

Improving the valve-regulated lead–acid battery

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Abstract

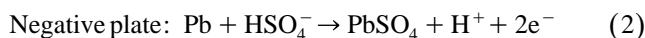
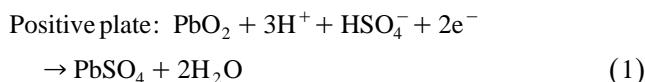
This paper outlines some of the improvements in the performance of valve-regulated lead–acid (VRLA) batteries that have been accomplished during the course of the 1990s and considers further advancements which might be achievable. Attention is focused on those aspects of the battery that have been changed in order to convert the original, flooded (vented) design into a valve-regulated unit. Refinements of the components which were modified during the course of the flooded-valve-regulated conversion could be a productive endeavour as research workers strive to raise the life of the VRLA battery to match, and exceed, that of its flooded predecessor. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Major targets in the research and development of lead – acid batteries are the achievement of maximum discharge capacity and, where deep-discharge duty is required, the sustaining of this maximum capacity through as many discharge–recharge cycles as possible.

The discharge reactions of the lead–acid cell are as follows:



The technical challenge to be met in maximizing discharge capacity involves facilitating the access of all the reactants to the site of the reaction. In order to produce high power, this access must be sustained at a high rate. Three key components in this strategy are the provision of: (i) high surface-area for the solid reactants; (ii) high flux of species in solution (e.g., through short diffusion lengths); (iii) low resistance to sustain the electronic current.

After each discharge, the optimum set of conditions, including high surface-area solids and low-resistance paths to the grid current-collectors are to be restored by charge reactions which are the reverse of Eqs. (1) and (2). In the

ideal case, the discharge capacity would be constant while the cell is cycled (as indicated by the horizontal line in Fig. 1). In practice, even at the start of life, the utilization of solid active materials in the lead – acid battery is generally limited to around 30%. As cycling proceeds, a number of processes (‘failure mechanisms’) can degrade even this performance.

Several of the possible failure mechanisms (FM1 to FM5, below) interfere with the supply of one or more of the discharge reactants in a flooded lead–acid battery, as follows.

FM1. *Expansion of the positive active-mass:* This can occur both in the plane of the plate (if the grid is stretched by a growing corrosion layer) and in the direction normal to the plate. Progressive expansion causes an increasing fraction of the positive active-material to be electronically disconnected from the current-collection process.

FM2. *Loss of water:* Production of oxygen and hydrogen during overcharge can reduce the volume of electrolyte so that some of the active material loses contact with the liquid phase. This process can be auto-accelerating. Impurities which affect the hydrogen overpotential exercise considerable influence on the propensity of a battery to gas [1].

FM3. *Stratification of the electrolyte:* On recharge, sulfuric acid is produced between the plates and there is a tendency for acid of higher concentration to collect at the bottom of the cell because it has a greater relative density than dilute acid. This segregation into layers of different

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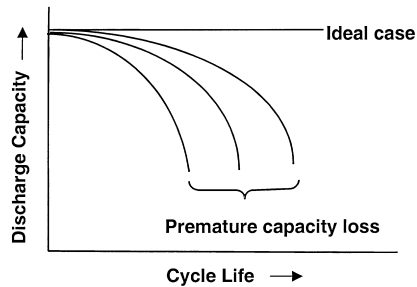


Fig. 1. Schematic representation of the variation of capacity with cycle-life of a lead-acid battery. The horizontal line represents the ideal case and the curves show the performance degraded by one or more forms of 'premature capacity loss'.

acid strength would be overcome either by diffusion, if the battery were left to stand for a very long time, or by turbulence, if the battery were set to heavy gassing during overcharge.

FM4. Incomplete charging: If either of the electrodes is left incompletely charged, either by a defective charge regime or as a result of physical changes that prevent adequate polarization, then the subsequent discharge will be impaired.

