

## Failure modes of lead/acid batteries\*

### B. Culpin

Chloride Industrial Batteries, P O Box 5, Clifton Junction, Swinton, Manchester M27 2LR (U K)

### D. A. J. Rand

CSIRO Division of Mineral Products, P O Box 124, Port Melbourne, Vic 3207 (Australia)

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### Abstract

The delivery and storage of electrical energy in lead/acid batteries via the conversion of lead dioxide and lead to, and from, lead sulphate is deceptively simple. In fact, battery performance depends upon the cell design, the materials of construction, a complex interplay between the multitudinous parameters involved in plate preparation, the chemical composition/structure of the active materials, and the duty/conditions of battery operation. It is not surprising, therefore, that the factors responsible for the degradation of battery performance, and eventual failure, are many and varied. Apart from occasional field surveys of automotive batteries in the U S A, comprehensive failure analyses of units removed from service are rarely published. In general, the information is kept proprietary, or appears as a *post mortem* report that is subsidiary to some other topic of interest. By contrast, the literature abounds with detailed laboratory investigations of phenomena that are likely to contribute, wholly or in part, to the demise of batteries. In broad terms, this review draws together the fragmented and scattered data presently available on the failure mechanisms of lead/acid batteries in order to provide a platform for further exploration of the phenomena, and for the planning of remedial strategies. The approach taken is to classify, first, the different lead/acid technologies in terms of required duty (i.e., float, cycling and automotive applications), unit design (i.e., flat or tubular plate, flooded or immobilized electrolyte), and grid alloy (i.e., lead-antimony or lead-calcium system). A distinction is then made between *catastrophic* failure, as characterized by a sudden inability of the battery to function, and *progressive* failure, as demonstrated by some more subtle deviation from optimum performance. Catastrophic failure is attributed to incorrect cell design, poor manufacturing practice, abuse, or misuse. These problems are obvious and, accordingly, have been afforded little discussion. Progressive life-limiting factors encountered with flooded-electrolyte batteries are discussed in detail. These are mainly associated with degradation of the positive plate, the negative plate and the separator. The technology of valve-regulated (i.e., immobilized-electrolyte) batteries is still at an early stage compared with that of flooded designs and, consequently, published information on failure modes is very limited. Nevertheless, based on the reports that are available and the authors' own knowledge, it is possible to make estimates of the major and minor causes of failure (note, these will also occur in flooded systems, but with shifted emphasis). Grid corrosion and growth are generally considered to be of major importance. Both negative-plate sulphation and water loss are also of concern, particularly

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in cycling applications. By contrast, the traditional problems associated with shedding, mossing and dendritic growth of the active material should be reduced in valve-regulated batteries.

## Introduction

For over a century, the lead/acid battery has provided a versatile, reliable and cost-effective means of storing and delivering electrical energy. Clearly, the mode(s) by which a battery eventually fails will depend largely upon the design and quality of the unit, the type of duty being undertaken, and the degree of care and maintenance that is exercised during operation. Therefore, in order to survey the whole field of failure modes, it is first necessary to examine the various applications of the lead/acid batteries and the approaches taken by manufacturers to design cells to withstand the rigours of such service.

## Classification of lead/acid batteries by duty

The different duties demanded of lead/acid batteries can be divided into the following three categories:

### *Float duty*

Float duty is encountered in the broad market for standby power. Traditionally, lead/acid batteries have been used as back-up power sources to ensure the operation of critical loads during breaks in the primary power supply, e.g., mains failure. Standby-power batteries have found service in power stations, telecommunications networks, emergency lighting, lift control, switch gear, signal systems, medical equipment, security devices, etc. More recently, advances in solid-state power electronics have allowed the development of uninterruptible power supply (UPS) systems [1]. These have extended the use of lead/acid batteries, particularly in the protection of computer-based equipment.

Depending upon the application, the required capacity of the batteries may be a few to several hundred ampere-hours. The batteries are designed for a life of 10 or more years. The major part of the service life is spent on float at a potential between 2.2 and 2.3 V/cell under well-controlled ambient temperatures, typically 25 to 30 °C. The batteries experience discharges, particularly deep discharges, only rarely. In regulated environments with secure power supplies, the batteries may be discharged as little as five times, or less, during their entire life.

### *Cycling duty*

The second category – cycling applications – covers a more varied range of duties and operating conditions. The most arduous work is en-

countered in motive-power service in which batteries are subjected to deep discharge on a regular (e.g., daily) basis. In countries where the mains supply is unpredictable, standby-power batteries may also be called upon to give deep discharge often in some cases, every day. Under such situations, the duty experienced by the standby batteries would be more akin to a cycling service than to a float regime, and the performance would be affected accordingly.

There is a burgeoning demand for sealed rechargeable batteries to power cordless appliances. The suitability of lead/acid batteries for portable devices has been strengthened by the recent introduction of valve-regulated technology [2]. The batteries are available over a wide range of sizes from around 1 to 25 A h. Given the existing wide diversity of battery-powered appliances and inevitable large differences in the usage patterns between owners, both the frequency and the extent of the discharge experienced by portable batteries are uncertain. A notable exception is the service required from miners' cap lamps for which a well-defined schedule of discharge and recharge can be established [3].

Increasing attention is being directed towards the development of stand-alone power supplies incorporating 'renewable' solar and/or wind technologies — with electricity storage in batteries — as more economic, reliable and environmentally acceptable alternatives to traditional diesel sets and diesel/battery hybrid arrangements [4]. The former systems offer an attractive prospect for the generation of power in remote areas (i.e., in navigational, telecommunications, village and homestead installations), as well as in space exploration. When intended for terrestrial operations, such a facility is commonly termed a 'remote-area power-supply' (RAPS) system. Lead/acid batteries are the most appropriate method for storing electricity derived from solar (i.e., photovoltaic) sources, but while RAPS duty has some features in common with those encountered in motive-power operations, solar-power batteries often undergo a more varied duty with poorly-defined discharge and recharge regimes. Furthermore, since photovoltaic-based RAPS systems offer the greatest benefits in sunny areas, the batteries have to withstand much higher temperatures than those prevailing under traditional cycling and float operations.

