

Review of factors that affect the deep cycling performance of valve-regulated lead/acid batteries

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Abstract

The effects of compression, positive-grid growth, electrolyte stratification and uniformity across a series string of cells during deep-cycling service of valve-regulated lead/acid batteries are considered. Without adequate control, each of these will cause premature failure. Although substantial improvements in cycleability have been made in recent years, more understanding and optimization of these factors is necessary for further improvements. In particular, little is known about the changes in the properties of separators during service that effect compressive forces on the positive plate, and more knowledge is required on the influence of grid growth and on the influence of cell design on electrolyte stratification in valve-regulated batteries. In addition, the paper considers the progressive variation between cells in long series strings, which is a major cause of early failure of these designs.

Keywords: Lead/acid batteries; Cycle life; Premature capacity loss; Compression; Grid growth; Electrolyte stratification; Charge management

1. Introduction

Valve-regulated lead/acid (VRLA) batteries have been in widespread commercial use for more than ten years. They were introduced at a time when there was a need for small maintenance free batteries suitable for operation in office environments. VRLA batteries have now substantially replaced the more traditional types of stand-by battery in many large telecommunications and UPS installations. In spite of early problems, continuing improvements together with a better understanding of the basic technology have resulted in designs for which manufacturers confidently expect more than ten years of trouble free service.

This is not yet the situation in deep-cycling applications. Whilst there has been considerable advances in recent years, 400 to 500 deep cycles is considered to be a good performance for VRLA batteries, compared with up to 2000 cycles for lead/acid traction cells used in typical motive-power applications. In these latter duties, the vehicle fleets usually have well organized, routine maintenance and the need for the newer, maintenance-free batteries is questionable. In the case of the modern electric vehicle (EV), however, not only is improved performance desirable, but because many may be privately owned, the batteries must require minimum maintenance and must be safe, i.e., free from excessive gas evolution or acid spillage.

The successful use of lead/acid batteries in the EV market depends upon their capability to give a reliable and long service-life. Accordingly, there have been major efforts to improve the cycling performance of VRLA designs. Whilst cycle life can be extended by reducing the depth-of-discharge (Fig. 1), thereby, increasing the calendar life and the total miles between battery replacement, the limitation to range would probably be unacceptable. The cycling performance of a present day VRLA battery is also shown in Fig. 1 and the data illustrate the difference between modern EV designs and the traditional industrial battery. The latter is a mature product that has been evolved over most of this century. It is

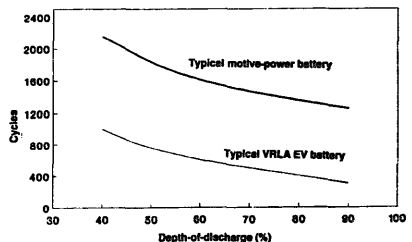


Fig. 1. Cycle life at various depths-of-discharge.

designed in such a way that corrosion of the positive grid limits the service life. This is not yet the situation with the newer products in which several, and often interacting, factors may cause failure. In addition, VRLA designs require higher standards of quality and many companies are only just appreciating the need to impose greater control over manufacturing operations in order to produce defect-free products.

Given that the product is manufactured with adequate care, certain design, material and operational features are essential to ensure reliability and to enhance deep cycling performance. This paper considers just four factors which, without some degree of optimization, will cause early failure. These factors are: (i) compression influences; (ii) choice of positive grid alloy; (iii) certain design aspects, and (iv) charge management. There are others. Whilst all these factors require more extensive consideration than is possible within the scope of this paper, the aim is to highlight their importance and encourage further work on their improvement.

2. Compression influences

A major concern with respect to the cycleability of VRLA batteries has been the phenomenon of premature capacity loss (PCL), traditionally associated with antimony-free designs. The poor cycling performance of batteries made with lead-calcium alloys or pure-lead grids has been recognized since their first use in submarine and stand-by batteries almost 50 years ago. Extensive studies have been performed throughout this period to try to explain PCL behaviour [1,2]. Whilst these studies were proceeding, other workers showed that constraint of the active material reduces capacity loss during cycling [3] and though explanations as to the cause were not forthcoming, it was demonstrated that compression exerts a major effect on cycle life. More recently, Constanti et al. [4] showed that changes in apparent density of the positive active material due to progressive expansion during cycling is probably the dominant cause PCL and that this can be greatly reduced by compressing the active material.