FM5. Corrosion: Corrosion layers can become substantial and can be more or less resistive given the duty cycle and/or the charging protocol. High resistance reduces the electronic current.

Motive-power batteries of the traditional, flooded design are able to avoid some of the above failure mechanisms, as follows.

FM1. Inclusion of antimony in the positive grid alloy prevents significant creep and tubular designs of positive plate have gauntlets that constrain the positive active-material and reduce its tendency to swell and to shed.

FM2. Water loss can be made good by the process of 'topping up'.

FM3. Stratification can be overcome by gassing excursions.

FM4. Gassing also copes with the problem of under-charge of either plate polarity.

As a result of these strategies, corrosion of the grid (FM5) becomes the life-limiting factor. The full range of failure mechanisms can be held at bay for over 1000 deep cycles of the flooded lead-acid battery. Is it possible, then, to achieve the same life with a valve-regulated design?

2. The valve-regulated lead-acid battery

The valve regulated lead-acid (VRLA) battery is designed to promote the recombination of oxygen at the

negative electrode in order to minimize water loss. Oxygen evolved at the positive electrode, i.e.,



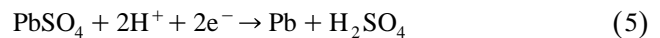
transfers through a gas space (Fig. 2 [2]) to the negative electrode where it is reduced, i.e.,



Thus, an internal 'oxygen cycle' is established.

There are two alternative designs which provide the gas space — in one, the electrolyte is held in an absorptive glass-mat (AGM) separator; in the other, the electrolyte is immobilized as a gel. In the former, gas passes through channels in the AGM, in the latter through fissures in the gel.

The oxygen discharges the negative plate and depolarizes the potential to a value at which hydrogen production is very low (i.e., much less than in a flooded battery). Since the plate is simultaneously on charge, the lead sulfate produced is immediately reduced to lead, i.e.,



This restores the chemical balance of the cell. The net sum of reactions (3) to (5) is zero. The electrical energy input into the cell during charge is thus converted to heat rather than to chemical energy [3].

Antimony is no longer included in the grid alloys for VRLA batteries because this element reduces the hydrogen overpotential and encourages gassing at the negative plate. Care needs to be taken against the introduction of other elements that might reduce the hydrogen overpotential [1].

If the cell is overfilled with acid initially, the oxygen cycle cannot function and the cell behaves as if it were a conventional, flooded design. Towards top-of-charge, first oxygen (from the positive), and then oxygen (from the positive) and hydrogen (from the negative), are evolved and released through the valve. This loss of water eventually opens gas spaces and allows the oxygen transfer to proceed. Gas release from the cell then falls to a very low level.

The oxygen cycle must be allowed to run in order to circumvent most of the loss of gas. If, however, the cycle is worked too hard then substantial heat is generated, charging of the negative electrode becomes difficult, and progressive sulfation begins from the bottom of the plate where acid concentration tends to be highest. The function of the oxygen cycle is subtly linked to the microstructure of the separator material (AGM designs) and to the details of the charge algorithm applied, especially near top-of-charge.

In summary, the move from the flooded to the valve-regulated design may allow several of the failure mechanisms the opportunity to recur, as follows.

