Fluid-transfer properties of recombinant battery separator media

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Abstract

The fluid-transfer properties of the separator play a critical role in both acid- and alkaline-based batteries. These properties are of particular importance in a lead–acid battery since the sulfuric acid is an active component of the battery reaction; the acid is depleted as the battery discharges. In a flooded lead–acid, the function of the separator to deliver acid is less significant than in a valve-regulated design. This paper discusses some issues with regards to this important interaction. © 2000 Elsevier Science S.A. All rights reserved.

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1. Background

Recombinant battery separator media (RBSM), better known as absorptive glass mat (AGM), is a critical component of the valve-regulated lead–acid (VRLA) system. Much attention has been devoted in recent years to understanding the physics of these separators. This is especially true of the way in which the separator applies force to the positive plate to restrict the expansion of the active material during battery service, and thus minimize premature capacity losses. This critical role of the separator should not be overshadowed by the fact that the other major function of the separator is to act as a reservoir for the sulfuric acid.

The fluid-transfer properties of the RBSM–battery systems are dependent on the fluid being employed (i.e., the electrolyte), the separator, and the nature of the positive and negative plates. The separator used in VRLA batteries has a fibrous structure. In most cases, the liquid movement in a fibrous, nonwoven material is an 'unsteady-state' flow [1]. The separator is not uniformly and completely saturated, and the liquid distribution throughout the medium changes with time. Absorbency phenomena in fibrous separators generally belong to this type of unsaturated flow. The microglass separator, once in contact with the

sulfuric acid, absorbs the acid with a saturation gradient in the direction of flow [2]. The degree of saturation (or filling) of the pores in the separator is highest at the liquid interphase. This gradient does not stay constant. The rate of change is dependent on the pore structure, that is, on the surface area of the separator (Fig. 1). As the battery is discharged and the acid concentration decreases, the saturation profile changes. In a new battery, the separator may be fully saturated and thus the driving force of capillarity is restricted. As the battery dries out, however, the separator becomes less saturated and greater gradients are developed with changes in capillarity.

The morphology, topography, physics and chemistry of a solid all influence its interaction with any fluid. The surface structure of the separator includes the overall physics and chemistry of the so-called 'capillary walls', not just the topography of the wall surface. Within a battery system, the fine pore structure and perfect wetting (i.e., zero contact angle) of the microglass separator allows for capillary movement of the acid.

Capillarity can be defined as ''the action by which the surface of a liquid where it is in contact with a solid is elevated or depressed as dictated by the relative attraction of the molecules of the liquid for each other and for those of the solid''. In a VRLA battery, there are three interfaces between the phases, namely: liquid–vapour, solid–vapour, solid–liquid. Depending on the degree of saturation, these interfaces will interact, more or less. The surface tension,

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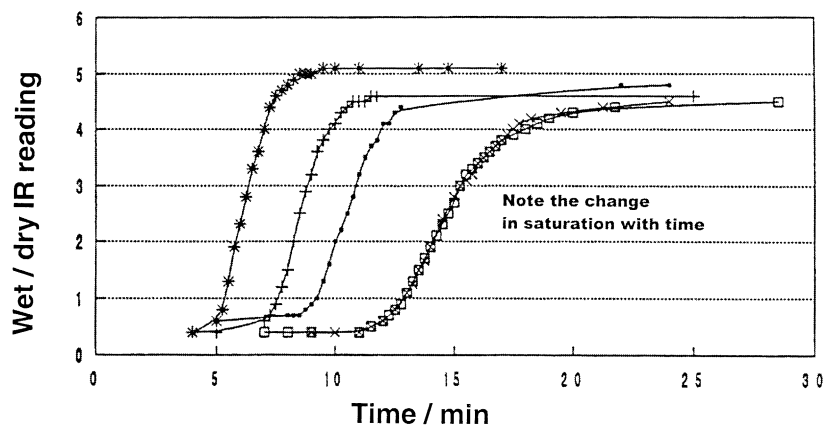*E-mail address:* gzguris@hovo.com (G.C. Zguris).

Fig. 1. Comparison of wicking times to a height of 17 cm for microglass fibre blends with fine:coarse ratios of: (●) 50%:50%; (+) 25%:75%; (*) 0%:100%; (□) 75%:25% (IR = infrared).

viscosity, density and polarity of the sulfuric acid will influence the wicking, surface and bulk characteristics of the solid, i.e., the contact angle of the solid and the porosity of the separator. The interfacial properties at the boundary or contact of the separator, electrolyte and the gas (oxygen or hydrogen) can be expressed in terms of interface energy and contact angle (Fig. 2).

Adhesive forces exist between liquid and solid molecules, while cohesive forces exist within the liquid. Absorption or wicking is the spontaneous physical imbibition of a liquid by a contact solid. The driving force in wicking derives from the free energies of the phase interfaces in the system. For wicking to occur, it is necessary for the interfacial area in the system to be large in comparison with the bulk volume.

2. Importance of separator porosity

The ability of the separator to have a high porosity is extremely important in VRLA technology. The one factor that made VRLA technology a reality was the discovery by the inventors, McClelland and Devitt [3], that microglass fibres could be used as the separator material. Microglass separator is still in use today, even after a period of over 20 years during which some of the best minds in the world have tried to develop a superior alternative. Present material has, however, been refined and customized towards the VRLA application compared with the samples that were first used. Nevertheless, today's materials still offer the main original benefits of that first microglass separator, viz.,

· good wettability
· good resilience
· high porosity
· small pores
· excellent corrosion resistance
· good 'spring' properties.

