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Benefits of controlling plate-group expansion: opening the door to advanced lead/acid batteries

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Abstract

Highly compressed, flooded-electrolyte cells have been constructed with pure-lead positive plates prepared from the following starting materials: (i) standard positive paste; (ii) standard negative paste; (iii) mixture of lead sulfate and barium sulfate; (iv) active-material removed from a cured negative-plate. All the cells return excellent cycle lives under deep-cycle service. The exceptional performance is attributed to the high level of cell-group compression that minimizes active-material shedding and maintains electrical conductivity within the positive active-mass. The results demand that traditional methods used to process battery plates be reviewed, especially in terms of positive-paste composition and curing conditions. Cost-effective strategies are identified to assist in the implementation of significant cell-group compression into commercial gelled- and flooded-electrolyte batteries. This involves the development of devices that apply accurate support to the cell group along with a compression-resistant separator system that can withstand high levels of compression. © 1997 Published by Elsevier Science S.A.

Keywords: Lead/acid batteries; Cell-group compression; Positive active-material constraint; Compression plates; Compression-resistant separators; Cycle-life tests

1. Background

As the move towards widespread implementation of electric vehicles (EVs) gathers momentum, the operational characteristics of likely candidate batteries come under closer scrutiny. The lead/acid battery is featured in many of the EVs that are either in production or in the final stages of development. This is an important position for what is regarded by many as an out-dated technology. Whether lead/acid remains near the forefront of developments depends on the extent to which the technology can be adapted to the specific requirements of EV duty. These requirements are known to be among the harshest to which batteries can be subjected. Accordingly, the successful deployment of lead/acid technology in EVs demands that the well-known deficiencies of the battery be addressed with renewed effort.

Today, the general utility of state-of-the-art lead/acid batteries is still limited in the areas of cycle life and active-material utilization (AMU). The former is arguably the greater problem because cycle life exerts a direct effect on the life-time cost of vehicle operation. Improvements in AMU are of course also sought because they are linked closely to the on-road performance of an EV. Before considering the paths that are available for the pursuit of improved battery characteristics, it is worthwhile to review briefly the reasons for the present limitation on performance.

The cycle life of the lead/acid battery under repetitive deep-discharge service is usually limited by a loss of discharge capacity of the positive plate. Of particular concern have been situations in which this loss of capacity is severe and occurs rapidly, without apparent cause. Although such cases are now less common, they have provided the focus for much of the research that has been carried out on 'premature capacity loss' (PCL) [1]. Extensive investigations into PCL have provided both a detailed description of the factors associated with capacity loss, as well as a great deal of information on the morphological and compositional changes that, in various ways, characterise the problem [2,3]. In spite of the comprehensive description, it was only recently that a clear understanding of the causes of PCL came to light [4,5].

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Among the investigations of positive-plate capacity loss, a relatively small number of studies has demonstrated how compression of the plate group is able to prolong cycle life [6–12]. On the basis of these findings, the present authors have investigated further the effects of compression and this has led to a full appreciation of the main determinants of positive-plate life. Compression exerts its benefit through restricting the volume to which the positive-plate material is allowed to expand. It is well-known that the material expands during discharging, and contracts during charging. More important, though, is the fact that the degree of expansion usually exceeds the degree of contraction, so that a net expansion occurs during cycling [13,14]. The problem with this progressive expansion is that it causes a concomitant fall in the packing density of the positive material which, in turn, is directly related to the bulk conductivity of the material. Unless the expansion of the positive material is controlled in some way, then, eventually, there is a breakdown in the conductivity of the positive material. This reduces greatly the extent to which the plate can be discharged.

If expansion of positive-plate material occurs close to the current collector, this gives rise to the severe form of capacity loss that is known as PCL-1 [2]. Here, the bulk of the positive material is in good condition, but is largely inaccessible during discharge because it is connected poorly to the current-collector. The provision of a certain minimum level of compression prevents this catastrophic form of capacity loss. Whether the positive plate is then able to survive long-term charge/discharge cycling is determined by the maintenance of this compression.

On the basis of the above information, an investigation has been made of the effects of constraining the expansion of positive active-material. This study has found that a variety of materials can be employed successfully as positive active-material, as long as adequate plate-group compression is available. At the same time, it has become obvious that the composition of the cured positive plate has a minimal effect on cycle life, again provided that plate-group compression is adequate. Finally, in order to expedite the implementation of plate-group compression on a commercial basis, a novel compression-resistant separator and the means for maintaining accurate levels of compression within lead/acid batteries have been identified.

