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Keeping up the pressure — strategies to maintain plate-group pressure and extend the cycle life of VRLA batteries

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Abstract

For valve regulated lead acid (VRLA) applications involving deep cycling, significant cycle life improvement can be achieved by applying pressure to the plates via the compressible recombinant battery separator mat (RBSM). However, the latest work is showing that the plate-group pressure needs to be much higher than previously assumed, in order to inhibit positive active material expansion and capacity loss. This will require changes not only to the separator, but also to the battery design and assembly techniques. Techniques to apply very high pressures to the cell group during battery assembly need to be developed. Changes to the container design and materials may also be needed, and the overall battery design may need to include an internal or external means to maintain the applied pressure throughout battery life. Less compressible separators may also enable higher plate-group pressures to be maintained.

This paper will review possible strategies to achieve these objectives of maintaining plate-group pressure and extending VRLA battery cycle life.

Keywords: RBSM; AGM; VRLA; Separator; Plate-group pressure; Cycle life

1. Introduction

VRLA batteries have found wide application in many market areas particularly stationary applications. However, in applications involving deep cycling, for example the emerging electric vehicle market, VRLA batteries can suffer from poor cycle life. This phenomenon has been termed ‘‘premature capacity loss’’. Several theories have been advanced to explain this, but essentially the problem arises from loss of positive particle to particle contact, paste softening and loss of positive plate capacity.

It has been found that significant cycle life improvement is possible by applying higher pressure to the plates via the compressible absorptive glass mat (AGM) separators. However, these separators may lose their springiness with time and also tend to contract on addition of liquid. It is also becoming apparent that it is the applied pressure rather than the % compression of the separator that is important. The plate-group pressure is probably the best way of defining the importance of the applied pressure to the life of the battery. Less compressible separators may have benefits because they may tolerate and maintain higher plate-group pressures.

The latest work is showing that the plate-group pressure needs to be much higher than previously assumed, in order to inhibit positive active material expansion and capacity loss. This will require changes not only to the separator, but also to the battery design and assembly techniques. Techniques to apply very high pressures to the cell group during battery assembly need to be developed. It may be possible to precompress the separators and ‘‘fix’’ the plate-group pressure in the early stages of cycling. Changes may need to be made to the container design and materials to avoid container distortion and tolerate thermal cycling. The overall battery design needs to include an internal or external means to maintain the applied pressure throughout battery life. Changes to the negative plates may also be necessary otherwise the high applied pressure may have an adverse effect on the negative plate performance. If less compressible separators are used, the overall battery design needs to be able to compensate for plate thickness tolerances and the ‘‘roughness’’ of plate surfaces.

Changes to the separator system and overall battery design may also require changes to the charge regime, as alternative separator systems may have different efficiencies of gas diffusion through the separator. A different charge regime and charge factor may be needed for different separator systems.

Possible strategies to achieve these objectives will be discussed.

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2. Background

Prior to the start of the first ALABC programme in 1992, a small, but detailed body of literature had been published which showed the beneficial effects of compression/active material constraint on positive plate cycle-ability [1–7]. One of the first tasks of the ALABC research programme was to establish the cause of "premature capacity loss", which appeared to have two distinct mechanisms that were called "PCL-1" and "PCL-2" [8,9]. At the time of commencing the research, strong arguments were being put forward that PCL was due to relatively subtle changes in key structural characteristics of the porous positive material [10,4]. These arguments were developed into the gel-crystal [10] and the aggregate-of-spheres [4] theories that seek to explain PCL-2.

Key research work by CSIRO in this first ALABC programme showed that if the separator is compressed against the positive plate at a high enough pressure, this can control the expansion and shedding of the positive active material, thereby extending battery life. In ALABC project AMC-003, work using a "capped" cell showed that the active material under the cap which remained under compression exhibited less swelling and expansion. From this work, CSIRO developed a unified theory of premature capacity loss [11]. This theory postulates compression of the active material via the separator as a critical factor in eliminating premature capacity loss. Subsequent work by CSIRO [12] indicated that the pressure applied to the plates via the separator might need to be as high as 80 kPa. The beneficial effect of compression in extending the cycle life of VRLA batteries was confirmed in one of the European ALABC projects [13]. This latter project also showed that the composition of the microfine glass separator has an important influence on cycle life, with a higher fine fibre content contributing to long cycle life.

The microfine glass (MFG) separator in the VRLA battery has always been designed to operate under compression and in fact the reference "uncompressed" separator thickness is actually measured under a controlled pressure of 10 kPa. For traditional "float" duty — originally the major application for VRLA batteries — the compression has been relatively low (e.g. 20%) and sometimes poorly controlled. The importance of high, controlled compression for deep cycle VRLA batteries has now been recognised, in particular from the ALABC research work mentioned above. In fact, it may now be more appropriate to talk about plate-group pressure rather than compression. New separator materials are now being developed which are relatively incompressible, but may be able to sustain a higher plate-group pressure than traditional microfine glass separators.

