative electrodes are schematically illustrated in Fig. 7. The instantaneous potential drop, A, is due to the resistance of the electrolyte in the pores of the separators, and the ohmic resistance of the grid/active-material/electrolyte interfaces. The potential drop B arises from the discharge of the active material in the pores of the active mass. In the positive electrode only, supersaturation of soluble Pb (II) ions and low availability of nucleation sites on the plate surface, followed by $PbSO_4$ crystallization phenomena, give rise to the voltage dip (or 'coup de fouet') C. The plateaux, D, represent the progressive discharge of the plate active materials to lead sulfate. Finally, a rapid decline in potential occurs, E, as a result of acid depletion (concentration polarization) in the pores, and blocking of the pores by lead sulfate crystals.

Typical charge − discharge 'half-cell' voltage curves of a lead − acid cell, measured against a cadmium reference electrode, are presented in Fig. 8 [5]. There is no merit in trying to be more specific as to the precise cadmium voltages expected for the positive and negative plates because of the influence of the many variables that are involved in battery/cell design.

### 4.2. Question: In automotive applications, what is the effect on cycle-life, water loss, grid corrosion / growth and other features when the positive / negative ratio (p:n) is changed, e.g., 6p:7n vs. 7p:6n or 7p:7n?

#### D.W.H. LAMBERT

Historically, it has become battery lore that the cell group should contain one more negative plate than positive plate. This is generally the case when the application demands a thick, heavy positive plate with an abundance of positive active-material. The edict is, however, now open to question, given the combined demands of in-
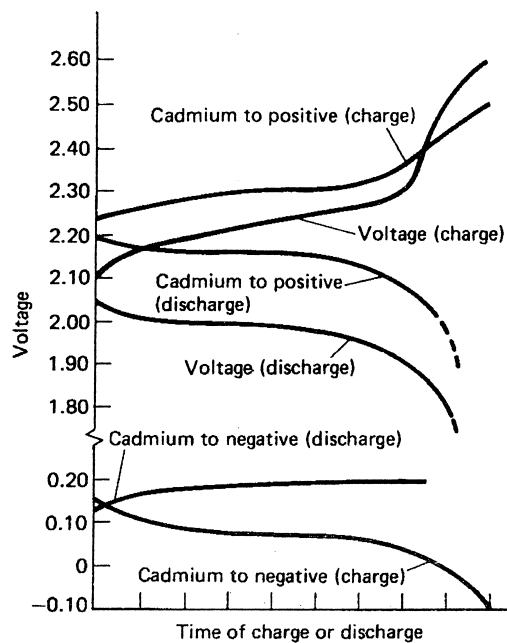
Fig. 8. Typical charge–discharge voltage curves for a lead–acid cell [5].

creased battery starting-current power, reserve-capacity performance and high-temperature durability (cycle-life) from thinner and thinner, low-cost plates, which are manufactured using high-volume continuous processes. To evaluate the optimum active-material balance and grid weight required to achieve the set performance criteria, it is now necessary to consider different plate and active-material ratios.

It is misguided to assume that changing the plate ratio in the component cell of an automotive battery will necessarily improve the performance of the battery. It is more appropriate to understand the effects of changing the size and number of plates in the cell on: (i) the positive-to-negative active-material ratio, commonly expressed as the ratio of the dry, active-material weight in the positive and negative plates after curing (or less frequently after formation); and (ii) the active-material utilization. Either weight comparison is valid, but the two must not be directly compared without first adjusting the data according to the changes in active-material morphology that occur between curing and formation.

A typical cycle-life 'benchmark' would be ~ 2800 cycles (SAE 'hot' J240 test at 75°C) from a Pb–Sb/Pb–Ca, 'hybrid', automotive battery which has tribasic lead sulfate curing, low water loss, and polyethylene envelope separators. The failure mode would be positive active-material degradation with, perhaps, a small amount of grid growth and corrosion. This assumes that other factors which affect performance have all been optimized for the particular battery design. These factors include: oxide purity; paste density; paste formulation; degree of overpasting; pasting

technique; composition and microstructure of the grid alloy; grid design; morphology, surface-area and porosity of the active material. Increasing the positive:negative active-material ratio improves cycle-life, but now at the risk of over-working the negative active-material (leading to lignin degradation)! For batteries with high positive:negative ratios, there is a tendency for negative-plate shrinkage to increase and become the predominant failure mode.

