

Advances in recombinant battery separator mat (RBSM) separators for lead-acid batteries—a review

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Abstract

Microglass separators have been used in lead-acid batteries for more than 20 years with excellent results. This type of separator (known as recombinant battery separator mat (RBSM)) has allowed valve-regulated lead-acid (VRLA) battery technology to become a commercial reality. When the concept of the VRLA battery was developed, the requirements of the RBSM separator were not fully known nor appreciated. In many cases, the direction charted for the separator has not been the most beneficial path to follow for separator performance and battery life. In some cases, such as the density of the separator media, experience has shown that the most correct path (low density) does not give rise to long battery life. As VRLA battery technology matures, greater pressure on cost and quality has arisen, especially with the proposed transition to 42 V automotive applications. This paper reviews some of the advances and changes in the RBSM separator made over the last 20 years, and provides some thoughts on future directions for this essential component of the VRLA battery. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Over the past few years, the valve-regulated lead-acid (VRLA) battery has been intensely studied. This work has resulted in advances in both the performance and the quality of VRLA batteries. The advent of the 36/42 V battery, however, is now giving rise to new requirements. Within a very short time, 42 V cars will take to the roads. In 6–9 years, it is probable that all new cars will be equipped with the system. This translates into a global original equipment market of around 12–15 million batteries. Lithium ion and nickel–metal–hydride chemistries, although more costly, threaten the hitherto dominance of lead-acid in automotive battery markets. For lead-acid batteries to remain the chemistry of first choice, improvements in quality, consistency and technology must be realised and deployed. These challenges are real and some manufacturers are already tackling them [1]. The 36/42 V battery application must not be viewed as the same product as the standard 12 V automotive battery. The new version will require more reliability and greater quality. The same attributes must also be sought in the components from which the batteries are made.

The separator has been shown to be an important contributor to the overall function of the VRLA battery and can be considered as a ‘third electrode’. Manufacturers are realising that quality, purity, uniformity and technology of the separator are more important factors than absolute cost. As separator technology matures, the fabrication process of VRLAs becomes faster and this enables manufacturing costs to be more in line with those of flooded-electrolyte batteries. Although, the basic cost is higher, a premium separator may result in overall cost reduction of the finished battery since such a separator may permit the use of higher speed equipment in battery production. Similar demands are placed on the other battery components. For example, VRLA batteries require lead of higher purity to minimise gassing, as well as stronger and better-engineered battery cases to sustain higher compression forces. The assembled battery costs should be the major concern, not the component costs.

With many of the high-speed wrapping machines, the separators can suffer greater surface abrasion than that experienced with slower machines or in hand assembly. If the correct separator is not selected, then the advantages of high-speed processes may not be fully realised. A separator that is suitable for a hand-wrapping operation may not be a suitable for an automatic operation if the production line cannot operate at maximum speed. Therefore, when changing a process, the properties of the existing separator must

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be examined to determine whether it has appropriate physical characteristics to run on high-speed equipment so that improved battery production is achieved.

Fast-production problems can be solved with technology. For example, the separator manufacturer can supply a tougher, more abrasion-resistant separator. In addition, increasing the bulk density will enhance surface toughness. This is accomplished by achieving better fibre–fibre contact of the microglass fibre, and by having fewer fibres protruding from the surface of the separator which otherwise would ‘catch’ during the manufacturing process. Moving from a 100% microglass separator to a hybrid (composite) material would also provide improved productivity for the battery manufacturer. Hybrid separators have gained in popularity due to their higher puncture resistance and burst strength when wet or dry. Such separators also have greater utility in thin-plate, expanded metal, or strip designs of battery.

2. Separator density

In the early days of VRLA batteries, the separator with the highest porosity was requested and used. High porosity means a low-density (high loft) separator. Density (gsm mm^{-1}) is defined as

$$\text{density} = \frac{\text{grammage (gsm)}}{\text{thickness (mm at 10 kPa)}} \quad (1)$$

where $\text{gsm}: \text{g m}^{-2}$.