The importance of compression is illustrated by the behaviour of valve-regulated automotive batteries (made with lead-calcium-tin alloys) on a deep-cycling schedule, see Fig. 2. Uncompressed designs failed within 40 cycles, whilst over 200 cycles were obtained with assemblies that con-

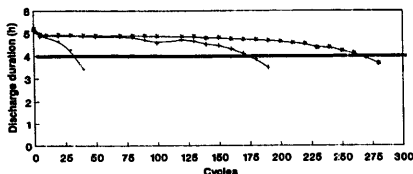


Fig. 2. Effect of compression on cycle life. 12 V/48 Ah batteries: discharged at 8 A to 11.2 V, and recharged at 14.8 V for 12 h; (□) no compression, (+) 15% compression, and (*) 25% compression.

strained the positive active material. Compression influences on cycleability are now universally accepted, but the optimum compression levels and how to achieve and maintain them, have not yet been defined.

The problem lies in the construction materials. First, the container must be sufficiently strong to support and maintain the compressive force to the assembled element. There should be no distortion of the container, either initially or throughout service. The second and more difficult factor concerns the separator. At the present time, VRLA designs in which the electrolyte is absorbed only use separators produced by wet-laying glass microfibrils (AGM variety). Mostly, the separators are made without a binder. The design compression is based upon the ratio of the nominal thickness of the separator (measured and quoted at 10 kPa) to the compressed thickness in the plate-group assembly. The compressive strength relates to the force that is necessary to compress the separator to a specific thickness. In the dry condition, these separators exhibit hysteresis effects and, after compression, they recover to their original thickness provided that they are not over-compressed. This limiting value of compression varies with the fibre source and the finish, but is generally around 45%, beyond which it is suggested that fibre breakage occurs and results in a loss of resilience.

The compressive strength is slightly higher in the wet than in the dry condition (Fig. 3). Presumably, this is a desirable characteristic, since materials with a low compressive strength when dry, and a high compressive strength when wet, would be easy to assemble but would produce a high force on the active material when wet. Nevertheless, there are no published data on how the resilience or plasticity of AGM separators changes during service, or on the long-term effects of compression. It is known that the grade of glass used in these products is slightly soluble in acid. The solubility, in

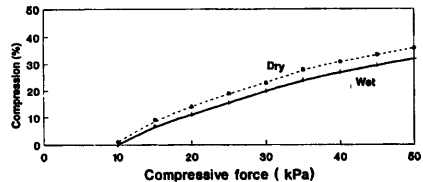


Fig. 3. Compression of wet and dry AGM separators. Mean of three samples. Basis weight = 240 g m⁻². Compression based on original caliper at 10 kPa load.

Table 1
Solubility of glass microfibre in sulfuric acid^a

Fibre source	A	A	B	B	C	C
Fibre diameter (μm)	0.9	2.9	0.8	3	0.8	3.4
Weight loss (g)	4.35	2.33	1.86	0.95	1.67	1.32

^a Tests carried out on 100 g fibre by soaking in sulfuric acid (sp. gr. 1.280) for 1 month at 25 °C.

terms of weight loss, of three sources of fibre in sulfuric acid (sp. gr. 1.280) at 25 °C for one month is given in Table 1. Whilst the solubility is small, it is likely that the fine fibres will be the most affected, with a probable reduction in resilience and compressive strength during service.

Both progressive degradation of the separator and distortion of the container will relax the compressive forces on the active material, and are likely to reduce the cycle life. Several manufacturers use strengthened containers to minimize distortion, but there is little reported work on variations in separator properties during service.

3. Choice of positive grid alloy

Several aspects of grid alloy may effect the cycling performance. The obvious ones are corrosion rate and type, and the effect of alloy composition (including trace elements) on voltage stability. Previous work in both these areas is well documented and requires no further comment. By contrast, a characteristic of lead alloys that has not been given much attention until recently is the naturally low creep resistance of all lead alloys that gives rise to grid growth during service.