In the electric utility industry, energy storage in lead/acid batteries provides a promising alternative to installing extremely costly continuous-duty plants to balance the power-generation requirements. Electrical energy is stored by charging of the batteries during off-peak hours (usually at night) and is supplied from the batteries when the demand is high. This is the concept of 'load levelling'. Battery facilities can also provide reserve energy to meet power emergencies. Located on the customer side of the meter, batteries can offset the customer's peak loads (note, the cost of electrical energy is determined not only by the total energy consumed (kW h) but also by the peak-power demand (kW)). This is the concept of 'peak shaving'. In both load-levelling and peak-shaving duties, the batteries will be subjected to a regular schedule of charge/discharge cycling. For example, the 8256

lead/acid cells comprising the load-levelling facility at Chino, CA, are required to supply, daily, 10 MW of power for 4 h [5]

### *Automotive duty*

Automotive batteries used for the starting, lighting and ignition of internal-combustion-engined vehicles (i.e., cars, buses, trucks and motorcycles) constitute the largest market for lead/acid. Once the engine is running, a generator or alternator system recharges the battery and maintains it on float at full charge. Thus, the duty is a mixture of cycling and float, again with the possibility of wide variations in ambient temperature. The latter problem is becoming a subject of major concern as the recent trend towards a decrease in vehicle size, combined with emission and fuel-efficiency requirements, has brought about smaller, hotter engine compartments that, in turn, result in higher battery temperatures.

From the above discussion of the wide diversity of battery duties, it can be readily appreciated that different failure mechanisms are likely to dominate under different circumstances. Nevertheless, drawing upon experience gained with the lead/acid system over the past 100 years or so, battery technologists have established empirical procedures to handle many of the problems associated with the various service routines.

## **Classification of lead/acid batteries by design**

### *Plate designs*

Three varieties of positive plate are used in the manufacture of lead/acid batteries, namely, the Planté, the flat pasted (or Faure) and the tubular configurations. By contrast, all negative plates are constructed as pasted types.

The Planté version of positive plate is made from a casting of pure lead that has numerous thin vertical grooves, strengthened by a series of horizontal cross-ribs, in order to increase the surface area. The active material (lead dioxide,  $\text{PbO}_2$ ) is formed electrochemically from the lead itself by carrying out a series of charge/discharge cycles in a mixture of dilute sulphuric and perchloric acids, and is held within the grooves cast in the plate. Planté batteries are used solely in standby-power service.

The pasted type of positive plate is produced by machine application of a stiff paste of active materials on to a lattice-type grid that is fabricated from a suitably selected lead alloy. The paste consists of a mixture of 'leady oxide', water and sulphuric acid blended together in proportions specific to each battery manufacturer. After pasting, the plates are passed rapidly through a high-temperature tunnel oven (so called 'flash drying') in order to reduce the surface moisture so that the plates will not stick together during subsequent handling. In the next process stage, the plates are 'cured' for a given period, preferably in an oven under controlled conditions of humidity and temperature. The latter are regulated to provide plates rich in either tribasic lead sulphate

(3BS) or tetrabasic lead sulphate (4BS) [6] The consolidation of the plate material is assisted by the production of these basic lead sulphates Finally, during the 'formation process', the cured material is converted to  $\text{PbO}_2$  by electrochemical oxidation in dilute sulphuric acid for a fixed period under controlled conditions of charging rate and temperature Pasted-plate designs are employed over the complete range of battery applications

The tubular form of positive-plate consists of a row of tubes containing coaxial lead-alloy rods (also known as 'spines') surrounded by active material Two types of tubes are commonly used single braided glass fibre or woven polyester fibre multi-tube 'gauntlets' After filling with oxide (usually a mixture of leady oxide and red lead), the tubes are soaked in sulphuric acid (the so-called 'pickling' process) in order to convert the majority of the lead oxide into lead sulphate This extensive sulphation assists the subsequent formation of the tubular plates Batteries with tubular plates are used predominantly in standby- and motive-power applications

### *Cell designs*

Recently, a new type of lead/acid technology has emerged to challenge the traditional, flooded-electrolyte, design of cell This has arisen as a result of a strong market pull for 'maintenance-free' batteries — that is, for batteries that do not require water replenishment during the course of their normal service life The new technology is based on the 'oxygen recombination cycle' [7], and uses an electrolyte that is immobilized either by adsorption within a glass-microfibre mat or by gelatinization with silica Gas recombination is achieved by arranging for oxygen generated at the positive plate on overcharge to pass via channels in either the glass-microfibre or the gel to the negative plate, where it reacts with excess lead to regenerate water A valve is fitted to allow the escape of small quantities of gas that are liberated on overcharge (note, recombination efficiency is  $< 100\%$  in most cases) and this prevents pressure build up and distortion of the container By virtue of this feature, the product has become known as the 'valve-regulated battery' (VRB) The absorbed-electrolyte design employs flat positive plates, although efforts are now underway [8] to develop batteries with tubular plates In these, the tubes have been converted to a square geometry in order to improve the contact between the glass-microfibre separator and the plate, and to equalize the stacking pressure in the cell assembly By contrast, both flat and tubular positive plates are commonly used in commercial gelled-electrolyte batteries

Batteries for float duty are now probably the largest single application of valve-regulated technology, this covers use in standby power, UPS and telecommunications systems [9] As mentioned above, VRBs are also proving extremely popular for powering portable devices and appliances, e g , miners' cap lamps [3]

The development of VRBs for true motive-power applications is still in its infancy Service lives of over 1000 cycles to 80% depth-of-discharge

(DOD) have recently been reported for both glass-microfibre [10] and gelled-electrolyte [11] batteries, but 500 cycles appears to be a more realistic limit with present designs [12]

The possibility of using VRBs in RAPS systems is also being investigated [1, 13–16] To date, results with glass-microfibre batteries have not been encouraging On the other hand, better performance has been obtained with gelled-electrolyte technology [15, 16] Under the relatively demanding conditions of RAPS duty, there is a clear need for more sophisticated regulation of battery charge/discharge operations when using VRBs

