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Absorptive glass-mat separators for valve-regulated lead/acid batteries — thoughts on compression

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Abstract

In the past few years, valve-regulated lead/acid (VRLA) batteries have come under increased study. Their use has become more widespread, yet their expected life has not always been realized. This paper discusses some thoughts relating to the property of compression of the microglass separator and the impact of compression on VRLA battery life. Ideas are suggested for the design engineer to consider in selecting a battery separator. Additionally, several long-term battery separator tests are described. As more is learned about the complex interactions that are taking place in the VRLA recombination process, a greater appreciation is being given to the role of the separator. Today, battery designers can help improve expected battery performance by incorporating the latest information regarding battery separators, compression factors, and impact on life. © 1997 Elsevier Science S.A.

Keywords: Microglass; Valve-regulated lead/acid batteries; Separators; Compression

1. Introduction

Microglass separator has been used in batteries since the inception of valve-regulated lead/acid (VRLA) technology. Based on recent research, there is increasing recognition that the separator plays a critical role in battery performance. This research supports the hypothesis that compression exerted by the separator can help diminish premature capacity loss (PCL). For example, some companies have suggested that the separator compression delays this failure mechanism in float applications, and ALABC studies have shown that designs with higher compression improve the cycle life of batteries. The separator in a VRLA battery is not an inactive spacer/barrier, as in a flooded lead/acid cell.

The attributes of the VRLA technology enabled these batteries to provide a very useful life in many applications. Nevertheless, the jury is still out with respect to the primary failure mode of VRLA batteries. In many occurrences, grid corrosion is not seen, while in many situations, dry-out/sulfation of the negative electrode has been observed. Garche et al. [1], made the following observation, see Fig. 1: 'the VRLA–AGM showed a rapid loss in capacity during the first year. The reason for this capacity loss was mainly the high sulfation of the bottom part, especially of the negative electrode, as a consequence of the acid stratification'.

This paper offers additional insights into mechanisms that are suspected to affect battery life and the role that the separator can play to improve performance.

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2. Background

The first commercial separator used in a VRLA battery was a microglass paper that was designed for a filter application. Through the twenty plus years of this technology, the microglass separator has gone through many changes. In many cases, the changes were driven more by cost considerations than by quality concerns. In general, a 100% pure microglass separator is still the material of choice.

In a microglass separator, the glass fiber has a zero contact angle with the sulfuric acid. This allows for excellent long-term wettability. The microglass is inherently durable in the acid environment. The fine fiber structure provides good resiliency to provide sustained pressure against the plates. Microglass separator having a porosity in the 90–95% range is also very conformable. This allows the separator to adapt to imperfections in the plate surface. A hard rigid material would have difficulty conforming to the plate, therefore, not wetting the total plate, or it can fracture. Another important attribute of microglass separators is the fact that the microglass fiber is inorganic, thus providing high-temperature stability. The microglass fiber structure will not melt in a thermal runaway situation. This can happen with all-organic separators manufactured with low-temperature polymers.

Recent studies have shown that higher levels of fine fiber and higher separator compression provide improved cycle performance in VRLA batteries. To understand the influence of fine fiber, it is useful to look at the number of fibers that are in the separator per unit weight of fiber. To give some idea of the number of fibers that are involved and how this number changes with fiber diameter, the following data are taken from a published report. For a 2 g sample of fine fiber (diameter of 0.8 μm), there are about 5.6 billion fibers present. This assumes a 0.3 mm length. A coarse fiber (diameter of 3.5 μm) would have only 28 million fibers. Remember this is for only a 2 g sample.

3. Critical aspects of separators

The grammage, thickness, compression resistance, and density of the separator are critical design criteria. Recent studies have reported improved performance by increasing the amount of microglass separator between the plates. ALABC and individual company studies have shown that higher design compression and separators with higher fine fiber result in batteries with better cycle life. Although many of these studies have focused on cycle applications [2], float applications should yield similar results. This is supported by the work of Nakamura [3].

In the past, a battery separator was selected primarily on the grounds of cost. Today, however, manufacturers are focusing on improved battery longevity in addition to maintaining a competitive cost. Use of separators that have higher density or are semi-compressed (to provide additional compressive force within the cell) can help achieve these objectives.