Traditionally, grid growth is more of a problem in stand-by batteries which operate for 20 years or more. In these situations, particular care is taken to ensure that minimum growth occurs, or that the design can tolerate it. Capacity loss during float service is normally due to a reduction in the grid-to-paste contact that results from the grid growth. Usually, 4% growth over the battery lifetime is the design limit. Beyond this value, growth increases more quickly and causes a rapid decline in capacity. This experience is related to stand-by batteries with massive grids and excess electrolyte.

Grid design, grain size and several other properties obviously have an influence, and the 4% limit is essentially an approximate guide. The grid sections are smaller in most VRLA batteries, particularly those designed for EV duties. Thus, growth rates should be higher, and there is some evidence that designs with absorbed and limited amounts of electrolyte are less tolerant to growth and, thereby, suffer greater capacity losses.

In addition, the operating potential of the positive electrode is higher VRLA designs. Studies on batteries in telephone service have shown [5] that grid growth is at a minimum when the positive-plate polarization is 40 mV above the reversible $PbO_2/PbSO_4$ potential, and increases to almost double at 150 mV above the reversible potential (see Fig. 4). In VRLA batteries, the oxygen-recombination process at the negative electrode changes the negative potential in a positive direction and, under typical float conditions, it operates at about the reversible $Pb/PbSO_4$ potential, i.e., with zero polarization. Consequently, the potential of the positive electrode is likely to be 50 to 100 mV higher than in a flooded-electrolyte counterpart and, therefore, encourages further increase in the growth rate.

Whilst it is traditionally accepted by designers of long-life industrial batteries that progressive grid growth results in

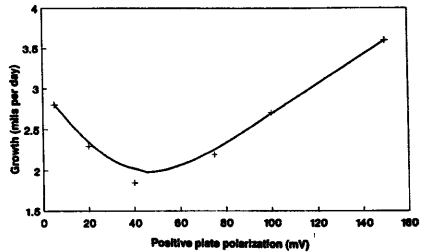


Fig. 4. Positive grid growth vs. polarization [5].

capacity loss, little attention has been given to this behaviour in attempts to improve cycleability, that is, until recently. Growth can, of course, be reduced by appropriate grid design and also by increasing the strength of the alloy. Giess [6] showed that ternary alloys of lead, calcium and tin with high tin levels have improved growth resistance and, recently, several manufacturers have introduced new alloys that should be beneficial in this respect.

4. Design aspects

There is still considerable uncertainty with regard to the design principles for VRLA batteries. Compared with traditional products (which are essentially designed around the number of plates required to give the nominal capacity with adequate plate thickness to ensure the expected life), several other criteria are important. As well as compression, the important considerations are acid volume, saturation level, and active-material ratio. For example, excess negative active material is claimed in the original patents in order to achieve good oxygen recombination rates, and this approach was adopted in many early designs. Later experience has shown, however, that the reaction at the surface of the negative plate does not, in general, control the rate of recombination and, in most applications, excess negative is not required. Progressively, the design features are being better understood and, as expected, the optimum design varies according to the application.

Certain K_v requirements for deep cycling are now widely accepted. In addition to high compression, excess positive-plate capacity is important because of the relatively poor charge acceptance of the positive plate, particularly in the deeply discharged condition. Charge acceptance is defined as the proportion of the charging energy that is used to convert lead sulfate to lead or lead dioxide; it varies according to the state-of-charge. The charge acceptance at the positive electrode is generally much lower than at the negative plate, at least with a clean system, i.e., one that is not contaminated with metals that depress the hydrogen overpotential. Charge acceptance also varies considerably with the strength of the electrolyte; it is much lower in strong acid.

In VRLA designs, the overcharge levels are kept to a minimum and, consequently, the charge efficiency is particularly important. Low levels of overcharge have a further adverse effect because without the mixing caused by gassing, regions of strong and weak acid are formed. Stratification of this nature greatly affects the charging efficiency and, without correction, causes a progressive decrease in capacity.