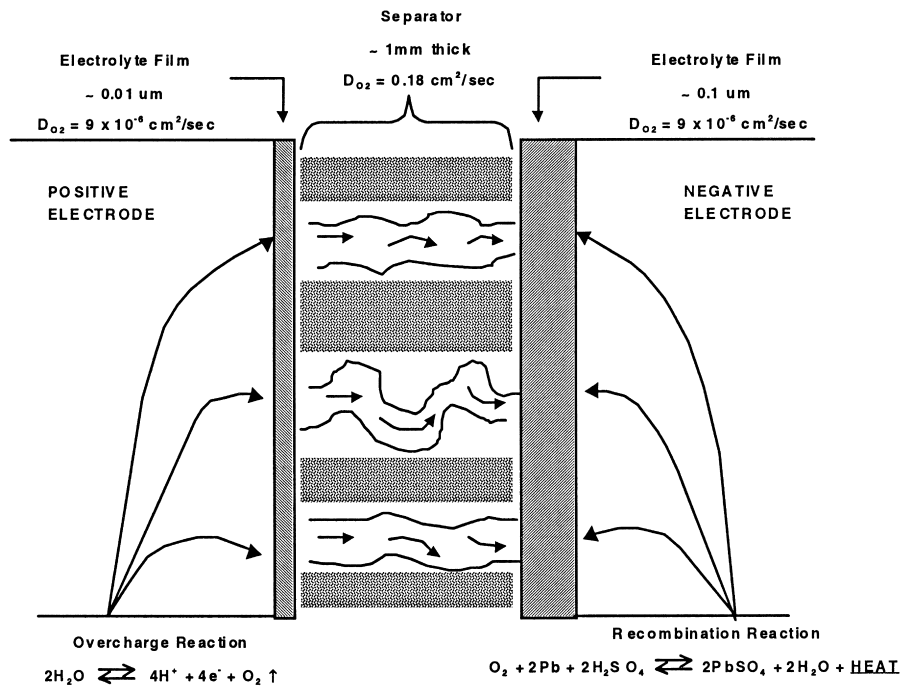


Fig. 2. Conceptual view of the oxygen cycle in an AGM design of valve-regulated battery [2].

FM1. Replacement of lead–antimony alloys with lead–calcium alternatives, as a means to discourage hydrogen evolution, reduces the creep strength so that expansion in the plane of the plate becomes once more a problem. Use of a separator with insufficient rigidity (i.e., too much ‘compressibility’) may allow expansion normal to the plane of the plate.

FM2. Water loss is minimized, as intended, but ...

FM3. Any stratification which occurs cannot be overcome by overcharging because there is little free electrolyte and, hence, ineffective mixing. Moreover, water lost cannot be replaced.

FM4. The presence of the oxygen cycle may cause incomplete charging of the negative plate [4].

As the result of some combination of the above failure mechanisms, the first attempts to deep-cycle VRLA batteries resulted in very short cycle-lives, as shown schematically in Fig. 1, and the term ‘‘premature capacity loss’’ [3] was devised to describe this shortfall in performance.

3. State of the art

In the early part of the decade, the lead–acid battery community united as the Advanced Lead–Acid Battery Consortium (ALABC) in a concerted effort ‘‘to make electric vehicles a reality’’ by overcoming the shortcomings of the VRLA battery. Much has been achieved during the global research and development programme joined by the ALABC.

3.1. Grid alloys

The creep resistance of the grid alloys has been restored, without loss of the hydrogen overpotential properties, by the addition of 1 to 1.5 wt.% tin to the lead–calcium alloy. An in-depth study of positive-grid alloys [5,6] has shown that the introduction of these levels of tin brings additional benefits in the form of enhanced corrosion resistance and reduced electronic resistance of the corrosion product layer. Positive grids that contain no antimony but have 1 to 1.5 wt.% tin do not suffer expansion in the plane of the plate and, as a result of the lower corrosion rate, it is possible to contemplate a substantial reduction in grid thickness (and weight) in pursuit of an increase in specific energy [7].

3.2. Positive plate

Swelling of the positive active-material in the direction normal to the plane of the plate remains a serious concern for VRLA batteries. There is some confusion over the details of the process(es) which give rise to this phenomenon. Some experimental programmes appear to show that the active mass expands during charge and contracts during discharge [8,9] while other programmes [10] have indicated that the active mass contracts during charge and expands during discharge. The tendency for the positive active-material to expand with repeated deep cycling is, however, beyond dispute and elegant experimental work at

the University of Brno [11] has demonstrated a clear correlation between loss of capacity with cycling and increase of active-material resistance (presumed to arise as a result of swelling).

