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RELATING RECOMBINATION MAT SEPARATOR PROPERTIES TO SEALED LEAD/ACID BATTERY PERFORMANCE

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Introduction

Sealed lead/acid batteries using binderless glass-fibre mat separators have been available for over 10 years. They have been used in a wide variety of no-maintenance applications, particularly those where high-rate performance is essential. These include stationary applications such as UPS systems, and portable applications such as cordless power tools, appliances and electronics. During the past decade, many companies have introduced new, sealed lead/acid batteries. The proliferation of this technology has resulted in a need for standard test methods for measuring those recombination mat-separator properties that affect battery performance. For example, the ohmic resistance of the separators can affect high-rate performance. During the past 10 years, the performance requirements for batteries have increased. The low resistance of today's separators has contributed to the success of the battery industry in meeting those requirements.

Performance is not the only issue. The separator must carry out its function over the life of the battery. One of the properties that is measured and that relates directly to the life of the battery is pore size. The distribution of pore diameters determines the ability of the separator to prevent internal shorting. In recombination mat separators, the pore-size distribution can also affect oxygen-recombination rates and acid retention.

Acid retention is not only a function of internal surface area and pore size. It is also affected by the cell geometry. As the height of the plate increases, the portion of the total void volume that is filled with acid decreases. This phenomenon has been called 'stratification', but that word already has another meaning in conventional flooded cells. Therefore, we refer to it as saturation *versus* height. Whatever term one uses, this important property determines the usable plate height of gas-recombination cells.

The total volume of acid in a sealed cell is determined, at least in part, by the porosity of the mat separator. The battery designer must know how much acid is in the separator to obtain the active material balance. The porosity of a given recombination mat varies with its thickness and, therefore, with the pressure that is used to assemble the battery element.

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Contaminants are of greatest concern when they affect the electrochemistry of the battery. It is important to keep the levels of these contaminants low enough to allow the battery to operate efficiently over its life span.

Measurement of separator properties

This paper will show the methods used and the data obtained when these properties are measured on typical samples of separator mat. For the most part, the methods are the traditional ones that have been used in the industry for many years. The unique properties of mat separators, however, require modifications to be made to traditional methods used to evaluate them. Take, for example, the measurement of partial saturation. In a sealed lead/acid battery, the mat separator cannot be fully saturated with acid. It must be only partially saturated to allow oxygen diffusion from the positive plate to the negative plate through the separator's pores. A method is therefore required to measure resistance when the separator is partially saturated. The maximum vertical dimension of a battery plate must also be known. The vertical wicking tests used by many companies are a first approximation of that height, but it is necessary to measure how much acid is in the mat (% saturation) at various heights in order to determine the maximum *usable* plate height.

Another unique property of recombination mat separators is compressibility. Since the separator and the plates are not fully saturated and there is no free acid surrounding the element, the separator and plates must be in virtual contact. Usually, this is accomplished by specifying the thickness of the mat such that the element must be compressed before it is inserted into the container and remains under compression for the life of the battery. Thus, the mat must be compressible. The compressibility of the mat requires the pressure to be specified when thickness is measured. Total porosity is also affected because the pressure used to measure the thickness of a given separator determines the apparent volume. When traditional methods are used to determine median pore size, the compressibility of the separator can be seen on the plot of pore volume *versus* pore diameter.

Separator resistance

The ohmic resistance of any separator is an important property, especially in high-rate applications. Theory suggests a low value for a mat separator because over 90% of its apparent volume is void space, even when it is compressed in a battery element. The fibrous structure also has a low tortuosity. What is unknown is the point at which 'drying out' results in unacceptably high internal resistance. For example, what is the shape of the curve of resistance *versus* % saturation?

To answer this question, a 1 kHz impedance bridge was connected to the cell as shown in Fig. 1. The sample of mat was weighed before, and after, saturation with acid. The acid weight, obtained by difference, was defined as

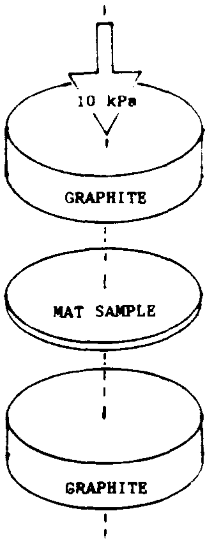

Fig. 1. Cell for measuring resistance of mat separators.

100% saturation. Lower levels of saturation were obtained by blotting the sample, re-weighing, and re-measuring the resistance. All of these measurements were done at a constant pressure of 10 kPa.

Figure 2 gives the level of saturation at which the resistance becomes too high. The shape of this curve is somewhat surprising. The flat portion of the curve, extending from 80% to 100% saturation, is quite reproducible. The transition to high resistance occurred between 60% and 80%. Whether this break-point shifts with changes in average fibre diameter (internal surface area) or pressure was not determined.