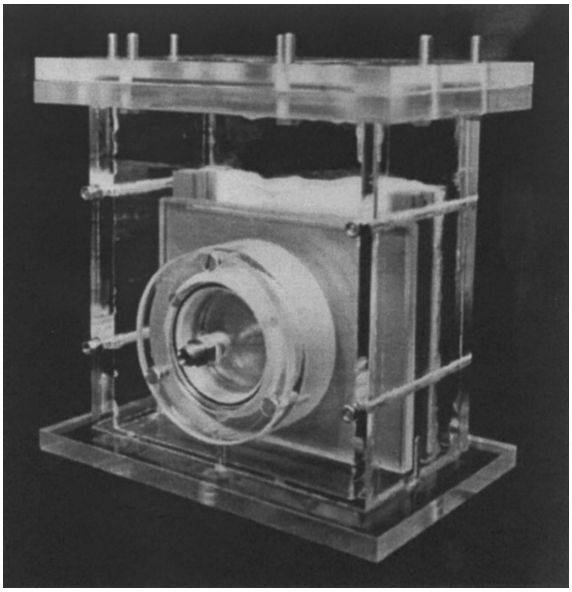

Fig. 1. CSIRO piston cell.

Much of the recent research work has been carried out on a laboratory scale often with "hand-built" batteries and laboratory based techniques for maintaining the applied pressure, for example external clamping or the piston cell developed by CSIRO (see Fig. 1). There is also some evidence from the most recent research work that the high applied pressures which are so beneficial for the positive plates, may have a harmful effect on the negative plates (contraction of the negative active material). A range of production and technical problems need to be resolved if VRLA batteries are to be constructed on a production scale which have been optimised for deep cycle duty by using techniques for controlling plate-group pressure.

3. The behaviour of RBSM separators under applied pressure

RBSM separators made from microfine glass, when compressed, act like springs and oppose any further compression in the direction of the applied force. When the force is removed, the separator will recover to a point close to the starting point, making its action more like a viscoelastic material. A viscoelastic material deforms under stress over a period of time, showing a creep effect and can relax under a constant strain. The compressive properties of the ideal separator should be reproducible when dry, and the separator should recover to its original thickness when the compressive force is released. Also, the separator should not contract when wetted with acid and should show the same compressive properties as the dry separator. The slope of the compression curve should accommodate small changes in plate thickness without an appreciable change in the compressive force. The behaviour of RBSM separators is characterised by carrying out compression/recovery curves, examples of which for AGM separators are shown in Figs. 2–5.

As can be seen from Figs. 2–5, the compression/recovery behaviour for microfine glass separators is not ideal, and typically shows the following features.

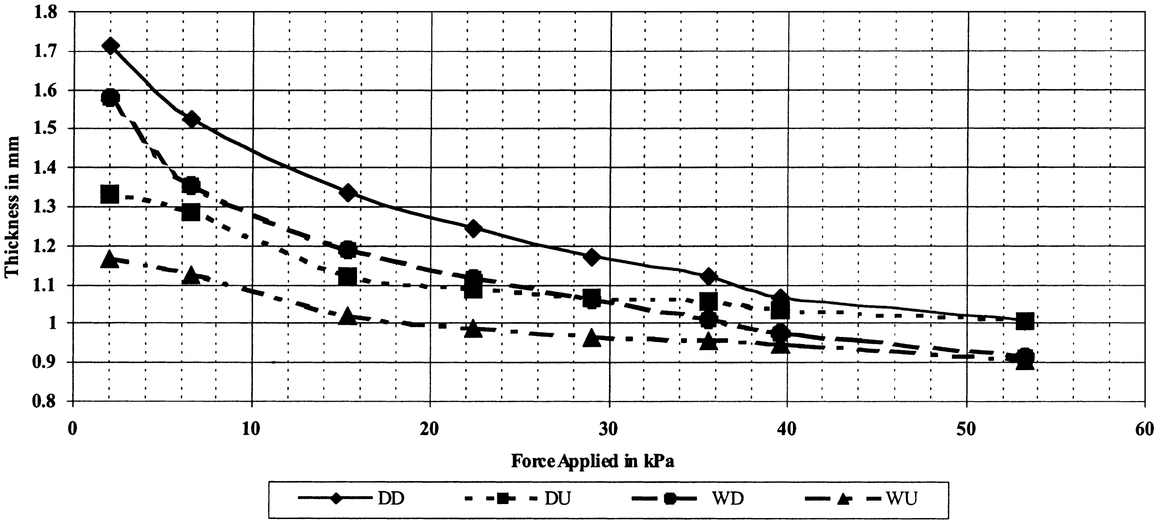

Fig. 2. Compression curve for 200 g/m^2–1.1 m^2/g.