The goal is for the separator to provide as much free space as possible for the sulphuric acid in the cell. In many cases, these very low densities, which were specified by the battery manufacturer, were at the upper limits of the wet-laid manufacturing process. This did not allow the separator manufacturer to control grammage and thickness to narrow limits. Often, wide ranges in weight tolerance (e.g. $\pm 20\%$) were needed to allow the manufacturer to meet the requirement for a separator of extremely low density. The weight was used as a control tool to achieve the desired thickness. Scrutiny of the historical specifications that were used in the early days shows grammage variations of 10–20% from the targeted weight of the separator. At that time, thickness was considered to be the primary variable, and weight was used to meet the high-loft requirements of separators.

Today’s manufacturing processes provide much tighter specifications than were possible in the past. This adds to the cost of the separator. Larger tolerances in weight and thickness mean that the separator manufacturer has to dispose of less material when adopting a specific grade of separator or switching to an alternative one.

There is still considerable debate on which property, viz. thickness or grammage, is essential when considering a separator. If all past and current data are examined, then the primary requirement for battery separators is grammage—not thickness—as this is the more important variable in determining good battery performance. Thickness is a

secondary, but an important, variable and provides the manufacturer with a useful means for checking that the production process is under good control and similar to past performance. This is not to say that a manufacturer should not have narrow limits on thickness, rather that thickness should not be the dominant variable.

The thickness is specified at a certain pressure, which varies from country to country. It would be best for the industry if the method for thickness measurement recommended by the Battery Council International (BCI) was adopted world-wide [2]. The BCI standard, which was approved by a consensus of major battery companies, would allow comparison of global designs. The design engineer would then use thickness and compression to insert the separator and plates into the battery case. Typically, the compression should be between 20 and 35%. Many designs are less than 20%, however, due to either cost or the fact that the plate group cannot be inserted into the jar. In many cases, the draft of the case can provide a change in compression of 10% from the top to the bottom of a plate. High compression can also lead to different compression levels within the battery. As the individual cells are inserted, additional force may be exerted on the outside cells do to bulging of the partition walls between cells. This can lead to leaks or different charge–discharge characteristics amongst the cells due to different plate-group forces within the battery.

After assembly with the plates and insertion into the case, acid is introduced into the separator. This results in a modulus change which, typically, yields 40–60% less force than with the dry separator. Thus, thickness is a secondary means to measure the true requirement of the separator within the battery, i.e. the wet-force exerted by the separator on the plates. Many studies by Hollingsworth and Vose and by CSIRO have confirmed that separator weight (grammage) is the principal physical parameter that controls the wet force in the cell. It should be pointed out, however, that changes in fibre composition would also have a large impact on the wet force of the separator inside the battery. For a given grammage or composition of separator, the manufacturing process (equipment and manufacturing instructions) can also have great influence on the resulting wet force inside a battery. Changes in fibre composition and the manufacturing process can result in separators with the same surface area having substantially greater wet compressive force. An example of how a change in the manufacturing process can generate much higher forces for a given fibre surface area is shown in Fig. 1. The curves show that for materials of the same specific surface area and thickness (~ 1.45 mm), the new-technology material retains a greater wet force (47 kPa) than the standard separator (18 kPa).

Since grammage is the controlling factor in determining battery performance and there is limited space (i.e. ‘thickness’) between the plates inside the cell, increased grammage can be best obtained by increasing the separator density. Both the grammage and the thickness of the product can be raised to provide a higher grammage amongst the

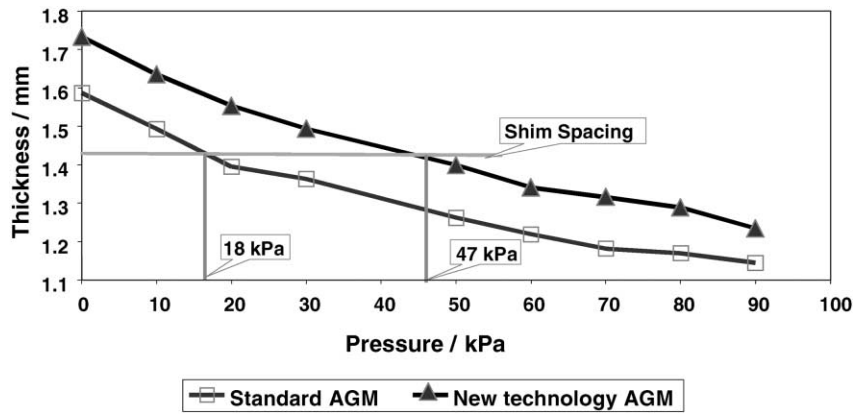


Fig. 1. FH block curve showing better compression properties with improved AGM. (The FH block test, developed by Hollingsworth and Vose, uses a low-cost assembly to mimic the behaviour of the separator force response inside a battery and to provide a numerical value of the forces retained.)