Since the resistance is constant at saturations greater than 80%, the readings were averaged for each of the samples and the separator resistance was isolated. The separator resistance is obtained by subtracting the cell resistance and the acid resistance from the total measured resistance. Direct measurement of the cell resistance without a sample proved to be unreliable.

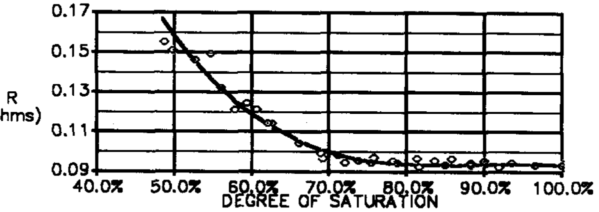

Fig. 2. Cell resistance as a function of separator saturation.

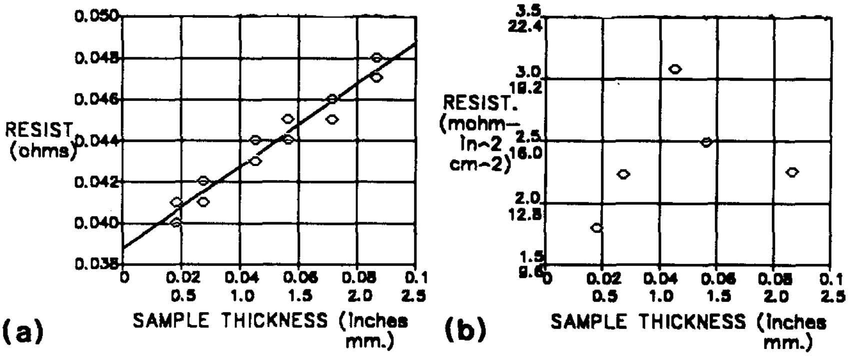

Fig. 3. Cell resistance *vs.* (a) sample thickness, (b) converted sample thickness.

The cell resistance was therefore obtained by extrapolating the resistance *versus* thickness curve to zero thickness. The acid resistance was calculated from the acid resistivity and the geometry of the sample. The raw separator resistance was then converted to the more familiar $\Omega\,cm^2$ and $\Omega\,in^2$ by multiplying the separator resistance by the apparent area of the sample.

Figure 3(a) and (b) shows the results of the measurements and calculations. It can be seen that the cell resistance is linearly-dependent on sample thickness. The resistance of mat separators is *very* low, being less than $20\,m\Omega\,cm^2$ at 1.5 mm thickness. The scatter in the data shows that these values are too low to be accurately measured with this equipment. Nevertheless, it can be concluded that recombination mat has the lowest resistance of any separator examined to date.

Separator saturation

As mentioned earlier, the degree of acid saturation varies with plate height. An engineer needs this information to specify materials and designs for new batteries. Many companies use a wicking test that lasts 24 h, or less, to determine the absorptivity of the mat separator. Remembering the resistance measurements shown earlier, any portion of the mat that has less than about 80% of its void space filled with acid can be an area of high resistance.

In order to determine the maximum usable plate height, a 24-h wicking test was carried out on samples of separator mat. The 60 cm samples were hung vertically with only 1 cm dipping into a tray of acid. The mat was cut at 5 cm intervals and the % saturation was determined for each piece. Similar tests were run on additional samples that were pre-saturated horizontally and then hung vertically for 17 days. The apparatus was enclosed in a clear plastic box to minimize the effect of evaporation.

The data in Fig. 4 indicate that the usable plate height is about 350 mm. Other factors that affect capillary saturation include pressure on the mat and total internal surface area. As either or both are increased, the usable plate height is increased.

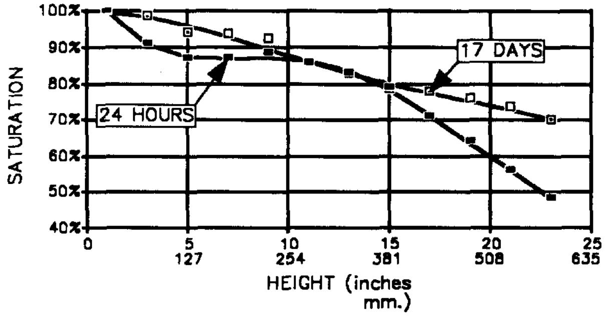

Fig. 4. Separator saturation as a function of plate height.

The degree of saturation is one factor that determines the total acid volume of a gas-recombination cell. Two other properties are the thickness and porosity of the separator. The compressibility of the mat affects the measurement of both of these properties.