2. Experimental

Studies of the effects of restraining material expansion were conducted on small scale, 2 V lead/acid cells. The key feature of these cells is a 'capped' design of positive plate with which the expansion of the positive material can be controlled to a large degree. A detailed description of the design and construction of these plates is available elsewhere [4]. The essential features of the capped plate are shown in Fig. 1. Each plate is based on a machined body (epoxy or perspex) that features a recess (diameter: 10 mm) in which the material is contained. A thread is cut on the narrow end of the body, so as to accommodate a plastic (polypropylene) retaining cap with the corresponding internal thread. The design allows a disc-shaped separator to be positioned between the cap and the porous material. In the studies described here, the separator is a piece of coarse glass-fibre matting, similar to that employed as a lining for some polymer separators. A disc of pure lead (the 'grid') is provided with an electrical contact and then sealed into the bottom of the recess.

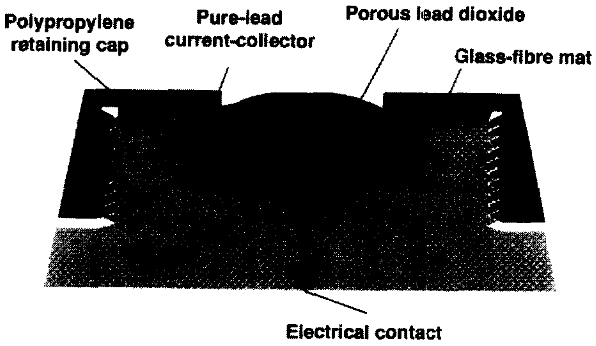

Fig. 1. Schematic representation of capped cell.

As will be described below, the material in these capped positive plates was prepared from a range of precursor states. For some of these, the preparation followed standard procedures of battery manufacturing. In those cases, pastes were mixed according to a typical formula for motive power plates. Curing was performed at 50 °C and 100% relative humidity for 24 h, followed by drying at the same temperature for 4 h. Details of the various non-standard methods of positive material preparation are described within the body of the Section 4, below. For all plates, the formation procedure was conducted at constant current and involved passing 300% of the theoretical charge requirement over a period of 64 h. The negative plates were constructed by cutting a portion from a typical automotive negative plate (Pb–Ca–Sn grid) so as to give at plate that was between five and ten times the size (by volume) of the positive plate. In this way, the capacity of the positive plate always determined the duration of discharge.

Electrodes were formed and cycled in an excess of 5 M H_2SO_4 by means of equipment built in the CSIRO laboratories. Initially, discharging was conducted at the 5 h rate, to 100% depth-of-discharge (DOD), until constant capacity was reached. The overcharge factor during this phase was set at ~ 20%. The discharging current was then adjusted, over several cycles, to a value near the desired rate of discharge. Once the required current had been ascertained, the overcharge factor was raised to ~ 50%. The charging current was set at 10 to 20% of the discharging current. No upper voltage limit was applied so that the highest voltages reached by the cells were in the range from 2.75 to 2.85 V.

3. Laboratory-scale investigations into the effects of cell-group compression

Operation of a range of cells with capped positive plates allowed a systematic characterization of the effects of compression, in the absence of other factors that influence cycle life. In effect, the capped design places a limit on the overall amount of expansion that can occur. To determine the ultimate effectiveness of such a highly constrained design, most of the positive plates examined were constructed from starting materials that are traditionally viewed as unsuitable for achieving even minimal cycling performance. These included negative-plate paste, a mixture of lead sulfate and barium sulfate, and ground (milled) material from a cycled negative plate. For comparison, plates based on a standard positive paste were also prepared and cycled under high plate-group compression. A summary of the starting materials and performance of the respective plates is provided in Table 1.