Battery water loss during overcharge ($2H_2O \rightarrow O_2 + 4H^+ + 4e^-$) is directly linked to positive-grid corrosion, and, therefore, any technological and design improvements that reduce grid corrosion will result in less water loss.

The grid weight per ampere-hour is almost directly proportional to the rate of positive-grid corrosion, particularly at elevated temperatures. Increasing the positive/negative ratio will, therefore, reduce the effect of this factor on battery life. Grid weights per ampere-hour (20-h rate), although a significant cost factor, are typically in the range 4.5–6.0 g. The growth of positive grids may decrease with increasing positive/negative ratio as a result of the effects of reducing the utilization of the positive active-mass, which, in turn, would exert less stretching stresses on the positive grid. The correct alloy specification and control of impurity levels are certainly of more critical importance in reducing the growth of positive grids.

Increasingly, batteries for automotive applications are designed with either equal numbers, or more positive than negative plates. The results from a survey have confirmed this, namely: 25%, 34% and 41% of batteries had p:n < 1, 1 and > 1, respectively. The true objective of this trend is, however, to achieve a desired positive/negative active-material ratio of, typically, 1:10 to 1:1.2.

*4.3. Question: Explain what is meant by 'local action' and what are its benefits and deficits?*

### D.W.H. LAMBERT

'Local action' is the term commonly used to describe any electrolytic reaction that takes place in a cell, other than the main charge–discharge reaction. Detrimental results of local action include, for example, the self-discharge of lead − acid batteries caused by the following.

· Localised $Fe^{2+}/Fe^{3+}$ redox reactions, due to impurities or contaminants in the electrolyte and/or in the active materials.
· The undesirable diffusion of antimony species from the positive grid/plate to the surface of the negative plate to form a galvanic cell, which, in the presence of sulfuric acid, results in a local self-discharge reaction with hydrogen evolution and the formation of lead sulfate, namely: $Pb + H_2SO_4 \rightarrow PbSO_4 + H_2$.
· Oxidation of alloying metals in the positive grid, such as antimony: $5PbO + 2Sb + 6H_2SO_4 \rightarrow (SbO_2)_2SO_4 + 5PbSO_4 + 6H_2O$.

- Sulfation of residual PbO, particularly in newly formed positive active material, i.e., $PbO + H_2SO_4 \rightarrow PbSO_4 + H_2O$.

Conversely, there is one major benefit of local action to the lead − acid battery system, namely, oxygen recombination at the negative electrode of a VRLA battery, i.e., $2Pb + 2H_2SO_4 + O_2 \rightarrow 2PbSO_4 + 2H_2O$.

## 4.4. Question: Do present-day negative-plate expanders display significant differences in performance?

### K. PETERS

Most battery-makers find it convenient to buy pre-mixed negative expanders. These may contain fibre (to improve paste consistency and handling) and dry-charge additives, but the main constituents are carbon, barium sulfate, and an organic expander. Carbon and barium sulfate are fairly standard components and vary little when obtained from different sources. Care should be taken that the carbon is free from oil and that there are no deleterious metallic impurities in the barium sulfate. It should be stressed that these expanders should always be purchased from a reputable supplier.

The type and composition of the organic component in the mixture may vary considerably. Most are derivatives of wood pulp. The extracted lignins are purified by removing sugars and various metals, and can be depolymerized to different degrees. Lignin molecules are formed from three primary precursors; the proportion of each varies with the origin of the lignin and exhibits a major influence on battery performance. They can be sulfonated to different degrees with sulfurous acid or with salts made with various cations. Partial oxidation of these lignosulfonates reduces the number of sulfonic and methoxyl groups and increases the number of the functional phenolic and carboxyl groups. These compounds are known as oxylignins. The high-molecular-weight fractions are the major constituent and contain about 10 wt.% methoxy groups and nearly 1 wt.% phenolic hydroxy groups. The conductivity of the low-molecular-weight fractions suggests that they are mostly colloidal with some dissociation or micelle formation, whereas the high-molecular-weight fractions behave as large and flexible polyelectrolytes.