The glass microfibers in battery separators essentially act like springs between the battery plates. Additional glass fibers (springs) can be added in one of two ways: (i) increase the designed compression, and (ii) use a separator with a higher density (lower porosity, i.e., semi-precompressed). Separators with higher glass density provide added glass-fiber springs between the plates while decreasing problems of assembling a cell using a high compression design.

Another trend in battery design is the use of precompressed separators, as evidenced by the growing list of precompressed patents [4–7]. A precompressed separator is a separator that has been compressed outside the jar. After the cell is assembled and the acid is added, the separator expands and, thereby, provides the designed compressive force inside the cell. The precompressed separator can also allow the manufacturer to add additional glass between the plates without excess bulging of the case. The use of a semi-precompressed separators is not new. Examples of semi-precompressed separators were cited by the author in a MABAT 1991 paper [8].

4. Compression

In designing a battery, a certain compression factor is typically selected. Achieving this selected compression factor must take into account many factors. One such factor is the consistency of the battery separator. Today, separators are supplied with tighter tolerances for thickness and grammage to accommodate some of the changes that occur after cell assembly and acid addition. Early separators were specified with thickness variations as wide as 35%, and commonly in the $\pm 10\%$ range. With a design of 15% compression and a total range of separator thickness variability of up to 35%, it can be seen that some of the earlier batteries may have not been under sufficient compression. This situation has improved. Today, some manufacturers are producing battery separator to a $\pm 5\%$ variability in thickness.

Another key factor in achieving a certain battery compression design is the separator thickness. The compression factor is based on a thickness value using a specified measurement protocol. Over the years, many different protocols have been developed utilizing different pressure and different loads. Therefore, the compression value cited must be viewed not only in terms of the separator fiber composition but also in terms of the method used to measure the compression.

The problem of different protocols, although better today, is still a problem. It is interesting that this problem was noted sometime ago, in 1987, by Fujita [9]. This author made the following comments: 'A special mention must be made concerning the method of measuring the thickness of separators. Several methods (or instruments) are available at present. Normally the separator is placed between the plates of the thickness-testing instrument under 15–25% compression above the stage of free compression. Since results depend, however, on the size of the anvil area, pressure, dwell time, speed of anvil drop, etc., it is extremely important that a standard for the test method be developed. In the meantime, customers specify a thickness and its method of measurement.'

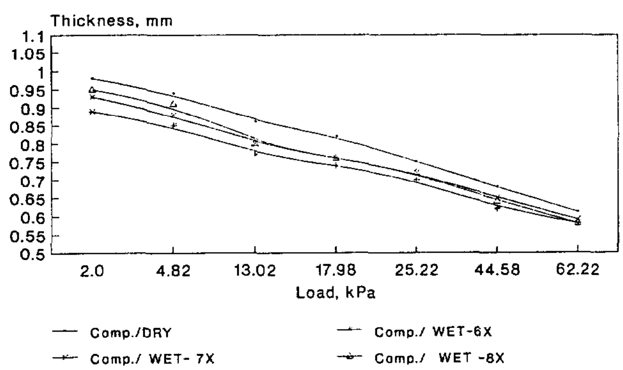

Fig. 1. Compression (BCI test) of microglass separator (grammage = 140 g m^{-2}; surface area 1.3 m^2 g^{-1}) in dry and wet (1.286 sp. gr. H_2SO_4) skates.

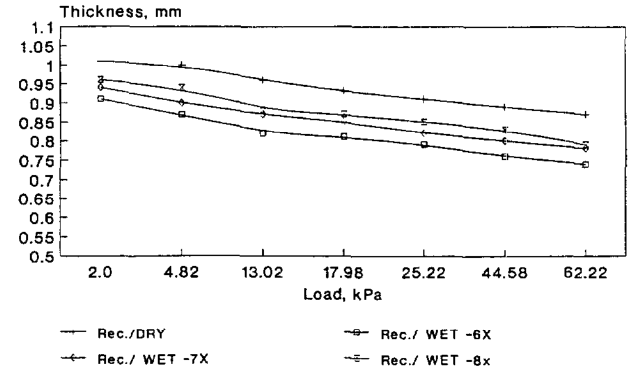

Fig. 2. Recovery of separator after being compressed, see Fig. 1.