- For an applied force up to — and possibly beyond — 50 kPa, the separator thickness is reduced with increasing applied force.
- When the applied force is released, the separator recovery is incomplete, and the separator does not return to the original thickness.
- The wet separator tends to contract, and for a given applied force has a lower thickness than the dry separator.
- To achieve a compression of 30% (reduction in thickness of 30% compared with the original thickness at 10 kPa) may require an applied force in excess of 50 kPa.

These figures also show that the compression/ recovery behaviour is influenced by the separator composition. For example a separator with the same grammage (basis weight in g/m^2) but different surface area will display a different compression behaviour (Fig. 2 compared with Fig. 5). To achieve a given % compression, a higher applied pressure will be needed for the separator mat with the higher surface area. The separator containing organic fibres (Hovosorb II) also needs a higher applied pressure for a given % compression. Of the examples shown, the Hovosorb II separator also shows the smallest difference between the dry and the wet thickness at an applied pressure of 10 kPa.

To date, no commercially viable alternative to the AGM separator — in terms of its overall mix of properties — has been found. However, its behaviour under high compressive forces is less than ideal, as shown by the comments above. A number of alternatives have therefore been tried — many of which have been evaluated as part of the ALABC research programme. Some of these alternative separator materials are less compressible than AGM, enabling higher pressures to be applied to the positive plates via the separator. However, these high applied pressures impose additional manufacturing and assembly problems as discussed later in this paper.

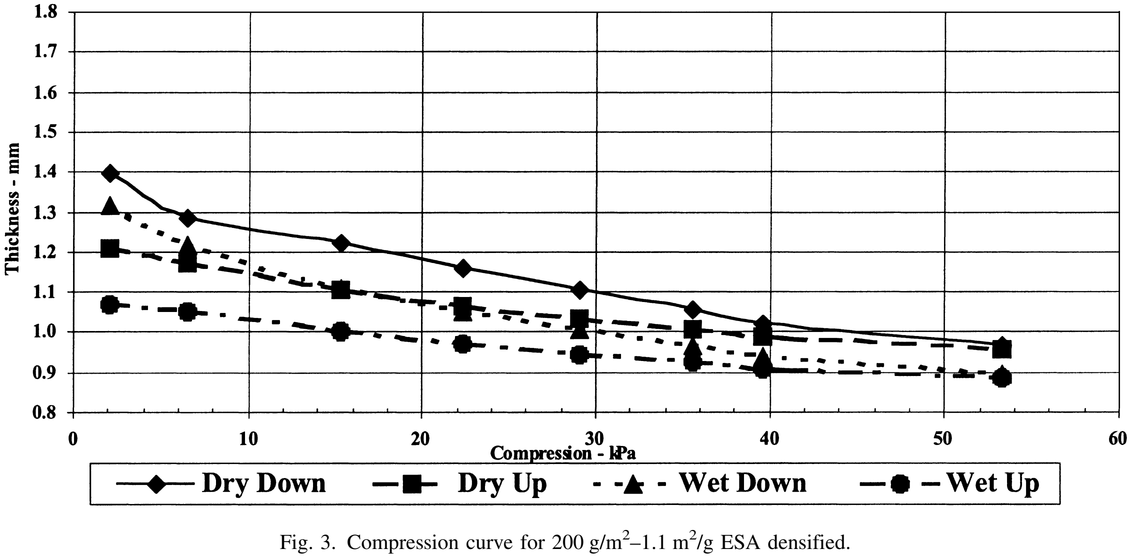

Fig. 3. Compression curve for 200 g/m^2–1.1 m^2/g ESA densified.