Table 7
Relative high-rate capacity of negative plates containing various organic expanders

| Additive | −18°C | 25°C |
|---|---|---|
| No organic expander | 1 | 6 |
| Additive A (lignin) | 5 | 25 |
| Additive B (metallic salt of oxylignin) | 6 | 27 |
| Additive C (oxylignin) | 7 | 28 |
| Additive D (metallic salt of oxylignin) | 8 | 30 |

Table 8
Effect of organic expander on negative charge potential

| Additive | Full charge potential at $0.1C_{20}$ A[a] (V) |
|---|---|
| No organic expander | −0.45 |
| 0.25 wt.% additive A (lignin) | −0.62 |
| 0.25 wt.% additive B (oxylignin) | −0.66 |
| 0.25 wt.% additive C (oxylignin) | −0.68 |

[a] With respect to the standard hydrogen potential (SHE).

These additives disperse lead and, thereby, reduce the particle size of the sponge to cause a very large increase in surface area. As a consequence, the additives exhibit the most beneficial effect on capacity — particularly, under cold conditions — as can be seen from a comparison of the relative performances of negatives made with various organics (Table 7). It is generally accepted that certain oxylignins and their metallic salts are more efficient in this respect than the lignins, and, thus, are often preferred in automotive batteries.

The retained activity over extended service of these materials may vary and the respective durabilities of these materials is not well defined. The general view is that the slightly less-efficient lignins are more durable and are often preferred in deep-cycling battery applications, where up to 2000 cycles are expected and the high-rate performance is not so demanding. The situation is confused by the influence of the organic materials on charge-acceptance and charge efficiency at pre-set charging voltages. While carbon and barium sulfate have little effect on the hydrogen-evolution potential, the organics have a considerable effect which varies according to the type of material used (Table 8).

Voltage differences as high as −80 mV per cell are possible with some additives and the charge-acceptance under certain charging conditions can be substantially decreased, which causes operational problems, particularly in deep-cycling applications and more so with long-string systems. This is further illustrated by the voltage response to constant-current charging of 12-V automotive batteries made with different organic expanders (Fig. 9). When charged under normal voltage conditions (say, to 14.5 V), each will be at a different state-of-charge (SoC) because of the varying charge efficiencies. When cycled frequently under similar conditions, the health and efficiency of the various negative plates will vary according to their overpotential characteristics.

A further property of these expanders, which should not be ignored, is their ability to prevent or inhibit passivation caused by impurities (so-called 'immunization'). This is also related to the polarization characteristics of the expanders, i.e., the higher the polarization, the more efficient the immunization or depassivation.
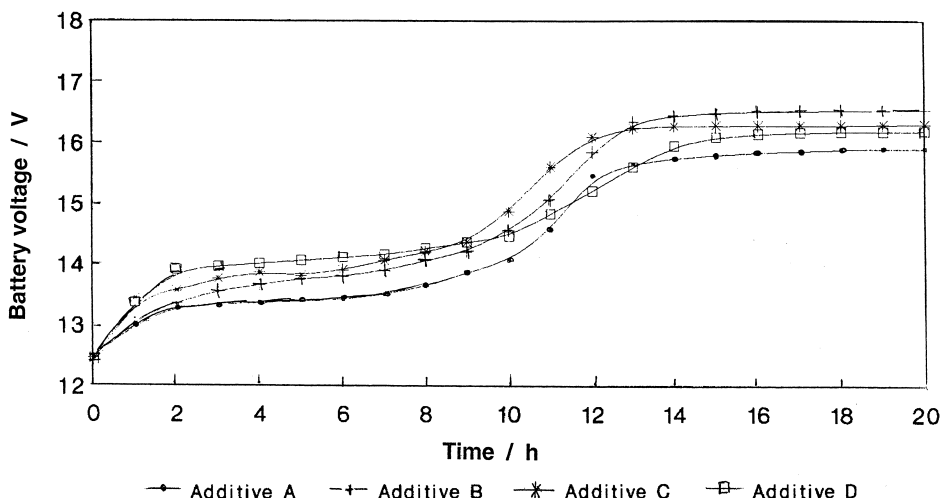
Fig. 9. Charge voltage with four types of organic expander. 12-V battery. Charging at $0.1C_{20}$ A. After 10 discharges to 50% SoC.