The date of this observation reflects how slow the industry moves, sometimes, even on important issues. Multiple testing protocols still exist today.

Through a consensus process, Battery Council International has developed a thickness test protocol using a 29 mm anvil and a 10.34 kPa load. The Japanese Industrial Standards (JIS) specifies a 20 kPa load with a 10 cm × 10 cm sample size and a stack of ten pieces [10]. In the past, thickness may have been determined with various anvils and different loading, from 2 to 50 kPa. In some cases, due to narrow slit width on the received separator, a 20 kPa load is obtained with only a 29 mm anvil (instead of the sample size required by JIS). This results in different values for the reported thickness, and can be significant, depending on the grade.

Compression can be determined by using the Battery Council International test [11]. This test measures the thickness of the separator under various loads. The thickness is obtained both under these loads and after the loads are removed. The latter is called compression-recovery. Both values are then plotted. Figs. 1 and 2 are curves obtained based on this test method. These curves are for a microglass separator at 140 g m^{-2} and with a surface area 1.3 m^2 g^{-1}. Fig. 1 reports the values obtained during compression, while Fig. 2 reflects the values obtained after the load is removed (recovery). These graphs are for values obtained on a dry and then acid-saturated separator at different levels. The amount of sulfuric acid added was chosen to represent typical saturation levels inside a battery. The data show that partial saturation changes the thickness of the separator at a given load and that the level of saturation will modify this curve.

One problem with this test is that it only defines the compressive force based on a short time-span. A low-cost test protocol is needed to understand better the change in separator thickness over time while under load in an acid condition. The acid condition is important, since the separator thickness will be different whether the material is dry or saturated.

This change in compressive force between the dry and acid-saturated separator condition is one reason that relaxation of the battery case can sometimes be observed when acid is added into the battery. The compression remaining inside the battery, after the acid is added, is the critical factor. The separator could lose contact with the plate if this phenomena is not considered. This lack of plate-to-separator contact may develop during the battery life as the battery dries out. The data in Figs. 1 and 2 support such a result. The loss of contact is especially significant if the design compression does not account for the saturated recovery curve of the glass separator at lower saturation levels. Supporting evidence for this effect has been presented by Culpin [12] who discussed the relationship of a microglass separator's thickness to the degree of saturation in the separator.

The correlation between separator thickness and saturation level is of great importance since VRLA batteries dry out. Dry-out can occur from plastic jar permeability, corrosion of the lead, and from the valves. The design release-pressure of the valves may be too low and, thereby, allow the valve to open unnecessarily and vent gases. The valve may stick in an open position and cause the negative electrode to sulfate from the oxygen entering from the outside air.

5. Long-term compression tests

5.1. Retention of thickness during saturation

A standard wicking column test can be used to understand better the thickness retention of a microglass separator after it has been compressed and then re-wetted.

The separator material is compressed and a fluid is allowed to wick up the column while maintaining compression. Usually, water is used for safety reasons and the test is conducted over a 24 h period. After the column is disassembled, thickness measurements are obtained on both the wet test piece and after drying it.

Test results suggest thickness changes in the 4–10% range. The variation is dependent on the amount of compression and the amount of fluid that has been imbibed by the wick column. Since the separator in a battery will be fully wet, the values obtained in the first few inches of the test piece should be the main concern. Studies indicate that the separator displays the greatest change from the original thickness at the higher saturation levels. Experiments also show that lower compression factors produced proportionally smaller thickness losses [13].

One interesting factor to consider is the change in the surface tension of the acid over time. During this 24 h wick test, the surface tension in the water reservoir used for the test changed from an initial value of 73 to 69 dyne cm^{-1}. Meanwhile, the fluid squeezed from the separator had a surface tension of only 51 dyne cm^{-1}. This is a rather significant change and, perhaps, an important attribute.