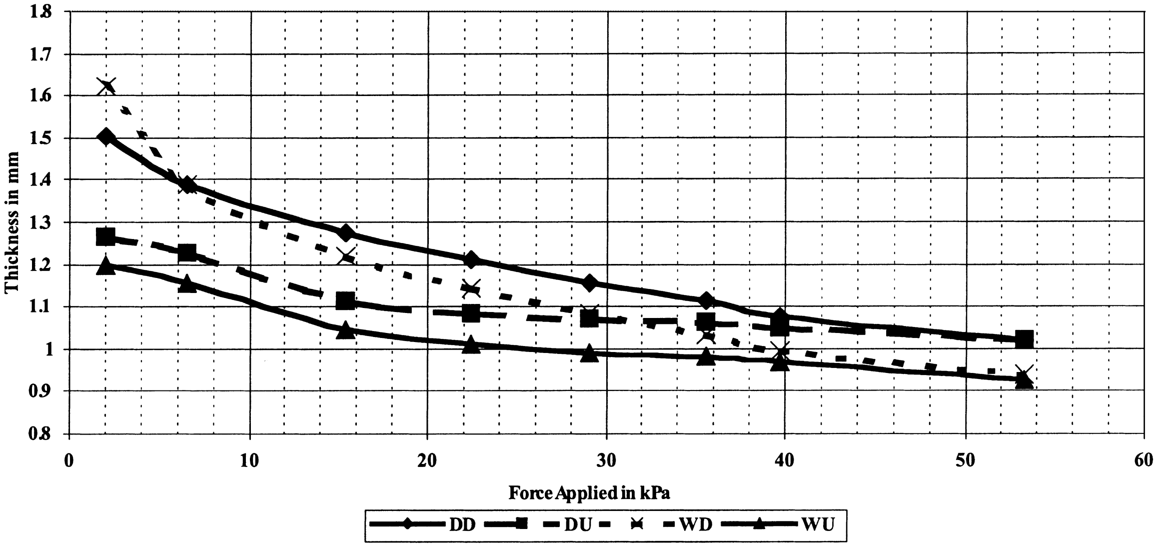

Fig. 4. Compression curve for 200 g/m^2, Hovosorb II.

An example of the data obtained using the CSIRO piston cell (Fig. 1) is given in Fig. 6. Fig. 6 shows the steady state behaviour of a range of different separator materials as tested by CSIRO for ALABC Project B-001.2 [14]. Note that these curves are somewhat different from the compression/recovery curves shown previously, as Figs. 2–5 were based on a single pass through the pressure range, whereas Fig. 6 shows the steady state behaviour. The data in Fig. 6 has also been normalised to 10 kPa, so that the greater the displacement of the thickness–pressure curve below the curve for the ceramic tile, the greater the separator compaction on wetting.

The ceramic tile exhibits the simplest behaviour because it is completely rigid. However, it is unsuitable for use as a battery separator material [14,23]. The pore size of currently available ceramic materials is too large, resulting in short circuits through the separator. Also, in preliminary experiments, the ceramic separator failed to inhibit positive active material shedding. In the starved electrolyte VRLA design, there were contact problems between the active mass and the separator, and it was also necessary to introduce a thin glass mat between the ceramic separator and the plates [23].

None of the separator materials used in the CSIRO study [14] proved to be superior to conventional AGM separators, or AGM separators containing some organic fibres, such as II-P15. However, further work is merited on materials such as the silica loaded glass mat (SLGM). The behaviour of this separator material is quite different from that of a conventional 100% microglass separator. It shows very little compaction on wetting and a relatively small change in thickness

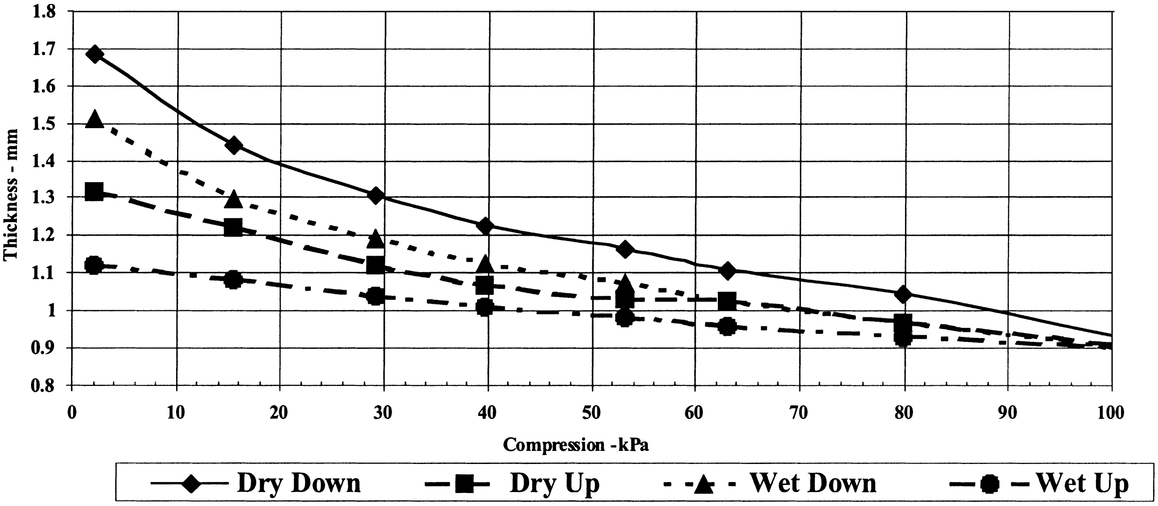

Fig. 5. Compression curve for 200 g/m^2–1.8 m^2/g.