The suitability of VRBs for load-levelling and peak-shaving duties was first demonstrated in 1989 in the USA [17] The success of this venture has given rise to the construction of two further plants One of these will be the largest single use, to date, of VRBs – 4 parallel strings of 144, 12-V modules rated at 5 MW and 5 MW h Since mid-1988, a major programme has been conducted by the Electric Power Research Institute (EPRI) to evaluate and compare the performance of glass-microfibre and gelled-electrolyte batteries as energy storage systems for electric utility companies

The world's first VRB for automotive service (a glass-microfibre variety) was introduced by Chloride Batteries Australia in the late 1970s – the Torque Starter<sup>®</sup> At that time, the emphasis was on good cold-cranking ability VRBs using glass-microfibre separators were attractive because of their low internal resistance and, therefore, superior cranking performance compared with equivalent flooded-electrolyte types (note, gelled-electrolyte batteries have much higher internal resistances) Furthermore, elimination of the need for an acid reservoir reduced both weight and size On the debit side, the low-rate capacity was inferior due to the acid-starved design The latter limitation assumed greater importance in the 1980s as the quiescent loads on automotive batteries increased This factor and the need for precise and consistent manufacturing specifications resulted in a high-cost product that, to date, has achieved little market penetration and, in some cases, has been withdrawn from the market completely Nevertheless, research still continues [18, 19] By contrast, VRBs – both glass-microfibre and gelled-electrolyte types – have gained widespread acceptance in motorcycle service

Not surprisingly, experience has shown that the marked differences in cell design and operational characteristics render both flooded and valve-regulated batteries susceptible to different failure modes

### **Classification of lead/acid batteries by grid alloy**

Conventional alloys for flooded-electrolyte traction batteries are based on the lead–antimony eutectic system Due to differences in the ease of fabrication, the spines of tubular plates have traditionally required an alloy with a higher antimony content (~10 wt %) than that appropriate for flat

plates ( $\sim 6$  wt %) Similar alloys are employed in the manufacture of standby-power batteries, but the use of pure lead in both Planté and pasted positive plates is also quite common

Antimony serves to improve the hardness, strength and castability of the grid It also exerts a subtle, beneficial effect on the structure and life of the positive active material There is, unfortunately, a major disadvantage with using antimony During battery charge, antimony dissolves (corrodes) from the positive grid, diffuses through the electrolyte, and deposits on the negative plate This results in a reduction of the hydrogen overpotential at the negative plate and, thereby, causes greater rates of gassing, water loss (and hence the need for more frequent maintenance) and self discharge These features are in opposition to the increasing demand for maintenance-free operation in all types of battery applications This, together with obvious cost savings, has resulted in the development and widespread use of 'low-antimony alloys' in flooded-electrolyte batteries At first, casting problems were experienced with low-antimony alloys but these have been largely overcome by the addition of grain-refining agents such as arsenic, copper, selenium, sulphur and tellurium Castability can also be improved by the presence of a small amount of tin ( $\sim 0.1$  wt %) which increases the fluidity of lead alloys

Low-antimony alloys used for the positive grids of present-day automotive batteries generally contain  $\sim 2$  wt % Sb In the USA — the world's largest market for automotive batteries — most units are built with lead-calcium or lead-calcium-tin alloys for the negative grids (so-called 'hybrid' units) There is also a growing proportion of batteries in service with positive and negative grids that are both made from calcium alloys These alloys exhibit a higher hydrogen overpotential than antimonial types (resulting in lower water loss during charging), have increased electrical conductivity, and are sufficiently malleable to allow grid fabrication by rapid and continuous techniques The calcium-containing alloys are produced by one of three processes (i) direct gravity casting (book-moulding or continuous strip), (ii) expansion of drum-cast strip, (iii) expansion of rolled (wrought) cast strip The different methods can give rise to variations in the metallurgy of the alloy and these, in turn, can be expected to influence performance in the battery

Lead-calcium-tin alloys are also preferred by most manufacturers of valve-regulated batteries (glass-microfibre and gelled-electrolyte types) and great emphasis is placed upon system purity to minimize water loss [20] The main exception is the Gates' glass-microfibre design [7] that employs grids punched from pure lead These grids require careful processing because of the low strength of the metal Glass-microfibre VRBs have also appeared on the market with low-antimony positive grids [17] These are based on a lead-antimony-cadmium system containing approximately equal amounts of the two alloying additions It would appear that the degree of antimony poisoning of the negative plate is minimal and that the alloys are suitable for deep-cycling service

Clearly, the use of the different alloys described above will affect grid corrosion rates and mechanisms, grid growth, and the leaching of impurities into solution. In turn, these will influence the life and failure modes of batteries—dependent, of course, upon the cell design.

### Categories of lead/acid battery failure

Before discussing battery failure modes in detail, it is first necessary to make a distinction between catastrophic battery failure, as characterized by a sudden inability to recharge and deliver useful electrical energy, and progressive deterioration in performance, as demonstrated by a gradual decline in capacity. Since batteries cannot be expected to last forever, the latter behaviour is obviously more desirable.

In general, *catastrophic failure* is easily diagnosed and characterized. In some instances, it arises simply from

- incorrect cell design and component selection, e.g., short-circuits due to plate and separator faults,
- poor quality control during manufacture, e.g., open-circuits arising from loose plates/terminals, and/or from the fracture of weak plate-to-busbar, busbar-to-terminal or cell-to-cell connections, attack from contaminants,
- abuse, e.g., undercharging, overcharging, low electrolyte level (flooded systems), vibration, high ambient temperature, entry of harmful foreign species, prolonged storage with insufficient recharging,
- external and/or internal damage, e.g., broken containers and covers, damaged terminals, electrolyte leakage.

There is a certain degree of overlap between some of these categories, and more than one may have indeed contributed to the demise of the battery. Under such circumstances, interpretation of the mechanism of failure can be difficult. There is also the problem of users not selecting the correct battery for the type of duty required. For example, automotive batteries are often used in caravans and in fish-trolling expeditions. This application to leisure activities must be regarded as an abuse of the battery, as modern automotive batteries are not designed for deep-discharge operation.