### 4.5. Question: What prompts the use of gas-recombining catalysts in VRLA batteries? How effective are these catalysts?

### K. PETERS

Gas-recombining catalysts have been used for many years in some lead − acid batteries, as well as in other battery systems, to recombine hydrogen gas with oxygen and produce water vapour, which condenses and reduces the need for water additions. In VRLA batteries, water replenishment occurs by virtue of the reaction of oxygen with the negative lead electrode and subsequent charge. Thus, the need for catalysts is generally perceived as unnecessary. Nevertheless, experience with long-life VRLA batteries, such as those used in standby applications with a projected service life of 20 years, suggests that the additional use of catalysts is beneficial and improves reliability over these extensive periods.

While gas recombination in a well-designed and operated VRLA battery works both efficiently and effectively, to give a smaller and compact battery with low water loss and that is capable of operating in an office environment, slow drying-out and progressive loss of negative-plate capacity may occur over extended periods. Loss of water in a well-regulated system may be due either to the kinetic hindrance of oxygen transport and reduction such that the recombination efficiency is less than 100%, or to side reactions such as positive-grid corrosion or self-discharge from impurities. While most designs allow for some short-fall in very long-life batteries, there is a risk that water loss could reduce the performance expectations. In addition, the oxygen-recombination reaction reduces the polarization of the negative plate with the further risk that it will become progressively undercharged and sulfated. In standby operations, where the battery is floated at pre-set voltage levels, this reduced polarization may cause variable negative-plate
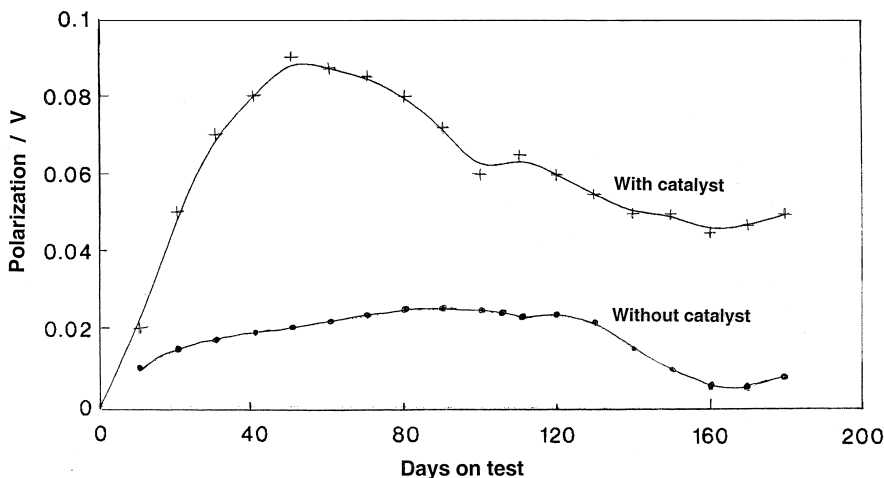


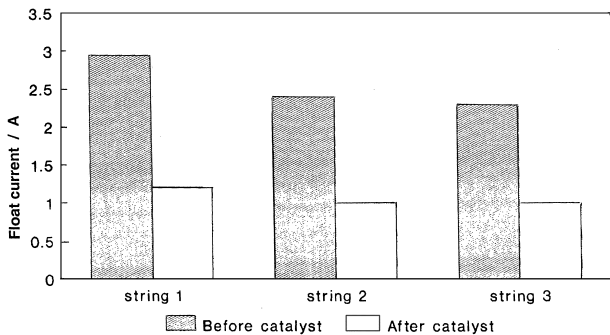Fig. 10. Negative polarization ($V$ vs. mercury/mercurous sulfate) at 2.27 V/cell, with and without catalyst.