3.3. Separator

Studies with flooded cells¹ have shown that the application of 40 kPa of pressure to the plate stack, with a view to preventing positive plate swelling, achieves a substantial increase in cycle-life compared with a stack which is only compressed by 8 kPa. In VRLA cells incorporating AGM separators, however, the application of this remedy is not always straightforward because sheets of AGM shrink when first wetted with electrolyte and are subject to substantial thickness reduction with applied pressure [13]. Both effects tend to reduce the pressure that is available to prevent the active-material from swelling.

Batteries with AGM separators are widely used and, under suitably engineered conditions, can provide a large number of deep-discharge cycles. Nevertheless, the changes in thickness (and microstructure) that occur as a result of wetting and/or compression certainly make it more difficult to achieve the best combination of wicking, gas transfer, and compression characteristics with such materials.

At present, a number of ALABC investigations are exploring the utility of different forms of AGM and indeed of other porous materials, to perform the separator function in VRLA batteries. The porosity and liquid retention properties of AGM vary with the dimensions of the primary fibre used, with the fraction of fine fibres that is incorporated, and with the degree of pressure applied to the mat [14]. Some of the alternative materials being considered offer little or no shrinkage or porosity change on being wetted or being subjected to applied pressure. Early tests with one of these materials show good cycling characteristics for at least 300 cycles (Fig. 3). A small change in limiting voltage of charge (from 2.4 to 2.45 V) was necessary to turn an initially nondescript performance with this material into an impressive behaviour. Throughout the test, the cell called for only a very low charge factor (about 1.02) and this may relate to the very fine pore size of the separator material.

3.4. Charging

The manner of charging exercises a dramatic effect on the performance of VRLA batteries. This is a particular area where the differences between flooded and valve-regulated designs are pronounced.

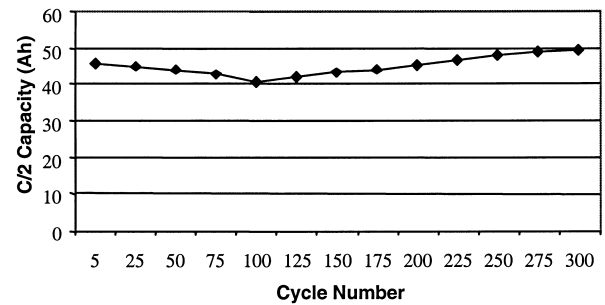


Fig. 3. Cycling performance (C2/2 discharge to 1.6 V followed by 15 min pause and constant-current (I)–constant-voltage (U) charge with $I = 1.5 \times I_5$, initially to 2.4 V but, from cycle 92, to 2.45 V) of a cell containing an incompressible separator with fine porosity (0.2 μm). (Taken from Brite-EuRam Project BE97-4085, Task 1b.)

An important factor is that the battery is thermodynamically unstable. The cell voltage of 2 V is far above the decomposition voltage of the water in the electrolyte, viz., 1.23 V. Water should therefore be split by electrolysis into hydrogen and oxygen gas spontaneously. Fortunately, however, at open-circuit and in the absence of elements which lower the gassing overpotential, these reactions are extremely slow. Fig. 4 shows the principal reactions that are to be expected in lead–acid batteries, in the normal potential range, on the basis of thermodynamic considerations [15].²

Apart from the charging and the discharging of the two electrode reactions, there are four secondary reactions which become particularly significant as the applied potential reaches beyond the open-circuit value.

At the positive electrode: (1) oxygen evolution (Eq. (3)) is possible above 1.23 V, but only becomes vigorous as the potential approaches the equilibrium value for the positive plate (around 1.75 V); (2) lead corrosion is the secondary reaction that should finally limit service life. Lead, which is the primary constituent of both grids, is stable only below the open-circuit potential of the negative electrode. At higher potentials, it is converted into lead sulfate or lead dioxide. On the negative grid, however, the recharge process can remove the corrosion product, while on the positive plate, progressive corrosion can be extremely slow due to the protective behaviour of a layer of PbO_2 at the metal surface. This layer also effectively hinders the oxidation of hydrogen at the positive electrode [15].