It should be remembered that as plates are discharged and charged, the plates will expand and contract. This causes the separator to experience compression and then relaxation.

5.2. *Instron®* long-term compression test

An Instron tensile machine has been used to investigate the force being exerted on the separator during long-term compression. The force data are collected on a computer for three days. The materials were tested both dry and with a sulfuric acid saturation level equivalent to 7 times the specimen dry weight. The saturated materials were enclosed in a plastic bag to seal in the acid. To improve the

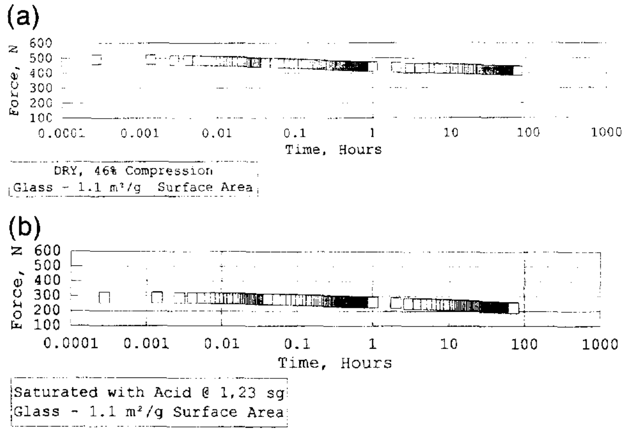

Fig. 3. Compressive force vs. time for (a) dry and (b) wet microglass separator.

accuracy of measurement, the data were obtained using a stack of ten pieces; each piece cut to 10 cm × 10 cm square. The stack was compressed to give a 46% compression, based on BCI thickness. Fig. 3(a) and (b) gives curves that compare thickness measurements of the test stacks over time for dry and acid-saturated samples, respectively. A standard glass separator of 1.1 $m^2\ g^{-1}$ was utilized. The force recorded with the saturated glass material was about 60% of the force recorded with the dry test. At the end of three days, the wet and dry curves displayed the same type of slope (curve). The change over the three days was about a 20% reduction in the initial force.

This type of measurement can capture much useful data. The drawback is that an expensive tension machine must be dedicated for this purpose for the time of the test.

5.3. Long-term JIS thickness change

A JIS thickness tester has also been used to monitor the change in thickness under a constant load over a period of time. The results of testing acid-saturated materials for a

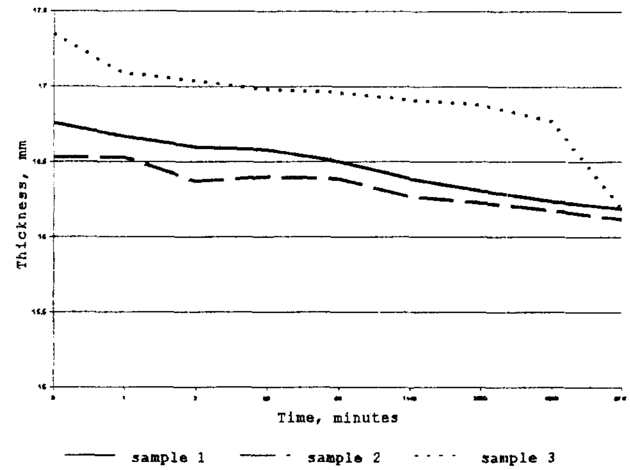

Fig. 4. Change in separator thickness under a constant load (long-term JIS test).

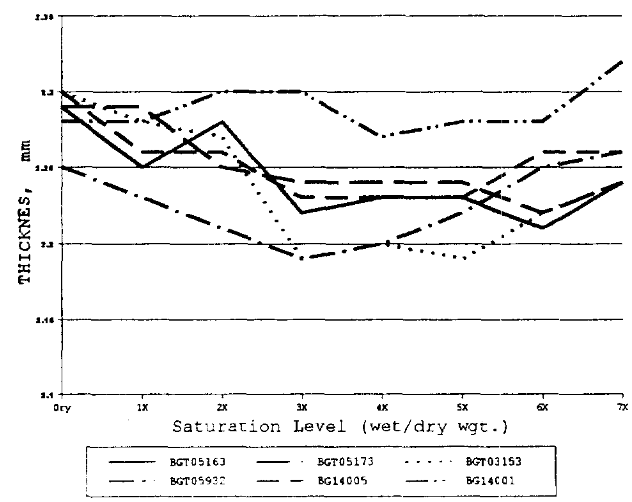

Fig. 5. Separator thickness vs. saturation (water) level (JIS test).