Fig. 11. Comparison of float currents in 6-month-old cells at 30°C to 35°C. 24 cells per string.

potentials and higher float currents with the risk of greater water loss.

Trials have shown that a well-designed catalytic agent fitted in the headspace reduces the gassing rate and water losses in VRLA cells still further. Additionally, the polarization of the negative plate is enhanced. The negative polarization of identical cells with and without catalysts is shown in Fig. 10. The variability over the first few weeks is not unusual, but the data show that the negative potentials of the cells fitted with catalysts stabilize at about 50 mV above that of cells without catalysts after 12 weeks of service. The float currents of cells after 6 months of service, before and after fitting catalysts, are presented in Fig. 11. With catalysts, the float current decreases to less than half the value recorded without catalysts. Catalytic systems are now commercially available in the USA for standby applications. Experience from 3 years of service supports the original view that battery reliability is improved.

There has been some concern expressed over the long-term reliability of the catalytic agents. For example, it is known that they are prone to loss in activity due to wetting and poisoning by certain metals, such as antimony. Designs of VRLA battery, however, have certain inherent

safeguards. First, they are made with relatively pure components and the risks of poisoning by impurities is much reduced. Second, the cells are, of course, not flooded, and, thus, there is little risk of wetting of the catalyst by acid spray. Third, since the catalysts are only combining a small proportion of the oxygen produced in the system (a much greater proportion reacts with the negative plate), the danger of saturation wetting of the catalyst is greatly diminished.

Results to date confirm the original view that the use of recombination catalysts in VRLA batteries minimizes gassing, maintains the negative potential at higher polarization levels (i.e., at more negative values), and stabilizes the cell potential. All of which assist reliability. It must be stressed, however, that catalysts will not compensate for VRLA batteries that are poorly made.

*4.6. Question: What causes the selective discharge of negative and positive plates in VRLA batteries under float duty and how can this problem be overcome?*

**D.A.J. RAND**

Consider the recharging of a VRLA battery from a totally discharged state, Fig. 12. In common practice, a constant-current − constant-voltage procedure is applied with a top-of-charge voltage of 2.45 V/cell average. As the SoC of the battery increases, the potential of the negative plate becomes more negative, and that of the positive plate becomes more positive. That is, the cell voltage increases.

For most VRLA designs, the current remains constant up to a SoC of about 70% and the voltage reaches the top-of-charge limit of 2.45 V/cell. Also, there is no (or very little) gas evolution at either plate polarity. Above 70% SoC, the charging switches to constant-voltage control, and the current starts to fall. Gas evolution now occurs at the electrodes. At 80% to 90% SoC, the portion of the total current ($I_T$) at each plate that is consumed by
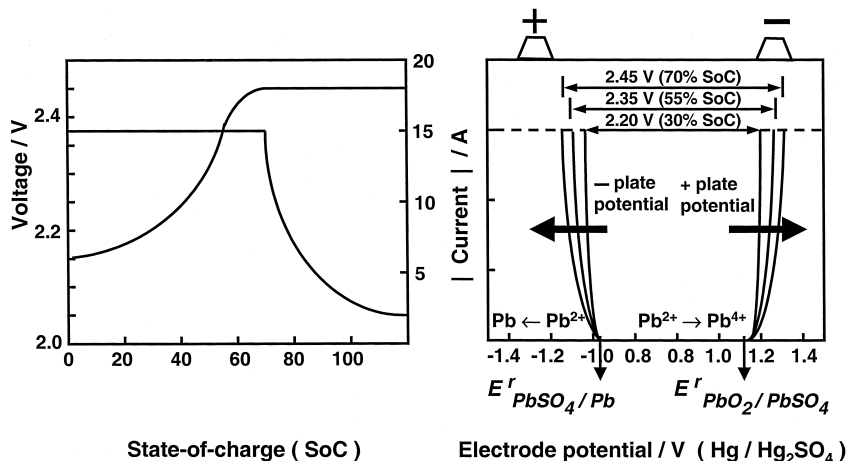