At the negative electrode: (3) hydrogen evolution, i.e.,

$$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \uparrow \quad (6)$$

is thermodynamically permitted at an electrode potential below 0 V on the scale shown in Fig. 4, but is rather slow until the potential falls to the equilibrium value of the negative. (4) Oxygen reduction [4] is possible at potentials below 1.23 V. This reaction is used to establish the oxygen

¹ R.H. Newnham, W.G.A. Balding, M. Barber, C.G. Phylant, D.G. Vella, L.H. Vu, N. Wilson, ALABC Project AMC-007. See Ref. [12].

² All electrode potentials are given with respect to the standard hydrogen electrode.

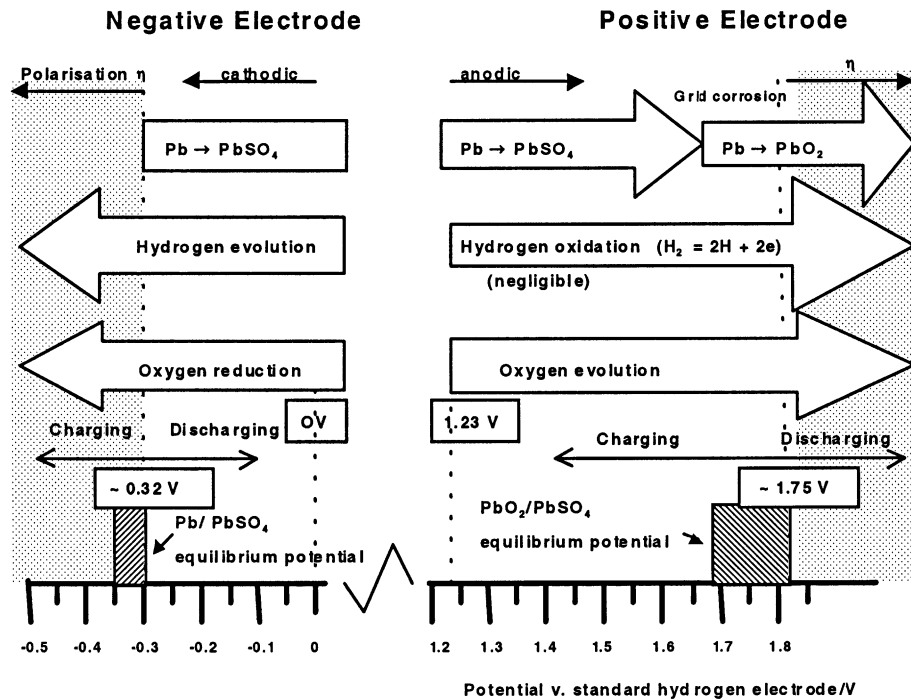


Fig. 4. Reactions which are thermodynamically permitted in lead–acid batteries within the normal range of potential. The equilibrium potentials (-0.32 and $+1.75$ V) of the reactions of the negative and positive plate correspond to an acid relative density of 1.23 and to an open-circuit voltage of 2.07 [15].

cycle in VRLA batteries. In flooded batteries, it is largely hindered by the low rate of diffusion of oxygen through the liquid phase.

During the return of approximately the first half of the charge to a discharged cell, virtually all of the current is consumed in the charge reactions and no gas is produced. In the later stages of the charging process, however, potentials are reached at which the gassing reactions increasingly share the input current with the charging reactions. In a flooded cell, oxygen and hydrogen are produced in approximately equal amounts but in a VRLA cell, the oxygen cycle shifts the potential of the negative electrode in the positive sense. Then, the main reactions in overcharge are the oxygen evolution at the positive electrode and oxygen reduction at the negative. The balance between current consumed by the desired charging reactions and the 'secondary' gassing reactions in a valve-regulated cell is a complex function of the cell design, the operating conditions, and the overcharge regime. This sensitively affects cycle-life.