Given the harsh conditions of service (v.s.), all cells have yielded excellent cycling performance. Perhaps the most impressive examples of the beneficial effect of constraining plate expansion are provided by the cells that contain barium sulfate (i.e., cells C, D and E, Table 1). It is well known that the presence of barium sulfate in the positive active-material causes early and catastrophic loss of discharge capacity, due to massive shedding of material. In sharp contrast, cell D delivered 339 cycles to 100% DOD and was still delivering in excess of 150% of its initial capacity when it was retired from duty. Further, it is worth noting that for cells D and E, there was no curing step. The starting material was crushed to a fine powder which was then packed into the plate body. In this way, any possible benefit associated with the development of a so-called 'backbone structure', via the curing process, is removed. The results demonstrate a definite ranking of the factors that are known to influence cycle life. Clearly, the effects of constraining the growth of plate material are much greater than those factors, such as strength/integrity of the cured state, that are traditionally viewed as the main determinants of positive-plate longevity. In other words, the composition of the starting material from which the positive plate was prepared has a minor effect on the cycling performance of the plate, as long as adequate plate-group compression is provided.

4. Achieving significant plate-group compression in commercial, flat-plate lead/acid batteries

In conjunction with a review of the literature and the extensive small-scale laboratory investigations into the effect of stack pressure on battery performance described above, CSIRO has developed, and filed, a provisional patent for a range of devices that maintain accurately high levels of plate-group compression in commercial lead/acid batteries [15]. For each device, the mechanism of operation allows for some expansion and contraction of the plate-group, as well as maintaining, overall, an accurate level of plate-group compression throughout the lifetime of the battery. Before describing the devices in detail, it is useful to review the design of state-of-the-art lead/acid batteries in terms of plate-group compression.

4.1. *Plate-group compression in state-of-the-art absorptive glass-microfibre batteries*

It has long been recognised by battery manufacturers that significant plate-group compression is imperative for the successful operation of absorptive glass-microfibre (AGM) batteries. This is based on the understanding that good contact between the AGM separator and the battery plates is required in order to ensure sufficient movement of

Table 1
Summary of performance for laboratory cells

Plate designation	Origin of positive material	Cycles completed (rate) [a,b]	Initial AMU (%) [c]	AMU at end of service (% of initial AMU)
A	Standard positive-paste	105 ($C_1/1$)	18.1	20.0 (110)
B	Standard positive-paste	111 ($C_1/1$) [d]	18.6	20.0 (107)
C	Negative material [e]	134 ($C_2/2$)	14.4	21.6 (150)
D	Negative material [f]	339 ($C_2/2$)	[g]	[g] (154)
E	Lead sulfate [h]	292 ($C_2/2$)	[g]	[g] (112)
F	Standard positive-paste	479 ($C_2/2$)	17.1	30.4 (178)

[a] Rate given applies to initial phase of service and was not adjusted later in service.

[b] No limit on top-of-charge voltage, 100% DOD, 150% overcharge.

[c] (actual discharged capacity)/(theoretical capacity) × 100%.

[d] Plate B also completed 200 cycles, to 70% DOD at $C_{0.05}/0.05$, prior to removal from service.

[e] Prepared from a standard SLI negative paste.

[f] Prepared by crushing and grinding material from a cycled negative plate.

[g] Data on material utilization are not available.

[h] Prepared from a mixture of finely ground lead sulfate and barium sulfate (0.3 wt.%), both chemicals supplied by BDH.

electrolyte around the cell. If the acid supply is not maintained in a uniform manner, areas of the plates can become isolated from the electrolyte and the capacity of the battery falls accordingly.

The level of compression used in the construction of AGM batteries has traditionally been defined by battery manufacturers as the extent to which the cell group is compressed. More specifically, compression is usually given as a percentage decrease in thickness of the cell group that occurs during insertion of the plate-group into the case. This compression is sometimes called the 'stack pressure'. It must be stated, however, that there are disadvantages with this approach. First, compression defined in these terms is reported as a percentage figure that is specific for a given plate-group configuration. On this point, it is recommended here that plate-group compression should, in future, be defined in terms of applied force, i.e. kg dm^{-2} (or, as a close approximation, kPa). Reporting compression in this way will facilitate meaningful comparisons from different configurations of cell groups.

Second, the maintenance of compression within AGM batteries relies upon the AGM separator behaving as a spring. Unfortunately, changes in the spring constant of the separator and plate-group compression can occur due to the following: (i) the addition of acid (i.e., wetting) is known to result in a relaxation/contraction of AGM; (ii) permanent 'crushing' under compression — AGM can relax/contract irreversibly over time; (iii) battery cases constructed from soft material (e.g., polypropylene) can deform and allow expansion of the plate group. Hence, given that very minor variations in cell-group thickness can result in significant changes in stack pressure, the compressive force within AGM batteries after acid filling and/or extended operation can be considerably less than that at the time of assembly.