Fig. 12. Schematic of recharging of a lead–acid battery from 0% to ∼ 70% SoC; constant-current–constant-voltage charging.
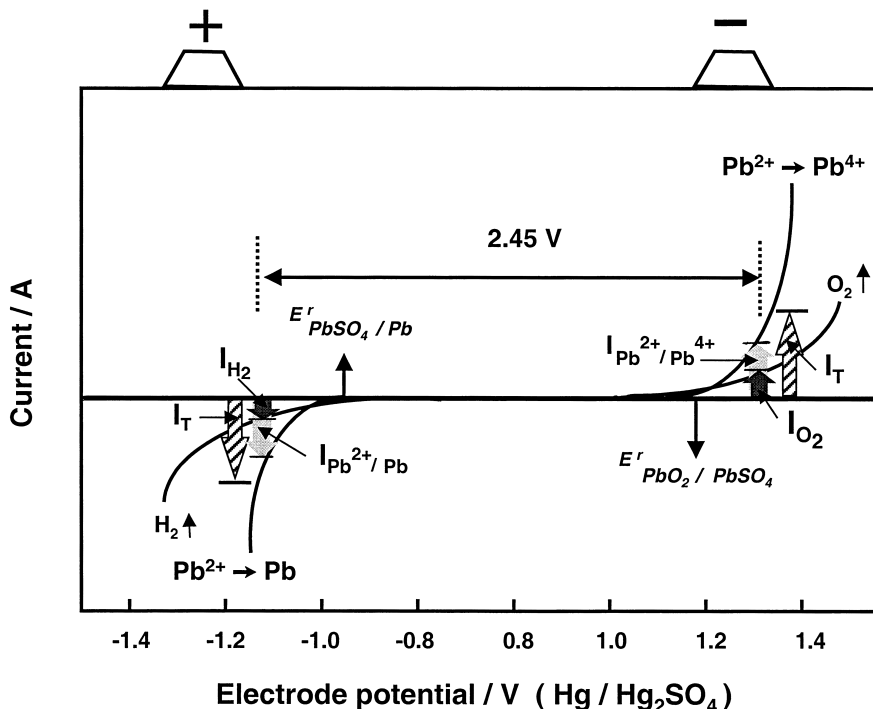
Fig. 13. Schematic of recharging a lead–acid battery from 0% to $\sim 90\%$ SoC; constant-current–constant-voltage charging.

the conversion of lead sulfate to the respective active material ($I_{Pb^{4+}/Pb^{2+}}$ and $I_{Pb^{2+}/Pb}$) is still greater than the portion consumed by the accompanying evolution of gas ($I_{O_2}$ and $I_{H_2}$) (see Fig. 13).

In float duty, the battery is maintained at full charge by applying of constant voltage ($V_a$) of, typically, 2.27 V/cell average (Fig. 14). For the battery to be kept in a fully charged state:

- the potential of the negative plate must be more negative than the reversible potential of the $PbSO_4/Pb$ couple ($E^r_{PbSO_4/Pb}$).
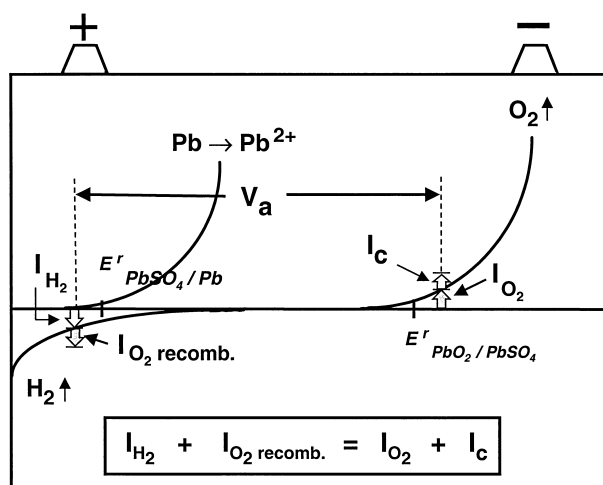


Fig. 14. Schematic of practical operational of a VRLA battery on float duty.

- the potential of the positive plate must be more positive than the reversible potential of the $PbO_2/PbSO_4$ couple ($E^r_{PbO_2/PbSO_4}$).