plates. Usually, this leads to serious battery-assembly problems, especially with group insertion and acid filling. The higher grammage and thickness increases the dry assembly force. The insertion operation then becomes almost impossible to perform. Also, difficulties may arise with the cast-on-strap operation. In addition, as consecutive cells are introduced into the jar, deformation of the interpartition walls may occur to such an extent that the cover and the case will not seal correctly. These problems increase costs to the manufacturer due to more rejections after inspection. By keeping the thickness constant and increasing the density of the separator, the same wet force inside the battery can be obtained with fewer manufacturing difficulties and reduced cost. This will also result in less deformation of the case during assembly, and thus will decrease any future memory effects shown by the case during the life of the battery. This is especially true in warm environments.

The wet force for a given composition of fibres will be dictated by the incoming density of the separator. The higher the density of the separator, the smaller is the decrease in the separator force from dry to wet after assembly. The key to

good battery cycle-life is the wet force, i.e. after filling the battery with acid. Many early separators had densities in the 130–140 p range ($p = \text{gsm mm}^{-1}$ of thickness at 10 kPa). Under high-compression loads, these high-porosity (low density) separators undergo a 40–60% decrease in force when wetted with acid. On increasing the density of the separator to levels such as 200 p, the change from dry to wet does not result in a significant loss of force to the plates. One of the goals for an ideal separator is to supply the same force wet as dry. This relationship is shown in Fig. 2 for a very high fine-fibre, all-glass separator (200 p). The plots show that the separator has equal or better compression characteristics when wet than when completely dry. That is, for a given thickness, the material exerts greater force in the wet state. One word of caution in understanding the data in Fig. 2: the wet curve has seven times its dry weight and the high density material would have a greater percentage of its void volume filled with acid than the low density material. The wet force exerted by a separator is dependent on the degree of saturation of the separator. A fully saturated separator can apply a higher wet force. As the saturation level decreases,

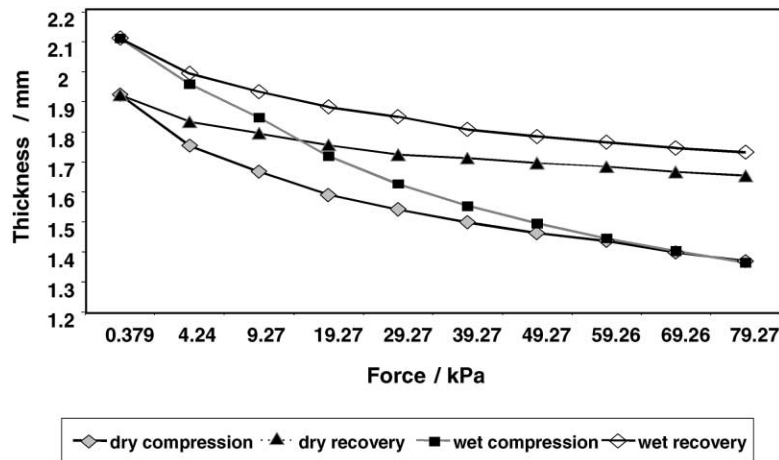


Fig. 2. BCI compression: all-glass separator at 200 p.

the wet force also decreases until a minimum level is reached. The impact of higher separator compression is analogous to the increase in battery life that a manufacturer obtains by increasing the density of the positive active-material.