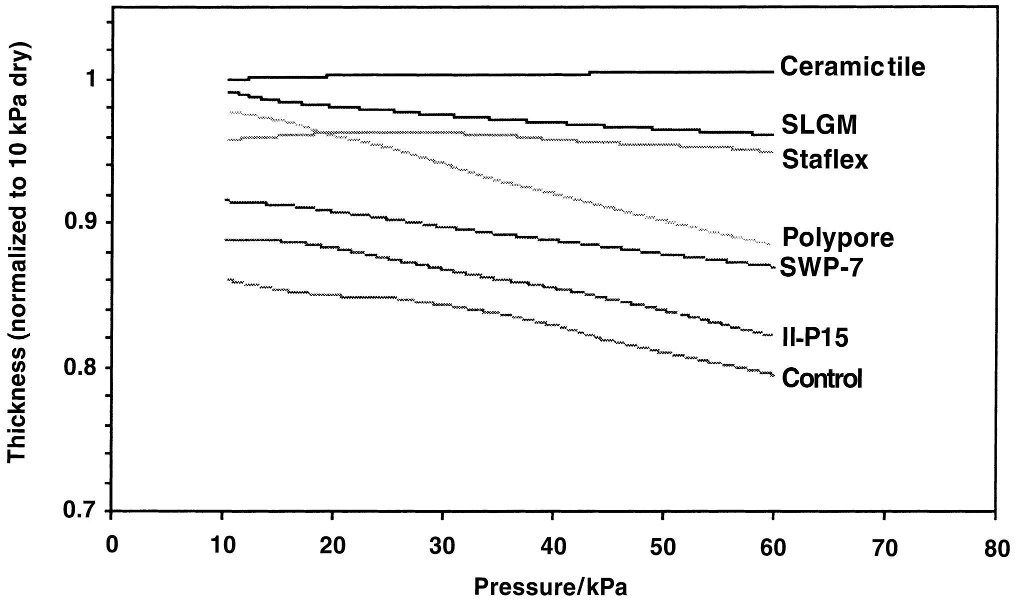

Fig. 6. Summary of thickness–pressure behaviour for candidate separator materials. Each line represents the steady-state behaviour for the acid-saturated material.

with increasing applied pressure. The Staflex separator also appeared to have an interesting thickness/pressure behaviour, but was let down by poor oxygen recombination.

Results from the European ALABC programme have been more encouraging. In this programme less compressible separators are being developed which are capable of withstanding high pressures without damage, and have also yielded encouraging cycle life data. In one of the projects the Daramic AJS separator is being tested. This separator is almost incompressible: the thickness remains almost constant at applied pressures up to 130 kPa. It has performed well both on initial performance tests and on life cycling [18]. Also of particular interest is one of the Amer-Sil separator variants that consisted of a high porosity microporous membrane between two layers of microfine glass. This also demonstrated an excellent performance and cycle life [17].

4. Influence of high plate-group pressures on the RBSM structure

If VRLA batteries are built in which the pressure applied to the plate-group via the separator is much higher than has been the case traditionally, then the effect of the high plate-group pressures on the structure of the separator needs to be considered. For example, it has been suggested that the high pressures may cause permanent crushing or damage/breakage of the fine fibres in AGM separators. However, a study by Hollingsworth and Vose has indicated that this should not be a major problem [15].

The experimental work reported by Hollingsworth and Vose [15] has demonstrated that RBSM separators can in fact maintain compression resilience at applied forces as high as 500 kPa. The observed reduction in tensile strength and increase in elongation during the compression test suggest that the matrix of the separator is changing as the force increases. The SEM study indicates that fibre displacement rather than fibre breakage is occurring, with fibres moving in and out of the focal plain, rotating, spreading out and even grouping together.

For standard Hovosorb separators, compression recoveries of over 92% have been observed. It may be possible to improve the tensile strength properties with modified separators (containing organic fibres). For example, Hovosorb II-P-15 maintains tensile strength across the range of applied forces.

This paper [15] only reported on the properties of separators in the dry state. Separators with a range of surface areas and grammages were tested, but the ratio of fine to coarse fibres in each separator was not reported. The compression tests were short term tests over a time period of 30 min. There may still be a question mark over the effect on fine glass fibres in the wet state of high compressive forces over a prolonged time period. However, the results are encouraging in indicating that the limitation on the maintenance of a high plate-group pressure within a VRLA battery is more likely to be due to the battery design and methods of assembly than the separator.

Separator manufacturers continue to work to improve the separator material so that the "spring" properties of the fibres are improved, reducing the tendency of the fibres to relax under a constant strain. As an example of this, a new 100% microglass material has been developed by Hollingsworth and Vose which can provide a much lower grammage at a given (BCI) thickness than a standard AGM: or alternatively a much thicker separator at a given grammage [16]. This new material is subjected to a higher compression level than the standard material. The BCI paper by G. Zguris [16] reports that compression tests on this separator saturated with sulphuric acid showed that after 1 week under compression, the new material retained three times the force of the standard material at the shimmed thickness.