In a VRLA battery, oxygen generated at the positive plate is transported to the negative plate, where it is chemically reduced (that is, 'recombined') to water at an efficiency of 95% to 98%. Thus, during float duty in the fully charged state, the current at the positive plate is consumed principally by oxygen evolution ($I_{O_2}$) and grid corrosion ($I_c$), and is balanced by a current at the negative plate that is consumed by hydrogen evolution ($I_{H_2}$) and oxygen recombination ($I_{O_2 \ recomb.}$) (see Fig. 14).

### 4.6.1. Selective discharge of negative plate

If the materials — particularly, the lead materials — used to construct the battery contain sufficient levels of certain impurities, then $H_2$ evolution may be enhanced (Fig. 15). If the rate of oxygen evolution and its recombination efficiency remain unaltered, then the potential of the negative plate will be driven to a value, which is less negative than the $PbSO_4/Pb$ reversible potential. In such a situation, the current consumed by hydrogen evolution will be greater than the sum of the currents consumed by the evolution of any unrecombined oxygen and by grid corrosion at the positive plate. To balance the current at the two plate polarities, the difference will be taken up by 'selective discharge' ($I_{sd}$) of the negative plate via the following reaction couple:

$$2H^+ + 2e^- \rightarrow H_2 \tag{4}$$

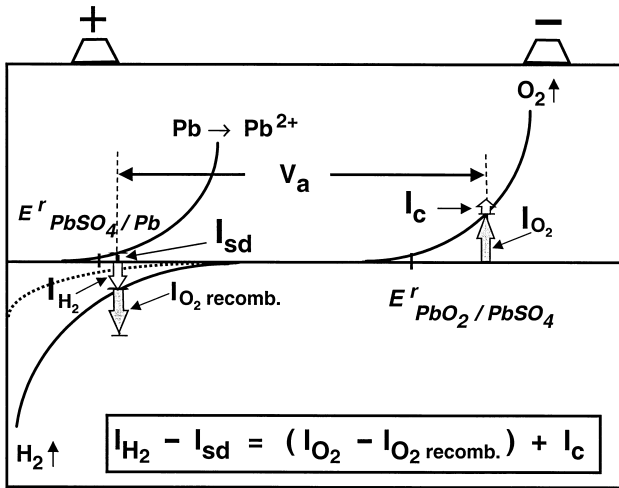$$Pb + H_2SO_4 \rightarrow PbSO_4 + 2H^+ + 2e^- \tag{5}$$
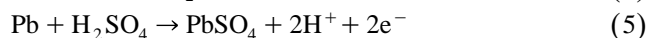
Fig. 15. Schematic of selective discharge of negative plates in a VRLA battery.
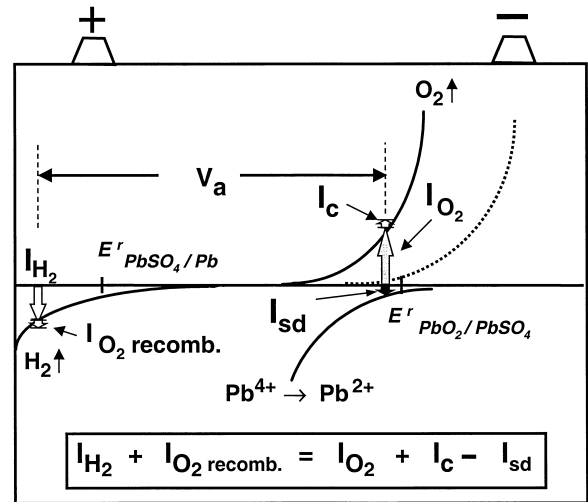


Fig. 17. Schematic of selective discharge of positive plates in a VRLA battery.

It should be noted that the problem of selective discharge of the negative plate is more severe if:

· the battery has a very high recombination efficiency (e.g., as a result of water loss during prolonged operation), or
· a highly corrosion-resistant grid alloy is used.