*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. The latter include the following:

- (i) the chemical composition and physical properties of leady oxide,
- (ii) the composition (including additives), density, method of application, loading and pellet size of the paste (for flat plates),
- (iii) chemical composition and structure of cured plates (flat type) or pickled plates (tubular type),
- (iv) chemical composition and structure of formed plates,
- (v) plate thickness,



- (vi) composition and processing conditions of grids,
- (vii) composition (including additives) of electrolyte,
- (viii) choice of separator,
- (ix) cell design,
- (x) storage time before use,
- (xi) frequency and current density of discharge,
- (xii) depth of discharge,
- (xiii) stand time in a state of partial or complete discharge,
- (xiv) current and voltage of recharge,
- (xv) degree of overcharge,
- (xvi) temperature,
- (xvii) uniformity of concentration and maintenance of electrolyte

Parameters (i) to (vii) depend upon the materials, processing and design of the battery and, hence, are known as 'inner parameters'. On the other hand, parameters (viii) to (xvi) are determined by the conditions of battery use, and are accordingly referred to as 'outer parameters'. Any deleterious effect of the inner parameters on service life can be minimized, and perhaps avoided, through control and optimization of the materials' processing stages, whilst any problems emanating from the outer parameters can be reduced by selecting the battery design and system features to match the operating requirements of the application. Nevertheless, both sets of parameters will act (to varying degrees) to cause the eventual failure of the battery, principally via progressive degradation of the positive plate, the negative plate, or the separator, or by some combination of the three.

### **Failure modes of flooded-electrolyte lead/acid batteries**

#### *Degradation of positive plates*

The most critical materials are those in the plates, in particular the active material and the grids. Furthermore, the service life of flooded-electrolyte batteries is generally limited by the performance of the positive plate, the capacity of which declines on cycling, especially under deep discharge. From the onset, 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 ( $\text{PbO}_2$ ) and the discharge product ( $\text{PbSO}_4$ ). There is considerable evidence to show that the structure of the active material tends to change with repeated charge/discharge cycling. According to Pavlov and Bashtavelova [21, 22], for example, the positive active material consists of small crystals (a 'crystalline' or 'micro' structure) grouped into porous agglomerates to form a macroporous network or skeleton (an 'agglomerate' or 'macro' structure). It is further suggested that the latter provides mechanical support for the active material, conducts the electric current, and retains a memory of the conditions under which the plate has been prepared. During cycling, the agglomerate structure is gradually and irreversibly transformed into the crystalline version which, in turn, is broken down into individual crystallites. This process causes degradation in the mechanical integrity of the plate.

through softening and shedding of the active material. The latter, in turn, promote the secondary problems of 'mossing' and 'leading-through' (discussed below). The loosening of the inter-particle contact, together with the fact that not all of the  $\text{PbSO}_4$  is necessarily converted back to  $\text{PbO}_2$  during charging, also causes a reduction in electrical performance.

In addition to interpretations of the loss of positive-plate capacity in terms of morphological changes, shedding and electrical isolation of the material, it has been suggested that the intrinsic electrochemical activity of the  $\text{PbO}_2$  itself decreases with charge/discharge cycling [23–28]. This hypothesis has become known as the 'hydrogen-loss model' for it is proposed that the activity of  $\text{PbO}_2$  is related to the abundance and nature of structural hydrogen atoms, as well as to the amount of disorder in the crystal structure of  $\text{PbO}_2$  (for a recent review see ref. 29). More specifically, the proponents of the model have argued that (i) electrochemically active  $\text{PbO}_2$  contains at least two types of hydrogen species, one of which does not correspond to the hydrogen present in water molecules, (ii) the amount of non-water hydrogen decreases with charge/discharge cycling and brings about a structural re-ordering of an amorphous/disordered component in the  $\text{PbO}_2$ .

The hydrogen-loss model attracted a great deal of interest as the low-hydrogen content and the well-ordered structure found for  $\text{PbO}_2$  in failed batteries could be equated with the characteristics of chemically prepared  $\text{PbO}_2$  which was considered to be electrochemically inactive. Moreover, the model was consistent with the so-called 'stoichiometry-changing current model' that was developed later [30–32] for the  $\text{PbO}_2$  electrode and suggested that non-water hydrogen was catalyst for, or an intermediate chemical species in, the deposition or dissolution of  $\text{PbO}_2$ .

Following numerous investigations employing sophisticated investigative techniques (for a review see ref. 33), it appears that most, if not all, of the hydrogen observed in samples of battery  $\text{PbO}_2$  is present as surface-adsorbed water or hydroxyl species [34–37]. Furthermore, extensive studies on plate material taken from healthy and failed batteries have revealed no correlation between electrochemical activity and hydrogen content [35, 36]. Parallel efforts [36, 38] to link capacity decline with a change in the structural order of the  $\text{PbO}_2$  have also proved unsuccessful. It would appear, therefore, that the hydrogen-loss model has little practical validity in accounting for the progressive failure of the positive plate.

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 grid alloy composition and microstructure, electrode potential, electrolyte composition and temperature. These parameters, together with the grid geometry and the creep properties of the alloy, also determine the growth, or elongation, of grid members during battery service.

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  $> 1$  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.

Early studies [39-41] attributed the antimony-free effect observed on lead-calcium or dilute lead-antimony ( $\text{Sb} \leq 1$  wt %) alloys to the irreversible formation of an insulating  $\text{PbSO}_4$  corrosion layer between the grid and the active material. In later work [42-45], performance losses were associated with the development of a highly resistive layer of  $\alpha\text{-PbO}$  on the grid. To explain the presence of this compound, which is stable only in an alkaline environment, it was suggested [46, 47] that the  $\text{PbSO}_4$  discharge product is impermeable to sulphate species. With such a property, deposition of  $\text{SO}_4^{2-}$  ions in the interior layer as lead sulphate or mixed basic sulphates, together with the net flow of  $\text{H}^+$  ions to the negative electrode during battery charging, will result in a rise in the local pH beneath the  $\text{PbSO}_4$  layer and, hence, will permit the formation of  $\alpha\text{-PbO}$ . At high positive-plate potentials, these conditions will also promote the formation of  $\alpha\text{-PbO}_2$ . Thus, it is concluded that the passivation, or 'barrier', layer has a mixed  $\text{PbSO}_4/\text{PbO}_2$  structure ( $1 \leq x < 2$ ) where  $\text{PbO}_2$  is probably  $\alpha\text{-PbO}$  and/or  $\alpha\text{-PbO}_2$  (for a review see ref. 48).