Separator compressibility and porosity

Figure 5 is a graph of thickness *versus* pressure that shows the compressibility of a sample mat separator with a basic weight of 225 g m^{-2}. The semi-logarithmic relationship holds for samples ranging from 80 to over 300 g m^{-2}.

The porosity of mat separators does not vary appreciably with changes in thickness at pressures normally seen in a battery element. In Fig. 6, porosity is defined as the ratio of void volume to total volume, expressed as a percentage. The plot shows that extreme changes in thickness (*i.e.*, increases in pressure) are needed to reduce the porosity to less than 90%. The equation in the box is derived from this definition of porosity when the void volume is defined as the difference between total and solid volume. The factor of 1000 is used when thickness is measured in mm. If mils (in./1000) are

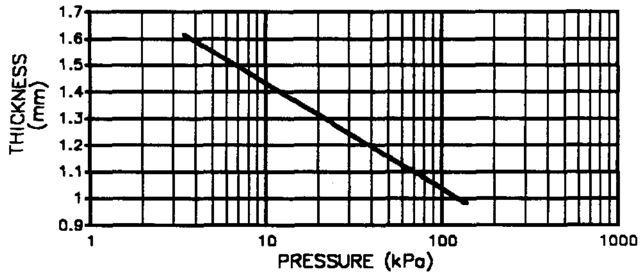

Fig. 5. Compressibility of mat separators.

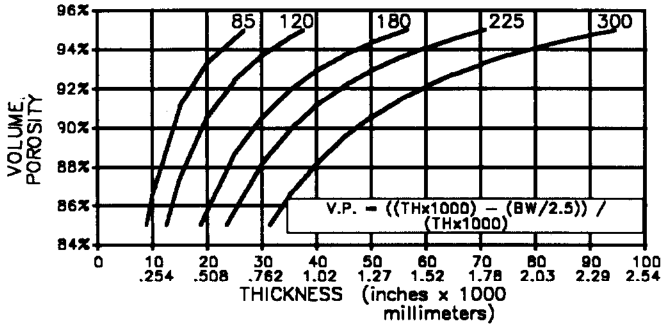

Fig. 6. Separator porosity *vs.* thickness at various basic weights.

used, the factor becomes 25.4. The porosities shown were calculated, but have been verified by measuring acid absorption. The lack of organic binders allows virtually all of the pore volume to be saturated with acid.

In Fig. 7, a mat with a basic weight of 225 g m^{-2} is compressed at pressures up to 140 kPa (about 20 psi), but the change in volume porosity is very small. It is difficult to imagine an element with a stacking pressure of even half the maximum value shown in Fig. 7 because the container walls would have to be very thick to prevent bulging. Since low contact resistance between the mat and the plates is essential, it is useful to know that a higher basic weight mat can be used at a higher stacking pressure in the same space with a minimal loss in total acid volume.

Compressibility also affects the measurement of median pore size. The standard method for determining the pore-size distribution of a separator is mercury intrusion. In this procedure, the porous sample is immersed in a pool of mercury while under vacuum. The pressure on the pool of mercury is gradually increased until no further intrusion occurs. The diameter of the pore opening is proportional to the pressure, so a plot of intrusion *versus* pressure can easily be translated to volume change *versus* pore diameter.

When applied to mat separators, we find that there are two possible phenomena in this test. As the pressure is increased, the mercury can compress the entire sample and penetrate the pores, or do both at the same

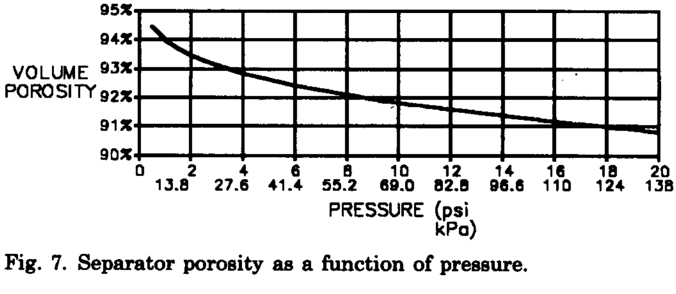

Fig. 7. Separator porosity as a function of pressure.

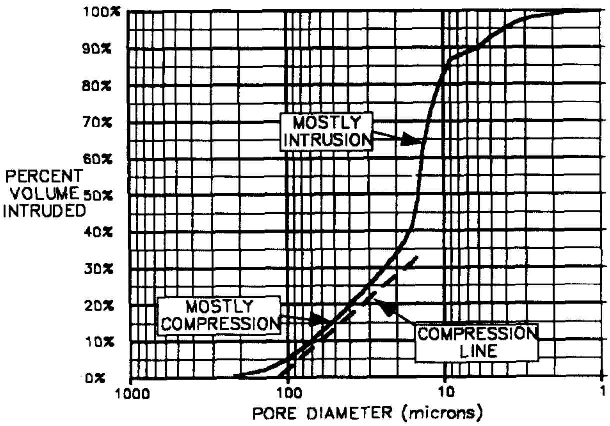

Fig. 8. Volume intended as a function of separator pore diameter.

time. Figure 5 showed that the plot of thickness *versus* pressure is a straight line. Thus, it is clear that a plot of change in volume *versus* log pressure is also a straight line for compression. It is not a straight line for intrusion.