Clearly, the design of AGM, and AGM-based lead/acid batteries, must do more than just ensure electrolyte contact between opposing plates. The traditional view of plate-group compression in AGM batteries must be modified to include the properties of AGM that contribute to the maintenance of conductivity within the positive active-material. In particular, the spring characteristics of AGM are of key significance. With these characteristics optimized, the cycling performance of AGM batteries should become far superior to that of uncompressed designs. The fact that the performance of AGM-based units is rarely superior poses questions about the maintenance of compression. To address this problem, it appears that AGM batteries should be provided with a supplementary source of plate-group compression.

4.2. Plate-group compression in state-of-the-art flat-plate, flooded- and gelled-electrolyte batteries

The majority of flat-plate, flooded-electrolyte and gelled-electrolyte batteries are assembled with low levels of plate-group compression. Increasing the stack pressures to higher levels (e.g., above 10 kg dm^{-2}) is difficult due to the ribbed nature of the separators typically used in such batteries. The ribbing does not provide even support across the entire positive plate. The ribs can also deform and fold, and this results in collapse of the plate stack and the possibility of short circuits. These problems can be overcome to some extent by strengthening both the backweb and the ribs, but the associated increase in thickness also raises the internal resistance of the separator and decreases the high-rate performance of the battery.

Another area that needs to be considered when implementing significant levels of plate-group compression into lead/acid batteries is the battery case/container. Battery containers used in state-of-the-art, flat-plate batteries generally have thin walls so that some distortion of the case occurs when the cell group is inserted. As described above, this can reduce the compression that is acting on the cell group. Manufacturers of motive-power power batteries have addressed this issue to some extent by forcing individual 2 V cells in totally rigid boxes — this can be used to apply a moderate level of compression to the cells.

Tubular-plate batteries have a significant advantage with respect to some of the problems associated with the application of plate-group compression. This advantage is mainly derived from the fact that the positive active-material is held tightly in a gauntlet around the central current-collector. Such an approach has provided good cycle lives for Pb–Ca based units, due to constraint of the positive active-material offered by the gauntlet. The obvious conclusion is that appropriate levels of compression suppress the debilitating effects of PCL associated with Pb–Ca batteries and can improve the performance of such battery systems relative to that of Pb–Sb units. This is supported by other CSIRO studies in which the performance of flat-plate Pb–Ca batteries constructed with appropriate levels of compression has been found to approach that of Pb–Sb equivalents.

4.3. Devices for achieving effective plate-group compression

If the implementation of plate-group compression is to be achieved successfully, it must be both cost effective in terms of production and provide permanent benefits in battery performance. With these criteria in mind, CSIRO has identified a number of options that will assist in achieving reliable plate-group compression. The options are described in the following sections.

4.3.1. Maintaining compression

Four different methods have been developed [15] for maintaining compression within lead/acid batteries. They differ in complexity, cost, benefit to battery performance, and in changes required to existing manufacturing processes for commercial implementation. The first method involves a flexible bag that is inserted between the plate-group and the battery-case wall. The bag is made from acid-proof material (e.g., natural rubber) and the pressure inside the bag can be adjusted by either introducing or removing a suitable fluid (in the first instance, compressed gas is suggested). The group of plates in the cell is maintained under compression by filling the bag to a certain pressure. In the simplest implementation of this strategy, the manufacturer elects to seal the bag, thereby fixing the compression at a reasonably constant level for the life of the unit. Alternatively, plate-group compression could be varied by inflating or deflating the bag, i.e. by applying an active load. This strategy forms part of a comprehensive approach to the optimization of compression. For example, it may be found that maintaining compression at a higher level during charging yields an extension of cycle life. If the benefit proves significant, then manufacturers may consider incorporating active control of compression into the management of large battery banks, such as those found in EVs.

A second method for maintaining the required level of compression is to replace the fluid-filled bag with a compressible member. The latter must have good elastic properties (i.e., behave like a spring) and be acid-resistant. It can be made of synthetic silicone rubber, closed-pore polyethylene foam, or natural rubber. Alternatively, it can take the form of a solid plate that has (i) multiple protrusions, each of which may be elastically deformed and act like a small spring or (ii) a wave-like structure that applies pressure when compressed. The latter device has been described by Alzieu and Robert [10] in their studies of the effects of plate compression.