The characteristics and influence of the barrier layer are thought to be moderated by the incorporation of tin — either alloyed into the positive grid, or as a laminated [49, 50] or electrodeposited [51] layer. When present in the alloy, tin has been shown to be effective in providing recovery from deep discharge [44, 52, 53], particularly during the early stages of battery cycle-life. Thus, the development of a passivating layer on non-antimonial grids has also been attributed to a 'tin-free effect' [44]. At present, there is considerable debate over the mechanism of the proposed tin effect, suggestions range from removal of the  $\alpha\text{-PbO}$  layer (via a simple redox process, i.e.,  $\text{SnO} + \text{PbO} \rightleftharpoons \text{Pb} + \text{SnO}_2$  [54]) to improved conductivity via complex semiconductor processes [55, 56]. By contrast, recent detailed studies have shown that, under certain operational conditions, tin exerts either only a transitory effect [48] or no clear benefit at all [57]. Obviously, further work is needed to determine what the true influence of tin may be in long-term cycling duties, with different cell designs (i.e., flooded-electrolyte versus VRB).

A second explanation for the antimony-free effect has been based on perceived differences in the nature and degree of cracking in the corrosion layers formed on antimonial and calcium alloys. The presence of cracks, together with poor adherence of the corrosion layer to the grid, will introduce electrical resistance losses. It appears that there is a reduced tendency for stress-cracking in the presence of antimony [58] and this has been related both to the additional space resulting from the preferential leaching of antimony-rich regions from the grid [59], and to a decreased hardness of the corrosion layer [60]. More recently, it has been suggested [61] that the

compound  $\text{PbSb}_2\text{O}_6$  is formed as a grid corrosion product and, by virtue of its layered-type structure, helps to relieve the stresses that accompany corrosion-product transformations during battery charge and discharge. Cracking of the corrosion layer occurs with prolonged cycling of batteries, irrespective of the choice of grid alloy. Lead-antimony alloys tend to exhibit radial fracture, whereas lead-calcium alloys tend to suffer concentric fracture [62]. Thus, under such conditions, there will be a better conduction path for electrons in the antimonial corrosion layer.

As opposed to  $\text{PbSO}_4/\alpha\text{-PbO}$  resistive layer or corrosion-layer cracking, a third school of thought advocates that the antimony-free effect is due to a varying current distribution from cycle to cycle brought about by changes in the conductivity of the lead dioxide [63]. In this respect, it is suggested that the antimony-free effect is better described as a 'relaxable insufficient mass utilization' (RIMU) because the phenomenon can occur in both the absence and the presence of antimony, and is caused by solid-state relaxation processes in the lead dioxide which is considered to be non-stoichiometric, i.e.,  $\text{PbO}_{2-\delta}$ . The morphology of the lead dioxide is regarded [64] as an aggregate of individual spheres (the 'Kugelhaufen' electrode) that provides an electrically conducting network via narrow passages, or necks, at the contact points of the spheres. With this model, it is claimed that the RIMU is caused by the formation of smaller neck zones of increased resistance. The latter modify the current distribution and, as a consequence, increasing amounts of active material become isolated from the electronic conduction network. It has also been shown [63, 65] that various electrode treatments can restore the capacity and this is believed to result from a broadening, or 'relaxation', of the neck zones.

During the cycling of batteries, sulphuric acid is either consumed (i.e., during discharging) or produced (i.e., during charging). These processes can result in high-density acid settling near the bottom of the plates and low-density acid near the top. The development of a resulting vertical concentration gradient of acid gives rise to non-uniformity in both current distribution and active-material utilization — factors that shorten service life through the irreversible formation of  $\text{PbSO}_4$  — as well as to irregular grid corrosion and growth. Acid stratification is a particular problem in tall cells and can be avoided through agitating the electrolyte, either by gassing during extended overcharge or by circulation with pumps.

In summary, the loss of capacity of the positive plate has been attributed to a combination of the following degradation mechanisms:

- (i) loss of inter-particle contact due to morphological changes,
- (ii) shedding of material from the plate due to grid corrosion and morphological changes,
- (iii) gradual conversion of material to an electrochemically inactive form,
- (iv) electrical isolation of parts of the material due to grid deterioration and growth, encapsulation by non-conductive  $\text{PbSO}_4$ , stress-cracking of the grid corrosion layer, formation of a barrier grid-corrosion film at the interface with the plate material,
- (v) plate sulphation due to acid stratification effects

These phenomena decrease the discharge capability both by reducing the amount of material available for reaction and by introducing large resistance losses. Furthermore, despite intensive research spanning three decades, the performance of the positive plate remains the principal life-limiting factor of the lead/acid battery. Innovations have been achieved in grid technology, but the design and processing criteria for the active material in all three types of plates have remained largely unchanged. Thus, extending the life of the positive without adversely affecting other important properties such as energy and power density, or increasing cost, is the major challenge facing battery scientists and engineers.

#### *Degradation of negative plates*

Negative plates require the presence of additives, known as 'expanders', to prevent the individual crystals of lead from growing and combining into a dense structure with low surface area and, therefore, low electrical capacity. Expanders usually comprise a mixture of barium sulphate, carbon black and a sulphonate derivative of lignin. The lignin has surfactant properties and is adsorbed both on the spongy lead and on the surface of the lead sulphate crystals formed during discharge. This has the effect of inhibiting crystal growth during the charge and discharge processes. The barium sulphate particles act as nuclei for the formation of lead sulphate crystals during discharge, and the end result is a uniform distribution of lead sulphate throughout the spongy lead active mass. The actions of lignin and barium sulphate are considered to be synergistic [66]. The carbon black has a lower hydrogen overpotential than the spongy lead, and during discharge, the hydrogen gas accumulates around the carbon particles to cause a mild expansion of the plate material. In summary, the expander counteracts the tendency for the spongy lead to coalesce, contract and densify. Thus, expanders impart desirable low-temperature and high-rate capabilities to the negative plate, in addition to inhibiting capacity-loss processes.