How can selective discharge of the negative plate be overcome? One approach (A in Fig. 16) would be to increase the rate of grid corrosion, but this would obviously shorten battery life. A second approach (B in Fig. 16) would be to lower the oxygen-recombination efficiency, either by allowing oxygen to escape from the cell
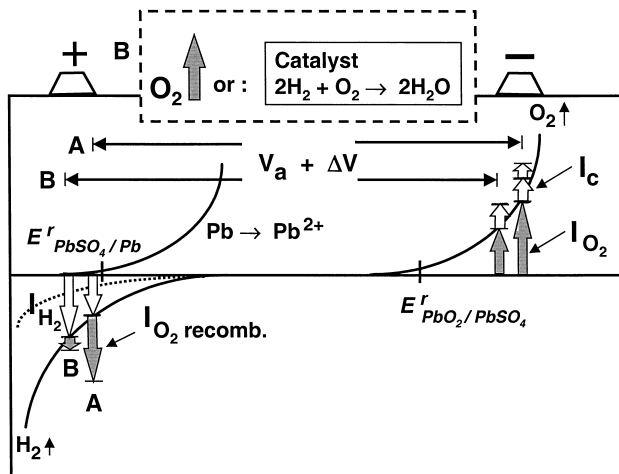


Fig. 16. Strategies (A and B) to overcome selective discharge of the negative plate in a VRLA battery. (A) Increase grid corrosion; no change in oxygen-recombination efficiency. (B) Lower oxygen-recombination efficiency; no change in grid corrosion. Both strategies involve an increase ($\Delta V$) in float voltage.

(but this would lower battery performance through cell dry-out) or by using a catalyst to reduce oxygen chemically. With both strategy A and strategy B, the battery would be operating at a higher voltage. Also, there would be an increase in hydrogen evolution. Here, a catalyst is useful as it combines the hydrogen with oxygen to produce water. It should be noted, however, that catalysts add complexity and cost, and possibly suffer reliability problems — not only with respect to their own operation, but also with respect to that of the battery itself.

The correct approach to safeguarding against the selective discharge of negative plates is to use purer lead. That is, to lower the tolerance limits of harmful metals which enhance hydrogen evolution, e.g., antimony, iron, nickel, selenium. It is for this reason that metal suppliers are now setting more rigorous specifications for soft lead and are offering lead with a quality and a purity that meets the special requirements of VRLA technology.
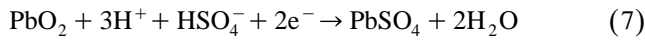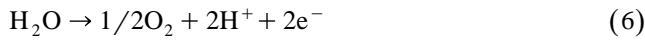
### 4.6.2. Selective discharge of positive plate

Positive plates in VRLA batteries can also suffer from selective discharge (Fig. 17). This discharge is particularly likely to occur during the early stages of service. The problem can be promoted by the following set of conditions:

· the rate of oxygen evolution at the positive plate in enhanced through the presence of impurities, e.g., antimony, cobalt, nickel, silver
· the oxygen-recombination efficiency at the negative plate is low ($< 80\%$).

These features move the potential of the positive plate towards the equilibrium potential. If the potential becomes less positive than the equilibrium value, and the combined

current due to oxygen evolution and grid corrosion ($I_{O_2}$ + $I_c$) is still higher than that consumed by hydrogen evolution and oxygen recombination ($I_{H_2} + I_{O_2 \text{ recomb.}}$) at the negative plate, then the difference will be taken up by selective discharge of the positive plate via the reaction couple:

$$H_2O \rightarrow 1/2 O_2 + 2H^+ + 2e^- \tag{6}$$

$$PbO_2 + 3H^+ + HSO_4^- + 2e^- \rightarrow PbSO_4 + 2H_2O \tag{7}$$

The selective discharge will be increased further if the positive plate uses a grid alloy which is highly corrodible.

Again, the solution to the problem is to use ultra-pure lead materials.

Note, as the battery dries out, the oxygen-recombination efficiency will increase. Thus, the negative-plate potential will become less negative, and, accordingly, the positive-plate potential will become more positive. Eventually, there will be no selective discharge of the positive. The persistently high evolution of oxygen will, however, cause excessive recombination of oxygen at the negative. This will produce considerable heat and may result in thermal runaway of the battery.

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