The phenomena are illustrated in Fig. 8. The line drawn under the intrusion curve shows the volume change that occurs when the same sample is compressed with a dead-weight dial micrometer. In samples that are not so compressible, this part of the intrusion curve is virtually flat.

The pore-size distribution of mats made with various mixtures of two different glass fibre diameters has been measured (Fig. 9). The surface area is calculated for the weighted average of the fibre diameters used in each sample. The median pore diameter is defined as the diameter that corresponds to the pressure where 50% of the total volume is measured. There is some change in median pore diameter as the fibre diameter is increased. Determining the effect of this change on cycle life would require extensive cell testing.

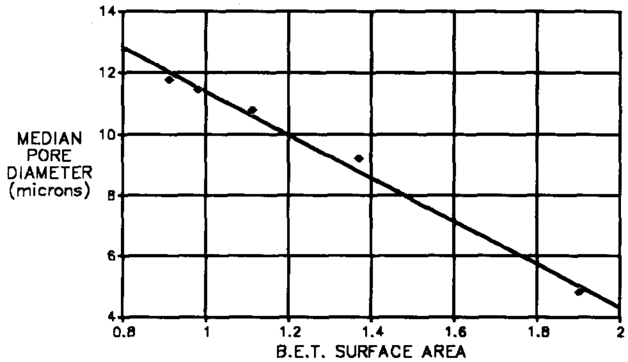

Fig. 9. Median pore diameter of mat separator as a function of surface area.

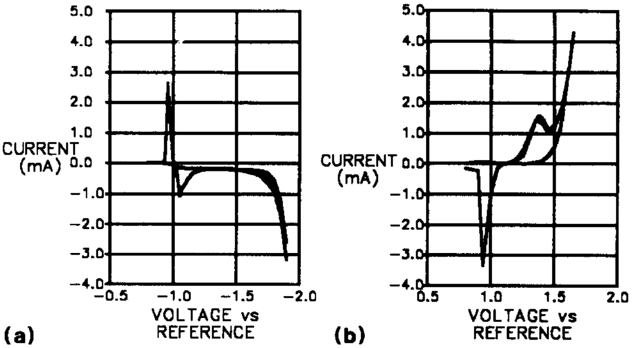

Fig. 10. Voltammetric scans to determine effect of separator purity: simulation of reaction at (a) negative plate, (b) positive plate.

Since most of the mat separator material sold in North America is being used in stationary float batteries, this testing has not been carried out to date.

Separator purity

In addition to having good physical properties, the separator must be chemically clean. It should not change the charge, discharge, or gas evolution reactions of either plate. The electrochemical compatibility test was developed by AT&T Bell Laboratories as part of the Round Cell program. It consists of voltammetric scans of fresh electrolyte and of electrolyte that has been exposed to the separator or other cell component for 7 days at 60 °C. The working electrode is a rotating disc made of lead. There are two kinds of scans — one simulates the negative plate and the other simulates the positive plate. Electrochemical compatibility is an effective screening test for battery components. If the voltammetric scans are clean, development can proceed. If they are not clean, the change in voltage and/or current gives a clear direction for further analysis.

The scans in Fig. 10 are for mat samples. There are two traces in each graph, one for clean acid and one for the leachate. The reproducibility of the results shows that the leachates from the separator do not alter the electrochemistry of the cell.

Conclusions

A summary of the results obtained from measurements of separator properties is as follows. The resistance of mat separators is so low that it is difficult to measure, but it increases dramatically when less than 70% of the void volume is filled with acid. The usable plate height is about 350 mm, but this can vary with pressure and internal surface area. The volume porosity changes only slightly with increasing pressure on the element. The median pore size ranges from 5 to 15 μm depending on the mixture of glass fibre diameters used to make the mat. Electrochemical compatibility testing indicates that the mat is free from contaminants.

The studies reported here are not industry-wide standards. Evanite is, however, a leading participant in the BCI Technical Subcommittee on Separators. This group of representatives from separator and battery companies is drafting a set of standard test methods for these and other mat separator properties. The performance criteria established by the present binderless glass-fibre separator material guides efforts to produce a lower cost of separator for sealed lead/acid batteries.