Degradation of the lignin fraction of the expander, and hence failure of the negative plate, may occur via one of the following three processes: (i) solubility in the electrolyte (allowing transport to the positive plate and destructive oxidation thereupon), (ii) thermal decomposition during paste mixing, flash drying, drying, curing, plate formation or battery use, (iii) chemical reaction with sulphuric acid in the electrolyte. Of these, thermal stability has become the most important criterion for expanders as certain applications (e.g., automotive and RAPS duties, see above) are requiring batteries to operate under increasingly aggressive conditions of elevated temperature.

#### *Degradation of separators*

The separator in a battery has a dual function. First, the separator serves as an electrical insulator that prevents short circuits between each adjoining positive and negative plate. Second, the separator is a mechanical spacer

that holds the plates in the prescribed position and helps to maintain the active mass in good contact with the grid. To fulfil these functions, the separator must be porous and wettable to allow the passage of acid as the battery is charged or discharged. Clearly, the separator must also be constructed from materials that are both resistant to the acidic and oxidative environment, and are of sufficient strength to withstand battery assembly operations and any thermal/vibrational shocks during service life.

Apart from obvious faults associated with mechanical defects, construction errors and damage during battery manufacture (including large pores/cracks and complete breakage), possible problems arising with separators include degradation under conditions of persistently high battery temperature, attack by the ingress of contaminants (e.g., via water additions), failure to resist penetration by lead dendrites growing from the negative plate (so called 'leading-through'). In recent years, however, advances in polymer science have made significant improvements in separators so that thin, low-cost materials with high porosity and small pore size can now be used with a high degree of reliability.

### *Influence of duty profile*

In standby-power applications, it is the float characteristics (i.e., voltage, temperature, a.c. ripple, etc.) that govern life. Principal failure mechanisms are associated with the gradual deterioration of the positive plate through loss of mechanical integrity [67] and growth/corrosion of the grid [68].

A detailed examination has been made [69] of the performance of various motive-power batteries under simulated electric-vehicle service. The findings demonstrated that battery failure modes vary with cell design, discharge rate and temperature, but again are determined mainly by the performance of the positive plate.

The failure modes of a wide range of battery designs under RAPS duty (both simulated in the laboratory and experienced in actual field service) showed [70] that losses in capacity for flat-plate types were usually related to softening/shedding of positive active material and corrosion/growth of positive grids. In extreme cases, massive inter-plate short circuits had developed across the lower parts of the negative and positive plates following build-up of conductive debris in the base of the container, and/or along the plates' edges as a consequence of 'mossing'. The latter relates to the formation of voluminous deposits at the negative plates through reduction of dispersed positive active material during charging. Short circuits were also found to result both from 'leading-through' of the separators and from grid growth that caused positive plates to come into contact with the negative busbar. Similar modes of failure under RAPS conditions have been observed by other workers [71].

In his classic text, Vinal [72] quotes data on the failure modes of automotive batteries in 1947 in which grid corrosion accounted for over one-third of all failures. The situation is the same today, some 40 years later! For example, from a field survey carried out in 1989, Hoover and

Boden [73] found that the most common cause of failure in batteries with antimonial grids was corrosion, while for batteries with calcium positive grids it was growth. The principal reason for this behaviour is the high under-the-bonnet temperatures encountered in modern automobiles. In this respect, analysis of the field data rather surprisingly revealed that both types of grid alloy were affected equally by temperature, despite the expected [74] acceleration in the corrosion of lead-calcium grids at elevated temperatures.

## Failure modes of valve-regulated lead/acid batteries

### *Major failure modes*

This section concentrates on failure modes that are most likely to affect VRBs to a greater extent than their flooded-electrolyte counterparts.

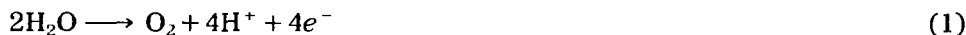
#### *Grid corrosion*

Grid corrosion is an important life-limiting process in float applications [75]. An accelerated life test has been developed for VRBs and uses the Arrhenius equation to predict service life under normal conditions [76]. In cycling duties, such as those required from miners' cap-lamp batteries, grid corrosion is also a significant failure mode. The same appears to hold for motive-power [10, 69] and RAPS [70] applications, although little information has been published on the performance of VRBs under this type of duty.

The importance of grid corrosion as a life-limiting factor in VRBs is not unexpected [77]. As shown by Tophorn [78], the polarization characteristics of electrodes in VRBs are different to those of electrodes in flooded-electrolyte systems. In particular, the float current is higher because of the depolarizing effect of the recombination reaction on the negative electrode [75]. Furthermore, on account of the different Tafel slopes, the positive electrode experiences a higher potential than its flooded-electrolyte equivalent (assuming the same applied cell potential). The increase in both current and potential will influence the rate of grid corrosion.

During overcharge, the net reactions at each electrode are

Positive electrode



Negative electrode



The net reaction for the cell is, of course, zero. Nevertheless, at the positive electrode, it gives rise to a depletion of water and an increased concentration of hydrogen ions. Both these factors increase the acidity around the positive electrode and, hence, will affect the corrosion rate. By contrast, the negative electrode undergoes a dilution effect. Although the recombination reaction can be very efficient (viz, 95–99%), some water will inevitably be lost during

service life (see below) This, too, results in increased acid concentration Finally, the partial saturation of the system and the oxygen environment around the positive electrode are also expected to enhance grid corrosion in VRBs, particularly later in life when the saturation falls below the initial level

The above corrosion effects are mitigated to a certain degree by the cell design of VRBs In this, the plates are held under compression by the glass-microfibre separator or the gelled electrolyte so that mechanical support of the grid is less of a problem than in flooded-electrolyte batteries Since the current-carrying capability is similar in both flooded-electrolyte and VRB systems, actual failure will depend to some extent on the duty For example, any increased grid corrosion in VRBs could be critical in high-rate applications (such as automotive service) due to the accompanying resistive losses In low-rate applications, however, degradation of the active material is more important and the added support given by the separator in VRBs will provide better life performance