5. Plate and separator tolerances

The accepted tolerances on plate thickness for the lead acid battery are quite wide compared with the very narrow, closely controlled tolerances widely accepted on other engineered components. Any variation in the cell group thickness caused by varying plate thickness is compensated for by the compressibility of the separator. However, the resultant variability in the compression of the separator will result in varying plate-group pressure and a possibly adverse effect on the cycle life of the battery. By way of example, the compression data in Fig. 5 has been used to calculate the influence of plate tolerances on the plate-group pressure for a 13-plate battery with 2.1 mm thick positive plates, 1.4 mm thick negative plates and an interplate spacing of 1.1 mm. The tolerance on plate thickness is assumed to be ±0.05 mm. If all the plates are at maximum thickness, the plate-group pressure will be ~85 kPa based on the dry separator, ~65 kPa based on the wet separator. If all the plates are at minimum thickness, the plate-group pressure will be ~60 kPa based on the dry separator, ~40 kPa based on the wet separator. This calculation shows that the influence of variation in plate thickness on the applied plate-group pressure can be quite significant.

Electric vehicle batteries and other large battery installations require a large number of cells to be connected in series (e.g. 100 cells for a nominally 200 V system). Inherent variability between cells can cause a number of problems including cell pack imbalance and incomplete charging resulting in a “walk down” in capacity of the battery. This is a particularly serious problem if the battery undergoes regular deep cycling duty. Even in automotive batteries, the likely move to 36 V batteries has highlighted the importance of product reliability and consistency. For example, if a particular application requires a battery pack with 156 cells in series, and the reliability of individual cells is 99.5%, then 50% of the battery packs will fail [25]. One of the key issues to be addressed in order to improve battery reliability is the tolerance on plate weight and thickness. This is an issue that the battery industry has to address anyway to retain existing markets and develop new markets. Tighter control of plate thickness will also enable the battery manufacturer to control separator compression/plate-group pressure, thereby extending battery life and improving reliability.

If less compressible separators are used — for example one of those mentioned earlier — this would also impact on the overall battery design. A less compressible separator will not compensate for variations in plate thickness, therefore it probably needs to be used in conjunction with some other means of controlling plate-group pressure, such as an additional internal or external compression device as mentioned later.

The latest pasting machines (e.g. orifice pasters) and continuous plate making techniques offer the possibility of significant improvements in plate weight and thickness tolerances, but further improvements may still be necessary. With the current technique of applying a paste of variable consistency to a grid, and “overpasting” the plate it remains very difficult to control the plate thickness to within very tight tolerances. With continuous plate making techniques the possibility may exist to pass the pasted plates between “planishing” rolls set at a preset thickness.

Separator thickness tolerances also need to be taken into account [26]. In the early days of AGM separators, the thickness variations could be as wide as 35%, and commonly in the ±10% range. Today, the variation has been reduced to ±5% typically: a big improvement, but still wide enough to cause significant variations in applied plate-group pressure.

6. Container design/construction/materials

The normal construction of containers formed by compression moulding is that the width/length of the cell compartment is less at the bottom of the container than it is at the top. This difference is termed “draft” and is necessary so that the battery case can be removed from the injection mould die after forming. This could have a significant influence on plate-group compression within the cell. It may be possible to compensate for this by introducing a “wedge” into the battery container. This approach was adopted by CSIRO in their development of a battery for the LR electric-hybrid bus (AMC 007) [20].

Battery container manufacturers such as Accuma are now starting to address the problem of container designs for VRLA batteries that are required to maintain high internal plate-group pressures and prevent relaxation of the compression of the separator [19]. The problem of container draft can be resolved by assembling single cells rather than monoblocs. For example, a motive power battery cell is already available with 3 mm thick walls in which the part is ejected from the mould utilising a 0° draft angle inside the cell. As well as ensuring uniform plate-group pressure, this design also maximises the acid volume within the cell. There is an additional advantage of using single cells rather than monoblocs. In a battery based on single cells it is easier to maintain a uniform temperature between the cells. High temperatures must be avoided because this may result in container distortion and loss of plate-group pressure.

It is also possible to design a battery case in which there are internal vertical, flexible ribs [19]. These ribs are designed to engage the element stack at an oblique angle to take advantage of their inherent flexibility. The ribs are able to fold out of the way as they are not connected to the case at the very bottom of the cell. The ribs provide a constant force to the element group to hold it in place. This container design is already available and in use for an automotive application. It may be possible to modify this design so that it has an application for VRLA batteries in order to control the internal plate-group pressure. Other design improvements include end rib patterns that are able to stiffen the end wall to resist the high internal pressures.

7. Plastic moulding materials

Thin walled polypropylene containers are widely used for automotive batteries, but are not suitable for most VRLA battery applications, which require anti-flame properties, stiffer side and end walls, and a carefully controlled venting system. Container materials for VRLA battery applications normally require a high flexural modulus to achieve stiffer end walls that will withstand higher internal battery pressures. ABS containers are normally used in this application. For example, a typical FR-ABS material has double the flexural modulus of a typical polypropylene material. [19]. For advanced VRLA deep cycle batteries in which very high internal plate-group pressures need to be maintained, other engineered plastics may need to be considered, that have even higher stiffness values.