Table 1
Long-term JIS thickness study

Sample	Dry thickness (mm)	Wet thickness (mm)	Change (dry vs. wet) (%)	End thickness after four days (mm)	Change after four days (%)	
					Wet	Dry to wet
3	18.85	17.35	8.0	16.7	4.0	11.7
2	17.38	16.53	4.9	16.1	2.5	7.2
1	17.61	16.76	4.8	16.2	3.4	8.0

test period of four days are given in Fig. 4, note the x-axis is not to scale. The dry-stack thickness was measured before wetting the test stack of samples and the difference is reported in the Table 1. The test was performed at a load of 20 kPa and with a stack of ten pieces; the data were manually collected. The acid-saturated stack was placed in a plastic bag to avoid evaporation and to prevent sulfuric acid damage to the equipment. All the samples had a targeted grammage of 300 g m^{-2}.

The data presented in Table 1 is from one set of tests. Note that test results are preliminary in that repeatability of this method has not been completely determined. The data would suggest that, based on a dry 20 kPa thickness, a 8–12% compression is needed to just accommodate the change observed.

5.4. *Effects of saturation on thickness measurements*

Microglass separator thickness will change in direct proportion to the level of fluid added to the separator. Fig. 5 presents show some measurements, using a JIS test method, on a 10 cm × 10 cm sample compressed to a 20 kPa load. The values were obtained after 10 min under dead-weight load. The fluid was water. The saturation level defined as 1 × means that fluid weight equal to the separator dry weight was added. 7 × means that 7 times the dry weight was added. All the material tested had a grammage of 140 g m^{-2}. The grades reflect different surface area compositions.

6. Other factors to consider

The draft of the battery case will influence the separator compression, and is of special concern in attempts to optimize the compression in the battery. A large draft could result in a 10% change in compression from the top to the bottom of the plate. If a compression of 25% is targeted for the middle of the cell, there could be a range of compression from 20–30%. Most would agree that a design change from 20% to 30% is significant. Similarly, this draft effect could take a target compression of 15% (at the middle of the cell) to 10% at the top of the case. The data reported in this paper (and by other authors) would suggest that the top of the plate would experience very little compression once acid is added under these conditions.

A high draft can also influence other separator properties. Since the separator has uniform grammage from the top to the bottom of the plate, the separator would then have a much smaller pore structure at the bottom of the plate under high draft conditions. This will cause slower acid drip speed as the acid approaches the bottom of the plate. Additionally, smaller separator pores have greater forces to attract liquid, and could drive the acid to greater stratification. These factors may suggest that VRLA battery design could benefit from a straight wall rigid case, or a design with the draft at the top of the case.

6.1. *Crush force of separator*

Crushed separator is defined as a separator that has lost its ability to rebound under a given load [13]. This condition can be observed when the separator is acid-saturated. Under dry conditions, 'crushing' of the separator may not be seen. This may be caused by the process of assembling the battery through use of feed rollers. This condition may warrant further investigation since separator crushing can result in the loss of compressive forces inside the battery. Material with a higher surface-area will have greater resistance to crushing.

7. Conclusions

1. Compression inside the battery is an important design consideration.

2. Battery designs should consider higher compressions to improve performance. Compressions of over 30% should be considered with minimum compression levels of at least 20%.

3. Present microglass separators have improved tolerances and characteristics that can help achieve design compression targets.

4. The level of compression should take into account:

- ▶ design of the battery
- ▶ density of the separator
- ▶ cell saturation
- ▶ surface area of the microglass separator
- ▶ jar drafts and wall thickness plus the history of how the battery was assemble.

5. Greater understanding of the various components, especially the separator, is still required to help this technology mature and, thereby, provide improved reliability.

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