It is clearly desirable for the charging process to be as efficient as possible. If too much charge is taken by the oxygen production process, then both electrodes can be adversely affected. Vigorous gassing at the positive plate contributes to the weakening of the microstructure of the active material. Too much oxygen recombination at the negative plate generates heat, brings strong depolarization, and makes it very difficult to complete the charging process.

The degree of overcharge drawn by the recharge process is a useful indicator of the extent to which the oxygen cycle is taking over from the charging reactions. In a test with packs of 40 Hawker batteries,³ limitation of the degree of overcharge was sufficient to extend the deep cycle-life from 38 to around 200 cycles.

If extensive overcharge is a threat to VRLA batteries, then a partial state-of-charge (PSoC) regime in which the top-of-charge is only approached occasionally and briefly might be expected to be beneficial. The demonstration by Cominco [17] of 1000 deep cycles with the Optima battery was achieved with a PSoC regime combined with rapid recharge. This formula is not, however, a universal panacea since the same regime produced a poor result with a flat plate battery (see Table 1) [18].

The assembly of experimental results gathered so far provides some indication of the importance of charging for the optimal performance of VRLA batteries and some pointers towards a strategy for development, namely:

- problems arise, particularly in the overcharge region where the charge process becomes inefficient — increasingly so, if the saturation of the separator progressively decreases;

³ H. Döring, F. Lang, H. Stelzer, W. Höhe, J. Garche, Brite-Euram Project BE-7297, Task 9. See Ref. [16].

Table 1
Cycle-lives of spiral-wound and flat-plate batteries under fast and partial state-of-charge (PSoC) regimes [18]

	Average cycles at full discharge	Average cycles under PSoC
<i>Spiral-wound</i>		
Conventional charge	275	300
Fast charge	100	900
<i>Flat-plate</i>		
Conventional charge	540	220
Fast charge	140	100

- too vigorous an oxygen cycle produces heat and inhibits charging of the negative plate;
- details of the charge regime, particularly the later stages and the charge-termination point, are important in the management of the oxygen cycle;
- undercharge also leads to a short life so that if refuge from gas problems is sought in a PSoC regime, then a full recharge must be employed occasionally in order to equalize strings of batteries.

3.5. Negative plate

Some of the very early failures which occurred when VRLA batteries went on deep-cycle duty were due to

expansion and shedding of the positive active mass. Once this failure mechanism had been overcome, by the use of creep-resistant alloys and by stack constraint, it became evident that the negative plate was becoming the life-limiting factor, both in cycling applications [18,19] and in float duty [20]. It is not uncommon to experience a pronounced difficulty in bringing the negative plate to a full state-of-charge [21] in the latter stages of the life of a VRLA battery.

There are a number of possible causes of the progressive capacity loss that besets the negative plate of valve-regulated lead–acid batteries. These include:

- reduction in the surface area of the electrodes, possibly following loss of the organic expander; this might be a problem which is peculiar to the VRLA battery design when oxygen reaching the negative plate proves destructive to organic molecules;
- electrolyte stratification, which is likely to be more severe the more open is the pore structure of the separator;
- depolarization due to highly efficient oxygen-recombination;
- recharge inefficiency due to selective discharge of the plate.