8. Compression devices

Compressible separators will compensate for minor changes in plate thickness, although as shown earlier this may have a significant effect on the actual plate-group pressure. However, separators that are almost incompressible will probably need to be used in conjunction with some other means of maintaining plate-group pressure. A number of options could be considered for maintaining plate-group pressure within each battery cell. Two that have been tested by CSIRO in their ALABC projects, for example AMC-007 and AMC-009 [12,20] are given below.

1. *Compression plate 1 ("WP").* This has a "wave-like" structure and is made from polycarbonate or fibreglass. The polycarbonate plates tended to lose their spring-like properties over a long period, but the fibreglass composite material performed well (see Fig. 7).
2. *Compression plate 2 ("LS").* This has a coated, spring steel backing plate with a series of fingers. When compressed to a specified level, the plate provides a high level of support to the cell group. This option may not be suitable for large scale use in commercial batteries (see Fig. 8).

Two other possibilities have been mentioned in the literature, although they have not been subjected to any detailed testing. One is a flexible hydrostatic pressure-bag. This exerts a constant compression on the cell plate-group. The pressure inside the bag can be adjusted by introducing or removing compressed air [20]. The other is an elastic compression device. This envelopes the whole cell group and is like a thick, porous stocking. This may be the most convenient to implement in production, and because the compression is maintained independent of the battery case or lid, a strong battery case may not be needed [20].

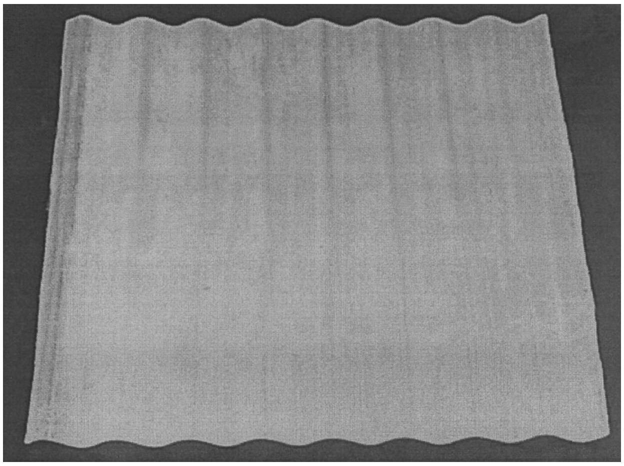

Fig. 7. CSIRO WP compression plate.

A more practical option may be to redesign the battery container, so that for example it contains flexible, vertical ribs, as mentioned in Section 6 above.

9. Cell assembly/formation

A number of problems need to be resolved during the assembly process to ensure that cell groups are assembled with a controlled, high plate-group pressure.

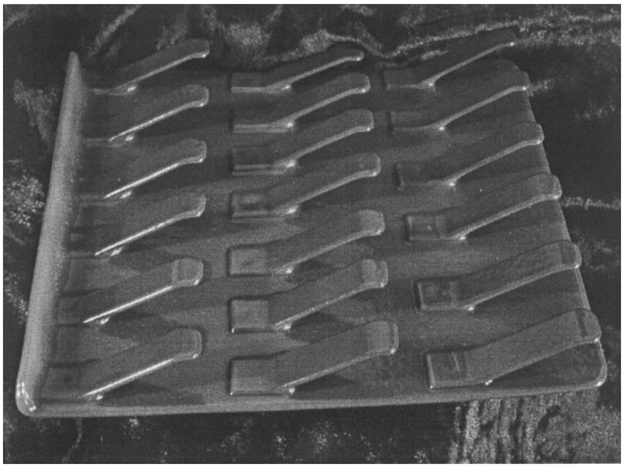

Fig. 8. CSIRO LS compression plate.

The plate-group pressure needs to be set, controlled and monitored immediately prior to insertion into the cell container. The pressure applied to the plate-group immediately prior to assembly may need to be higher than in the actual cell container. This may have implications for possible damage or irreversible crushing of the separator material. The maximum pressure of any assembly process will be controlled by the ability to carry out one of the following:

1. Slide the compressed cell into the container while maintaining it under pressure.
2. Force the uncompressed cell through a tapered "compression shoe" into the container.
3. Force an uncompressed cell into a tapered container (which would yield uneven pressure vertically in the cell).
4. "Overcompress" the cell in a clamping device to make it sufficiently smaller than the container opening in order to be able to extract the clamping means from the cell space after insertion.

All of this must be done at high speed without damaging the cell or losing alignment.

The high internal plate-group pressures and compression of the separator may result in additional problems in filling and formation of the cells/batteries, particularly with high energy thin plate battery designs [21]. The possibility of pre-wetting and/or pre-compression of the separator needs to be considered. Significant re-design of the battery assembly process would be needed to achieve this.