#### *Grid growth*

Grid growth is closely associated with corrosion The incidence and severity of the phenomenon 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 For flooded-electrolyte systems, Lander [79] concluded that lead-calcium-tin alloys were superior to either pure lead or lead-antimony in terms of resistance to grid growth The growth was low, or immeasurable, during the early stages of corrosion, but then attained a steady rate as the corrosion product became thicker and the grid member became correspondingly thinner 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 three main mechanisms [80], i.e., as a result of recombination inefficiencies, permeation through the container material and grid corrosion

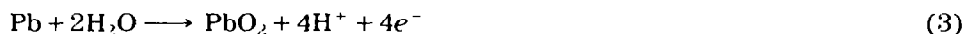
Under float duty, recombination efficiencies are typically 97–98% and, therefore, this is rarely a life-limiting mechanism In cycling service, however, significant gassing occurs with each recharge This can be minimized by keeping the potential at a low value but, unfortunately, the recharge duration is then long and often inefficient Higher voltage will give a more rapid recharge, but introduces the danger of significant water loss [81]

Permeation of water through the case is obviously dependent upon the nature and thickness of the chosen material The major driving force for this mechanism is, however, the difference in water vapour pressure between the inside and the outside of the case The relative humidity of the ambient



atmosphere in battery rooms is less easy to define and is likely to be quite variable. In high-humidity climates, it is even conceivable that the mechanism will be reversed and water will enter the battery.

Grid corrosion will cause the consumption of water via the net reaction



As it is simply a function of the corrosion rate, the loss of water can be easily calculated.

The effect of water loss on failure modes is dependent upon the duty that the battery has to perform. Water loss will reduce the degree of saturation of the system and, consequently, will increase the resistance of the separator [82]. This is particularly important in automotive applications where the batteries are required to deliver high currents for engine starting. Even a small loss of water will cause a large drop in battery voltage at these high currents and, consequently, will reduce cranking performance and, eventually, will cause failure of the battery. 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.

#### *Sulphation of negative plate*

Irreversible sulphation of the negative plate, with subsequent capacity loss, might be expected to be an important failure mode of VRBs. There are two possible reasons for adopting such a view. First, the oxygen-recombination reaction effectively depolarizes the negative electrode so that it never reaches the low potentials experienced in flooded-electrolyte batteries. Excessive overcharge to drive the negative electrode to these low potentials is best avoided because of the resultant water loss. In practice, however, sulphation via this route rarely appears to be a problem with VRBs. It seems that the recombination inefficiency, usually 1–5%, is sufficient to keep the negative in a reasonable state of charge. This, together with the fact that cell designs normally contain an excess of negative active material, ensures that sulphation associated with the gas-recombination process is not a life-limiting factor.

The second possible cause of irreversible sulphation could emanate from the effects of acid stratification. As mentioned above, sulphuric acid produced during battery charging will tend to sink to the bottom of the cell and give rise to a vertical concentration gradient. The latter will render the reduction of  $\text{PbSO}_4$  more difficult at the bottom than at the top of the cell. In flooded-electrolyte systems, gassing on overcharge is an effective means of mixing the electrolyte and equalizing the acid concentration. Clearly, this is not possible in VRBs. As with other designs, the severity of acid stratification in VRBs depends on both the cycling regime and the cell design [83]. Nevertheless, it is generally found not to be a serious problem, especially

in VRBs using gelled-electrolyte [78] In tall designs, the problem can be alleviated by operating the cells in a horizontal position

### *Voltage variation*

In large series-connected strings of either flooded-electrolyte or valve-regulated cells, charged at constant potential, there is a tendency for the cells to get out of step when used in a regular cycling duty During charging, any weak cell will not become fully charged and on the next discharge will be discharged to a greater depth This will result in a greater degree of undercharging on the subsequent recharge The process continues with each cycle until, eventually, the weakest cell becomes grossly over-discharged The possibility of cell failure by this mechanism is increased if the quality of the product is variable, the series string is very large, or the cycling is deep and continuous On the other hand, if the cells experience long recharges, or appreciable periods on float between discharges, the problem is alleviated by allowing the weak cells to reach top-of-charge before the next discharge

In VRBs, the problem becomes more complex because of the bi-stable nature of the cell on recharge The two stable areas are (i) below 2.4 V, if gas recombination is occurring, (ii) 2.5 to 2.6 V, if significant quantities of hydrogen are being evolved Although little has been published in this area for VRBs, the available literature does indeed suggest the incidence of such a bi-modal distribution of cell voltage [75] In particular, under conditions where the charging voltage is high (e.g., 2.45 V/cell for a cycling duty), it is easy for cells to flip from one stable state to the other In float applications, however, the voltage is considerably lower (typically 2.27 V/cell) and, therefore, it is more difficult for a cell to reach a gassing state as this would result in severe depression of the voltages of the other cells Again, large strings would be expected to be more prone to this problem Furthermore, data indicate that the variability is greatest at the beginning of life, presumably due to differences between the recombination efficiencies of the cells at this stage [84]

The effect of voltage variability on the performance and life of VRBs is a matter of some debate Tests reported by Harrison and Bullough [85] showed no correlation between the voltage of a VRB on float and the delivered capacity In other work, Deshpande [84] demonstrated that strings of up to 180 cells could be floated at 2.26 V/cell, with all cells registering a voltage within  $\pm 30$  mV of the mean value The same author repetitively deep-discharged a battery consisting of three strings of 48 cells connected in parallel It was found that the current sharing between the strings was even, and that each string provided close to the expected 33.3% of the capacity In a further test, the same battery was abused by overdischarge to give some cell reversal Nevertheless, the battery was recharged satisfactorily with further cycling, this indicated that none of the cells had become out of step In all cases, the recharge was performed at a constant potential equivalent to 2.37 V/cell for 60 to 70 h Thus, a critical feature in maintaining string stability appears to be a long recharge at a low potential, as opposed to a shorter

recharge at a high potential. Clearly, battery design and series/parallel connections become important in those cases where duty requirements demand a rapid recharge.