The effects of stratification have been demonstrated by tests on 2 V/60 Ah VRLA cells designed for telecommunications duties. The cells were cycled in a group of six by discharging at 9.85 A for 3 h and then recharging at 14.4 V (i.e., 2.4 V/cell) for 9 h. It was intended to carry out capacity checks at a current of 3 A on each cell after every 50 cycles but, at the first check discharge, the capacities averaged only 66% of the initial value. This loss of capacity was accompanied by a progressive decrease in both the end-of-charge current and the finishing voltage on the 3 h discharge. The ratio of Ah(in) to Ah(out) decreased from an initial value of 107–109% to 103–104% at 50 cycles. At cycle 73, all the cells were inverted and the end-of-charge current and the Ah ratios increased within two or three subsequent cycles. At cycle 78, the capacity of all cells had recovered to approximately the nominal value. Table 2 and Fig. 5 show the capacity before and after inverting the cells. The differences in charge acceptance are clearly demonstrated. As cycling continued, the capacity of all cells decreased, but at a slower rate than previously.

In certain applications, such as in submarine batteries, the above effects are prevented by agitating the electrolyte with air, but this is not practicable in many designs. Low cell height reduces the problem, but Sunu and Burrows [7] showed that even in a 12 cm high automotive battery there was a marked difference in acid strength from the top to the bottom after 40 cycles (viz., 1.21 versus 1.34 sp. gr.), and it took three weeks to mix without agitation.

Due to gravitational flow constraints, it is to be expected that cells in which a substantial proportion of the electrolyte is absorbed in glass-microfibre separators would exhibit less stratification effects than in batteries with free-flowing electrolyte. Indeed, Tuphorn [8] claims there is a 50% reduction in these designs. This depends, however, upon certain impor-

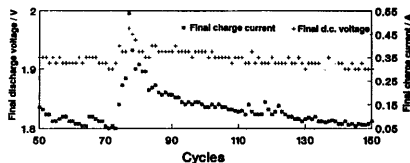


Fig. 5. Cycling tests on 2 V/60 Ah telecommunications cells. Discharge: 3 h at 9.85 A, recharge: 9 h at 2.4 V/cell. Note, all cells were inverted after cycle 73.

tant design parameters. Culpin [9] showed that the high electrolyte retention properties of AGM separators when compressed, limit the drainage of acid to a considerable extent, particularly for drainage heights below 400 mm. Clearly, the design target should be to ensure that there is sufficient pore volume to take up all the electrolyte under the normal conditions of charge and discharge. Under these conditions, stratification effects are greatly reduced.

5. Charge management

Several charging algorithms have been proposed in recent years. Most manufacturers have their own preferred schedules for gaining maximum cycle life. These vary considerably, but they all aim to provide sufficient coulombic input to replace the output with some allowance for the charging inefficiencies. Invariably, the strategies have some form of overcharge and overdischarge protection, plus precautions against excessive temperature. Most of these systems treat the battery as a whole unit and the techniques and associated equipment are relatively easy to arrange. They do not take account of the variability of cells within the long series strings that are typically used, for example, in EV applications.

As mentioned previously, overcharge in maintenance-free designs is kept to a minimum, but the consequence of this limited overcharge in a series string is that cells attain different levels of charge over relatively few cycles. Every attempt is made to ensure uniform product quality — sometimes, by capacity checks prior to shipping and cell-matching within the string. Nevertheless, minor deviations in, say, acid concentration or inherent differences such as temperature variations within the battery, can result in some cells being overcharged and some undercharged and, consequently, can lead to a subsequent reduction in cycle life.