3. Separator uniformity

An issue facing the VRLA battery is its reliability, especially in long strings. The separator plays an important role in the repeatability of the performance of each cell. The uniformity of the grammage is the important factor. In a 12 V battery, the six cells must be uniformly matched. With the advent of the 36/42 V battery, 18 cells will similarly have to be matched. As already mentioned, the key parameters of the separator are the force it exerts in each cell and its level of saturation throughout the battery. Variations in grammage are also critical, especially when using precision filling equipment. If an $\pm 8\%$ variance is allowed, then, in total, a 16% variability could occur. If an 8% variance in thickness is also permitted, then a huge incoming glass bulk density is allowed. For example, a 300 gsm separator at a target thickness of 2.13 mm would result in a density between 120 and 165 p (note, density = grammage/thickness). This is a swing in density from low to high of 37.5%.

Let us assume that the target separator is 300 gsm. With an 8% variance, this allows for a maximum swing in weight of 48 gsm. Between the plates, the separator should hold seven to eight times its own weight in acid. If a manufacturer requires a certain saturation level, then a difference of 384 cm³ of acid (at eight times) would be required from the low end of the density range to the high end. Also, with precision filling (i.e. cells are filled with a precise volume of acid), a separator at the low end of the specification would be fully saturated but would be below the desired saturation level (typically 95%) at the high end. Thus, the rate of oxygen recombination would change from slow (low weight) to fast (high weight). Within a battery, however, the inter-plate spacing does tend to moderate this effect. For a variation in weight of 48 g for an area of separator, the change in the glass volume, at a density of 2.5 g cm⁻³, is only 19 cm³. Therefore, the void volume of the separator will only change by 19 cm³ in an area, or for a 200 mm × 250 mm plate the difference will be about 1 cm³ between each plate. The total change in allowed void volume would be 12 cm³ (based on target weight). This acid difference can result in a significant variation in initial capacity, especially at low rates.

4. Glass composition

Another area of concern for battery manufacturers is the composition of the glass. The manufacturer must provide a separator for which the surface area, the fibre blend ratio and

the glass composition are all constant. These parameters are critical to providing uniform and consistent cell performance. It is tempting for a manufacturer to modify the glass composition due to a lower spot price of the raw material. This can cause problems, however, since the glass composition usually differs between manufacturers. There can also be differences in both the targeted surface area and the diameter of the fibres. Moreover, different manufacturing processes can result in fibres with unique physical attributes. For example, the patented CAT[®] process [3] of the Evanite Fibre Corporation produces a fibre that gives a separator increase in loft and elongation. This can provide a superior compression force inside the battery.

The glass chemistry of microglass fibres plays a significant role in battery performance since all such fibres will leach certain beneficial or detrimental elements into the battery acid. Usually, the solubility in acid differs with the silica content; in general, higher silica loadings result in lower solubility. Depending on the quality of the raw materials, different elements could be leached into the acid. The release of large quantities would cause the battery to experience a marked decay in voltage on stand. More sodium or more calcium could be leached and this may change the negative- or positive-plate potential of the cell. Although all the fibres may be suitable in a battery, modifying the chemistry could result in the battery floating at a lower or a higher voltage. If the manufacturer is not aware of these changes, mixing batteries with different separator glass chemistry could result in a battery string that has individual cells wanting to float at different voltages.

5. Concluding remarks

Tremendous improvement has been made in separator technology since the introduction of VRLA batteries by the Gates Company. This is especially true in the last few years. The challenges ahead for the lead-acid industry are great, especially with the transition of the automotive battery to a 36/42 V standard. Alternative battery chemistries are already threatening the automotive markets for lead-acid batteries. The industry must highlight the advances made in quality, uniformity and life of VRLA batteries. Cost should be a secondary consideration with respect to quality, otherwise nickel–metal–hydride or lithium ion batteries, although many times more expensive, will become the units of choice for the car manufacturer.

The selection of battery components must be considered in terms of quality and uniformity. For separators, there is a variety of choice and careful consideration must be given to the uniformity and quality of the manufacture, and to the application of the separator. Today, manufacturers can no longer accept the large tolerances of the past, where thickness and surface area may have been the only considerations. With present-day technology, separator hybrids offer improvements such as greater puncture strength and

improved battery cycle-life. With the addition of special additives/binders to the separator, these benefits can be realised over the standard 100% microglass separator.

Acknowledgements

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