Assembly techniques are already available which may solve some of the battery assembly problems mentioned above. One example is the Sealed Energy Systems (SES) technology assembly method and apparatus mentioned in US Patents 5,344,466 and 5,407, 450 (EP 0510083) [22]. The application of this technology to batteries containing AGM separators involves:

- precise and automatic severing of AGM separators from coiled stock,
- automatic alignment of the plates, lugs, and separators within each cell,
- automatic removal of the aligned cell stack from the assembly zone,
- precise compression of each cell to any desired degree,
- automatic insertion of the compressed cell into the battery container to a precise depth with lugs properly positioned and aligned,
- automatic removal of the filled containers from the assembly machine, and
- automatic transport of the container to downstream assembly operations.

Of particular interest in this process is the ability to apply controlled compression to the cell group and automatically insert the compressed cell into the case. Combining the SES technology with automated downstream processing permits manufacturers of VRLA batteries to fully automate production and achieve maximum production efficiency and product consistency.

For reasons of cost and convenience, many VRLA battery manufacturers prefer to assemble the batteries with unformed plates and use container formation, rather than assemble from dry-charged plates. Problems with container formation may be aggravated if the cell groups are assembled with a very high stack pressure [24]. When the separator is compressed it reduces the pore size significantly and also reduces the space available for electrolyte between the plates. This adversely affects the wicking properties of the electrolyte. During the filling process, the separator tends to hold the electrolyte fairly strongly due to capillary forces, and the positive and negative plate-groups are also drawing electrolyte away from the separator. The reaction of the electrolyte with the plate active materials is exothermic, so that as the liquid penetrates into the plate stack it becomes more dilute and is getting hotter. In the extreme case, lead sulphate from the plates dissolves into the dilute electrolyte, releasing soluble Pb^{2+} ions into the separator, and resulting in the formation of lead dendrites and/or hydration shorts. This problem is aggravated if the plates are relatively tall and/or have small interplate spacing, and if the separator is under high compression.

Another potential problem with the filling process is that individual cells after filling may have dry areas in which little or no liquid is present. These dry areas will slowly become wetted during and after formation, but there is a risk of massive grid corrosion due to the high temperatures and alkaline conditions prior to and during formation [24].

Where it is felt particularly important to have a very accurate control of plate-group pressure, an additional problem arises with container formation. The volume of the battery plates changes significantly during the formation process, resulting in changes in the plate-group pressure. All these factors mentioned above may cause the battery manufacturer to re-consider the use of dry-charged plates rather than unformed plates in the assembly of VRLA batteries that are intended for long life under deep cycle duty.

The problem of changes in plate volume during formation (and in subsequent cycling) may be reduced if some additional form of internal or external cell constraint is used.

10. Cylindrical cells

The discussion so far has concentrated on prismatic cell construction. However, many VRLA cells are of cylindrical construction, particularly for high rate or automotive applications. From the viewpoint of maintaining a high, uniform internal plate-group pressure the cylindrical construction does have certain advantages. Nevertheless, the problem of separator contraction on wetting, and reduced resilience of the separator during cycling still remains. It may be possible to incorporate an idea from lithium cell design into cylindrical VRLA cells, in order to maintain internal plate-group pressure throughout the life of the battery. Some cylindrical lithium batteries contain an internal spring that expands as the lithium at the anode is depleted, to prevent any gap occurring. It is possible that a modification of this idea could be used for cylindrical VRLA cells. If a suitable spring could be found, this could be placed at the centre of the cell to maintain a controlled pressure against the plate-group and compensate for any changes in plate-group pressure caused by relaxation of the separator during the life of the battery.

11. Conclusions

For advanced VRLA batteries it will be necessary to modify battery design and assembly techniques so that high plate-group pressures can be set and maintained. This applies whether the separators used are conventional AGM separators or alternative, less compressible separators. Advanced separator designs may enable higher plate-group pressures to be achieved than with AGM separators. Therefore, the overall battery design and assembly techniques will need to take into account the compression or thickness versus pressure characteristics of the separator. Different separators may require changes to the battery design and assembly processes so that the plate-group pressure is set at the optimum value to match the properties of the separator being used.

Novel battery assembly and formation techniques need to be considered. For example, it may be feasible to use separators that have been pre-compressed and possibly also pre-wetted. Serious consideration has to be given to whether dry charged plates are used instead of unformed plates and container formation.

Battery container manufacturers need to be pro-actively involved with battery manufacturers in developing new battery case designs, which assist in maintaining the required plate-group pressure throughout the life of the battery.

Finally, the possible adverse impact on the negative plates of very high plate-group pressures should not be forgotten. This will undoubtedly be addressed in future research. However, it should be practical to resolve this problem by redesigning the negative grid so that the grid frame rather than the negative active material supports the pressure.

Acknowledgements

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