#### *Thermal runaway*

Thermal runaway is a possible problem with many battery systems and is caused by the heat generated during charge and overcharge depressing the cell potential and causing an increase in current. In VRBs, the recombination reaction results in an increased heat input into the system and this enhances the possibility of thermal runaway. Fortunately, however, this is normally a small effect. For example, a float current of 50 mA at 2 V will liberate a maximum of 100 mW of heat so that, as long as the battery layout is correctly arranged, failure via thermal runaway should not be a common occurrence.

#### *Antimony-free effect*

As with all non-antimonial batteries, the possibility exists of the antimony-free effect limiting the life of VRBs in cycling applications. As described in detail above, this is characterized by a loss in capacity of the positive plate, despite its often healthy appearance. Batteries can, however, be designed with active-material/acid ratios that largely eliminate this problem [50].

#### *Minor failure modes*

This section briefly discusses failure modes that are less likely to affect VRBs than flooded-electrolyte types.

#### *Leading-through of separator*

In flooded-electrolyte batteries, leading-through is a process by which very fine particulate (even colloidal) matter in suspension in the electrolyte becomes attracted to protrusions on the plate and forms thin dendrites that can grow through the separator. This problem can be largely eliminated by increasing the tortuosity and reducing the pore size of the separator.

In VRBs, the electrolyte is completely immobilized and the circulation of particulate matter in the electrolyte cannot occur. Thus, the development of leading-through via such a mechanism is not possible. Despite this, a different type of leading-through, common to both flooded-electrolyte batteries and VRBs, can occur if the acid gravity reaches very low levels, e.g., as a result of overdischarge or prolonged stand on an open-circuit in the discharged condition. In these situations, the pH can increase and give rise to soluble lead species that promote the growth of dendrites from the plates. As this involves a solution mechanism, it is generally unaffected by separator characteristics and can be largely avoided by careful cell design. In Chloride's Powersafe<sup>®</sup> range, for instance, this type of failure is very rare, it only occurs under conditions of severe abuse.

#### *Shedding of active material*

Because the positive plates in VRBs are held under compression by the glass-microfibre separator or by the gelled electrolyte, the active material

cannot shed in the classical sense. This eliminates the need for a mud space of the type usually present in flooded-electrolyte batteries, and prevents failure not only by leading-through (see above), but also by mossing and other types of edge shorts. Even in deep-cycling applications, experience has shown that the integrity of the active material is maintained and the traditional 'sludging' behaviour of the positive plate is largely avoided.

#### *Degradation of separator*

As discussed above, the highly oxidizing environment of the positive electrode requires care to be exercised in the choice and use of organic-based separators in flooded-electrolyte batteries. For one class of VRBs, 100% glass microfibre is used almost universally and this has very good oxidation resistance. Therefore, failure due to separator degradation does not occur, even after extensive periods of duty. Gelled-electrolyte VRBs do not require a separator.

#### *Explosion*

Oxygen and hydrogen are generated on overcharge and, therefore, explosion is a potential hazard in any type of lead/acid battery. The possibility of detonation from an external source is reduced by the use of explosion-minimizing vents. In VRBs, the danger from internally generated sparks is also largely eliminated. This is because the gas in the head space rarely reaches flammable proportions due to the efficient recombination reaction that maintains the oxygen level below the critical 4% threshold. Thus, VRBs can be used in applications such as miners' cap lamps where safety is of paramount importance.

### **Concluding remarks**

Perhaps the most important aspect of lead/acid science is understanding how and why batteries fail. The benefits of such information would be two-fold: first, the information would enable optimization of design for a given application, second, it would offer the possibility of extending the life of the product.

This review shows that considerable progress has been made in recent years in the search for a clearer understanding of the nature and mechanisms of battery failure modes. In particular, the decline in performance of the positive plate through active-material degradation has received special attention. Nevertheless, there is still much to be done as these studies have not resulted in any major improvement in the life of positive plates under the various duties required from lead/acid batteries. Indeed, the basic design parameters established many years ago are still valid today. Furthermore, in contrast to the wealth of published data obtained from scientific investigations of the physicochemical characteristics of positive active material,

very little has been documented on the technology and causes of failure of the material in the different designs of practical batteries. Considering the large resources needed to carry out either life testing in the laboratory or the collection and analysis of failure modes in the field, it is unfortunate that such work, when performed, is not reported more widely. Clearly, a combined investigation of both scientific and technological aspects is essential to the success of efforts directed towards unravelling the complex nature of positive-plate failure.

As this review shows, the other major cause of battery failure is corrosion of the positive grid. One of the major changes in battery design in recent years has been the widespread use of lead-calcium alloys. This has arisen through a market pull for maintenance-free batteries – both flooded-electrolyte and VRB types. This has introduced the problem of premature failure via the antimony-free effect. In automotive and standby applications, which experience infrequent deep discharges, batteries can be designed so that premature failure is not a serious problem. In deep-cycling duties (e.g., motive-power, load-levelling and RAPS service), however, the antimony-free effect must be a major consideration.

The extent of the present knowledge on the antimony-free effect poses several vital questions:

- Is the phenomenon truly understood?
- Is the inclusion of tin beneficial or necessary, and if a thin surface film of tin is effective, how does it influence the corrosion product later in battery life when the corrosion layer is much thicker than the original tin-rich film?
- Is the metallurgy of lead-calcium alloys fully characterized, and how can it be controlled during grid production?
- By what mechanism(s) do lead-calcium alloys corrode?
- Are calcium alloys the best route for cycling batteries, or are low-antimony alloys a more effective approach? In which case, is there an antimony level that will give good deep-cycle life but not affect the maintenance-free characteristics of the battery?
- Given the limitations of the Periodic Table, are there any alternative alloys?
- In view of recent advances in materials science, does the future lie in non-lead grid structures with markedly improved corrosion resistance, or does the cycleability of positive plates depend on the nature of the corrosion product of the lead alloy itself?

In the past, the success of the lead/acid battery has been due principally to its ability to adapt to changing market needs. One of the major consumer requirements today is for a maintenance-free (preferably sealed) design that has a good deep-cycling performance (1500 to 2000 cycles) and still maintains the traditional cost-effectiveness of the system. Success in this area would greatly expand the scope and demand for batteries and must be seen as the greatest challenge for both scientists and technologists engaged in the further development of the lead/acid system.

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