In any event, it is instructive to note that, whichever of these is (are) the culprit(s), the problem is not of universal

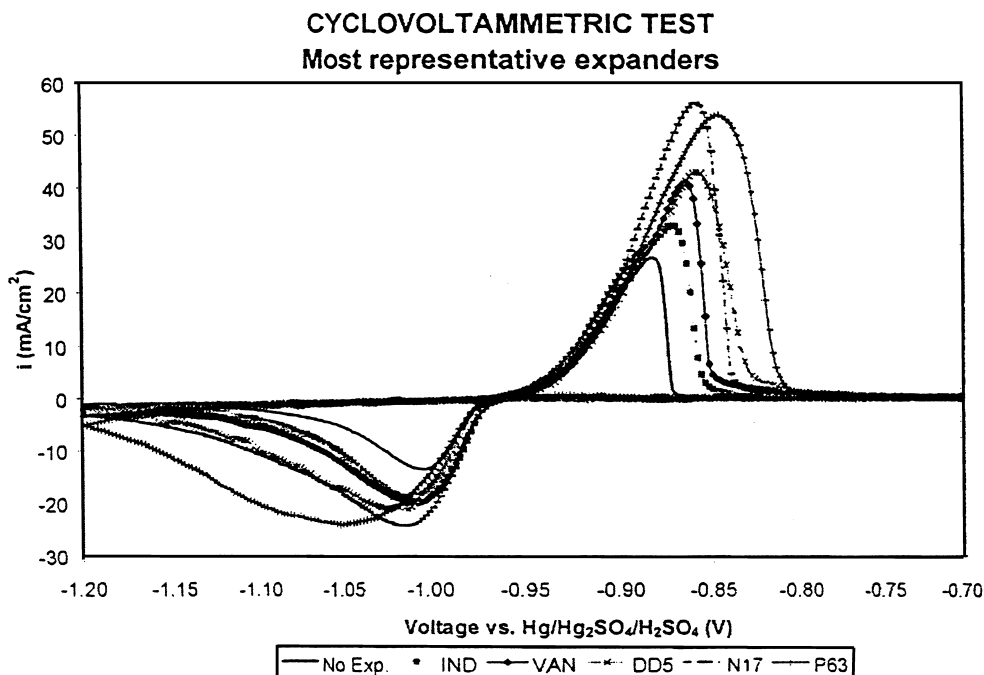


Fig. 5. Cyclic voltammograms for a lead electrode with a variety of expanders: IND-Indulin; VAN-Vanisperse A; DD5 (a blend of kraft lignosulphonate and condensed naphthalene sulphonate); N17 (sodium lignosulphonate); P63 (sodium naphthalene sulphonate). Increased anodic peak area signifies improved expander efficiency, but increased cathodic peak polarization signifies increased charge inhibition.

severity. As noted in Table 1 and Ref. [18], there are some cases when a long life is achieved and in these instances the degradation of the negative plate is evidently being held at bay.

Three of the potential problems listed above may implicate the separator to some degree. Of course, it is possible that a new expander, with an improved balance between its efficiency and its tendency to inhibit charging, especially at elevated temperature (Fig. 5), might be a valuable contribution. On the other hand, a separator offering a microstructure that would prevent an excess of oxygen access from destroying the expander, and would not depolarize the electrode too far, while simultaneously discouraging stratification, could offer a greater contribution. Both possibilities are being actively pursued in the present ALABC programme.

The remaining problem — selective discharge [4] — could involve an impurity. Control of the balance between the reactions that decide the life-limiting function may yet be achievable through the use of catalysts [20].

4. Conclusions and future directions

Much of the recent research and development effort devoted to improving the life of VRLA batteries has focused on performance under deep-discharge duty, with a view to application in electric vehicles. A good deal of progress has been made. Life-limiting factors in the first 300 to 500 cycles that involve the positive plate have been largely overcome and a major task now is the management of processes that threaten the negative plate, so that life is extended reliably to approach that of the flooded battery.

A good deal of what has been learned in the work on deep cycling will undoubtedly benefit the use of batteries in partial state-of-charge or float operation. Nevertheless, some aspects of the battery function in these latter two regimes will be different.

A new phase of the ALABC programme is scheduled to commence in January 2000. Research and development will concentrate on fundamental issues as they relate to all three modes of operation, namely: deep-discharge, partial

state-of-charge, and float. This is likely to be a profitable and fascinating study.

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