The third method for providing plate-group compression is to manufacture battery containers with collapsible bridges moulded on the inside of the case. On insertion of the plate group into the container, the bridges are compressed and thus apply pressure to the plates.

The final procedure, and possibly the most convenient to implement, involves the use of an elastic device that envelopes the whole cell-group. The device would resemble a thick, porous 'stocking'. The method is attractive in that a strong battery case is not needed, i.e. the compression is maintained independent of the battery case and lid.

4.3.2. Compression-resistant separator

Having developed several options for maintaining accurate compression within the battery, it is recognised that existing separator technology used in current gelled- and flooded-electrolyte batteries is inadequate to withstand the relatively high levels of compression required. Hence, a separator system for flooded- and gelled-electrolyte batteries has been devised that can withstand up to 200 kPa of pressure, does not significantly affect acid diffusion, occupies minimal volume and guarantees even compression across the face of the positive plates. It has the added benefit of removing the need for a microporous separator (gelled-electrolyte type only) which improves the high-rate performance of the battery significantly.

The separator design consists of the following two parts: (i) a main body that is constructed from an acid-resistant material, and (ii) a thin outer layer that is located on both sides of the main body. The construction of the main body is such that thin outer sheets are separated by a series of ribs that form a series of compartments. The ribs provide the main body with most of its mechanical strength. The thickness of both the outer sheets and ribs, and the rib spacing, are determined by the strength of the material used. Holes are drilled through the main body of the separator to allow for the movement of electrolyte. The holes are located along the ribs to allow diffusion of acid from one compartment to another. The location and size of the holes, termed the 'hole pattern', depends upon the intended application of the battery and the required compression resistance of the whole separator.

The thin outer layer comprises a sheet of glass mat, polyester cloth, microporous separator or combination thereof, depending upon the required duty of the battery. This layer provides support to the active-material not constrained directly by the separator, i.e. where holes have been drilled through the main body.

5. Conclusions

The present study has confirmed the beneficial effects of plate-group compression on lead/acid battery cycle life. It has also been demonstrated that the composition of positive active-material is not as important as traditionally thought, provided that adequate compression is applied. Finally, several strategies have been identified that will assist in achieving the cost-effective implementation of plate-group compression into lead/acid batteries on a commercial scale.

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References

[1] A.F. Hollenkamp, *J. Power Sources, 36* (1991) 567.
[2] In R.F. Nelson and D.A.J. Rand (eds.), *Proc. 1st Meet. The ALABC PCL Study Group, Lower Beeding, West Sussex, UK, 23–24 Sept. 1993*, International Lead Zinc Research Organization, Inc., Research Triangle Park, NC, USA.

[3] In R.F. Nelson and D.A.J. Rand (eds.), *Proc. 2nd Meet. The ALABC PCL Study Group, Montreux, Switzerland, 19–20 Sept. 1994*, International Lead Zinc Research Organization, Inc., Research Triangle Park, NC, USA.

[4] A.F. Hollenkamp, K.K. Constanti, M.J. Koop and K. McGregor, *J. Power Sources, 55* (1995) 269.

[5] A.F. Hollenkamp, *J. Power Sources, 59* (1996) 87.

[6] K. Takahashi, M. Tsubota, K. Yonezu and K. Ando, *J. Electrochem. Soc., 130* (1983) 2144.

[7] J. Landfors, *J. Power Sources, 52* (1994) 99.

[8] S. Atlung and B. Zachau-Christiansen, *J. Power Sources, 30* (1990) 131.

[9] J. Alzieu, B. Geoffrion, N. Lecaude and J. Robert, *Proc. 5th Int. Vehicle Symp., EVS-5, Com. 783205, Philadelphia, PA, USA, 2–5 Oct. 1978*, Electric Vehicle Council, 90 Park Avenue, New York, NY, USA.

[10] J. Alzieu and J. Robert, *J. Power Sources, 13* (1984) 93.

[11] J. Alzieu, N. Koechlin and J. Robert, *J. Electrochem. Soc., 134* (1987) 1881.

[12] D. Pavlov, *J. Power Sources, 33* (1991) 221.

[13] K. Micka, M. Svata and V. Koudelka, *J. Power Sources, 4* (1979) 43.

[14] D. Pavlov and E. Bashtavelova, *J. Electrochem. Soc., 133* (1986) 241.

[15] A.F. Hollenkamp and R.H. Newnham, A Battery and Components Therefor, *Aust. Provisional Patent No. PN 8080.*