The changes that can occur in a few cycles in a series string of 105 cells are shown in Figs. 6 and 7. Initially, the voltages of all cells at the end of discharge to a final voltage of 200 V (i.e., 1.90 V/cell) and at the end of the charge period to a finishing voltage of 260 V (i.e., 2.48 V/cell) were reasonably uniform. After only 45 cycles on a typical EV schedule, both the discharge and charge voltages displayed much greater variation from cell-to-cell. There was a risk that, with continued cycling, certain cells, particularly cells 12, 23 and 87, would fail prematurely. Subsequent examination showed that

Table 2
Capacity (Ah) of 2 V/6 Ah telecommunications batteries discharged at 3 A to 10.5 V*

Cell no.	Cycles				
	1	50	78	128	150
7	62.3	42.2	59.4	56.7	52.3
8	64.2	47.9	60.1	58.1	54.4
9	62.3	47.2	60.3	56.1	51.6
10	63.5	42.2	59.4	53.9	50.7
11	62.8	46.6	60.4	55.9	52.2
12	61.8	42.2	58.4	55.5	50.9

* All cells were inverted at cycle 73.

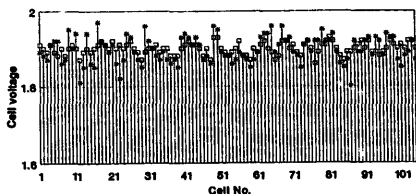


Fig. 6. Discharge voltages of cells before and after cycling. 210 V battery discharged to 200 V; (□) before cycling, and (*) after 45 cycles.

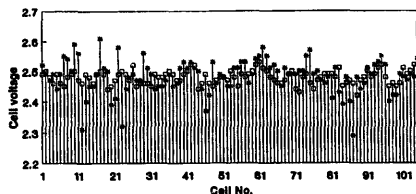


Fig. 7. Top-of-charge voltage of cells before and after cycling. 210 V battery charged to 260 V; (□) before cycling, and (*) after 45 cycles.

these cells were of good quality, with no design or manufacturing defects but, clearly, they had not accepted charge as efficiently as the other cells in the battery.

These inhomogeneities in the state-of-charge of cells within a long string are well known. Manufacturers of industrial traction batteries admit that some form of regular equalizing charge is necessary to achieve the guaranteed cycle life. Whilst increased overcharge, within limits, is not detrimental because water losses can be easily replaced, this is not possible with VRLA designs. Consequently, regular and frequent equalizing charges is not an option, and the type of variability demonstrated above is one of the main causes of early failure of VRLA batteries when regularly and deeply cycled. Furthermore, this 'out of phase' behaviour is increased as the depth-of-discharge increases.

Several ways of resolving this problem are presently being assessed. Schmidt and Siedle [10] have developed equipment that controls the voltages of single modules during charge and discharge. If the voltage of one module decreases, the majority of the battery will be supported by the stronger modules. A similar behaviour occurs during charge. In addition, several other means of equalizing without excessive charge are being tested. They all require individual modules or cells to be monitored. Naturally, this adds to the cost of the charge-management system.

6. Further considerations

Several reasons for the poor cycling performance of VRLA batteries have been proposed in recent times. These include

barrier-layer effects caused by the different corrosion-layer structures with antimony-free grids, agglomeration of the dioxide particles in the positive active material and, more recently, changes in the apparent density of the active material. It is conceivable that all these mechanisms contribute to early failure during cycling. The purpose of this paper, however, is to review certain design and operating criteria that have a major effect on cycling performance.

Each of the four factors considered can cause premature failure if not controlled to a satisfactory level. Furthermore, they interact to a considerable extent and it is difficult to consider any one in isolation. In 1992, the Advanced Lead-Acid Battery Consortium [11] proposed a target battery life of 500 cycles on the simplified federal urban driving schedule (SFUDS). Recent improvements indicate that this is within reach of several major manufacturers. Further improvement in the cycling performance requires a better understanding, and a greater control, of these key parameters, i.e., compression, grid growth, electrolyte stratification and cell uniformity during cycling.

Once this capability is reached, the limiting failure mode is likely to be corrosion of the positive grid. This is a familiar area of technology for battery designers and, given this situation, they can more easily design for specific cycle-life requirements. Moreover, with the likely introduction of more corrosion-resistant alloys, the key objectives of high specific energy and cycle lives much greater than the present target of 500 SFUDS cycles will be achievable. Since the cost of battery amortization and replacement generally far exceeds the operating costs, usually by a factor of three or four, an extension of cycle life will have a major impact on the commercial use of lead/acid batteries for the new traffic-compatible electric vehicles.

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