The porosity plays an important role: without adequate porosity, not enough acid can be added to the battery and
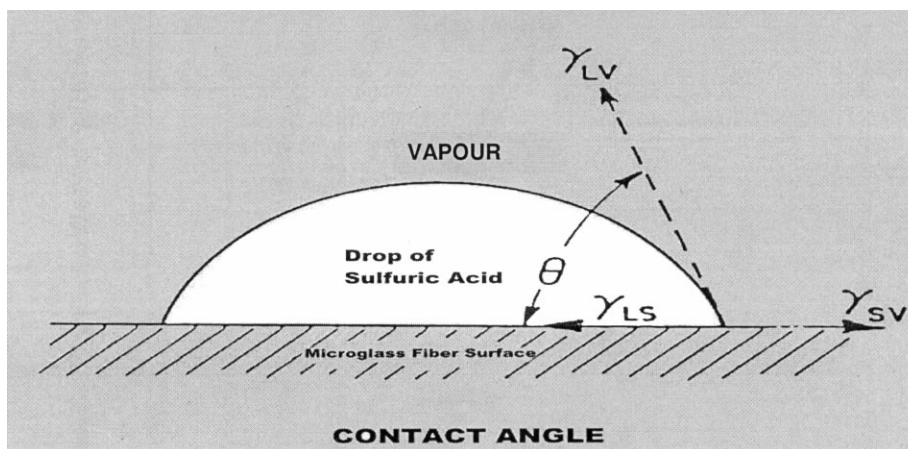

Fig. 2. Schematic of the contact angle in a drop of acid on a microglass fibre surface.
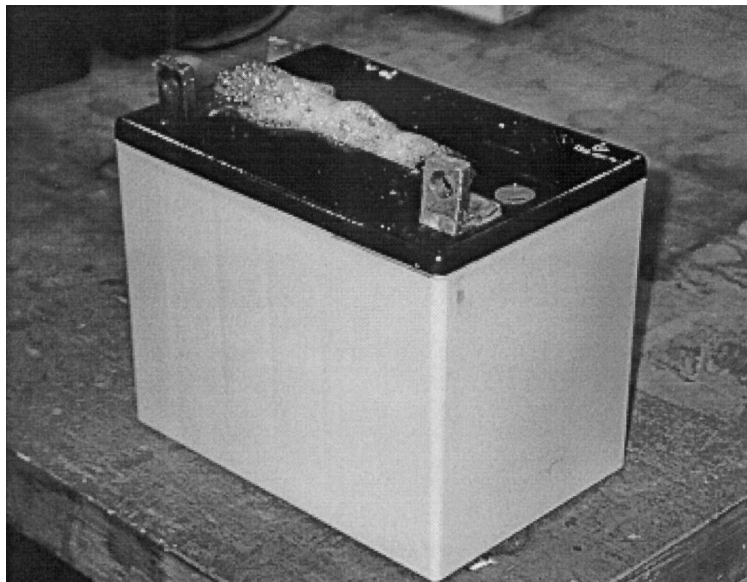
Fig. 3. Foaming during cycling tests of a battery using a separator with 100% organic separator.

the battery performance is negatively effected, e.g., low-rate capacities are poorer or lower. A drawback of VRLA batteries versus flooded types is that the former batteries have less acid. Most VRLA batteries are designed to hold just the minimum amount of acid. The thickness of the separator in many designs is determined on the 'gas tank principal'. In determining how much acid a separator can hold, designing in a greater fringe area would provide for greater acid holding of the separator. A greater fringe area can be obtained by: (i) narrowing the widths of the plates; (ii) wrapping the negatives instead of the positives; (iii) using the head space to hold acid; (iv) including more space between the plates, i.e., by the use of thinner plates. When the battery is acid-limited, as in the case of many small-size batteries, it is possible that cost savings can be realized by removal of lead, while maintaining the same or better capacity. If the design is truly acid-limited, then all the capacity of the plates is not being used. Changing the design so that additional acid is within the cell will also improve the heat capacity of the battery, and will thus allow for better control of any temperature rise. Employment of a thicker separator between the plates will also impact the shock-absorbing properties. The presence of more acid will also slow down the rate of dry-out of the separator. If the separator thickness is doubled for a given amount of corrosion or outgassing, the percentage change in the acid saturation of the separator is reduced by 50%.

The porosity of the separator, besides effecting the acid-holding characteristics, can also influence the impact of changes in the modulus of the separator as it goes from a dry to a semisaturated state. It should be remembered that if the separator were fully saturated, it would have good compression characteristics since fluids are not com-pressible. A sheet with 80% porosity compared with a sheet with 95% porosity (i.e., the standard for AGM, at same material density) will change the solidity from 5% to 20%. It is reasonable to assume that a similar material with four times the solidity is harder to compress, or has less of a modulus change from the dry to the wet state. This is a simplistic view of why many battery designs are moving to higher-density separators.

Another factor which influences the porosity is the density of the separator material itself. A separator which is composed of an organic material such as polypropylene at 0.9 g cm^{-3} versus a standard microglass with a density of 2.5 g cm^{-3} would have 2.8 times the solidity at the same grammage and thickness. A further feature that must be considered, especially with the use of organic-containing separators, is the overall degree of wettability of the separator. Mixing hydrophobic fibres with hydrophilic fibres (glass) may act adversely on long-term battery performance, as well as on safety if a thermal runaway condition develops. If the hydrophobic material is made wettable
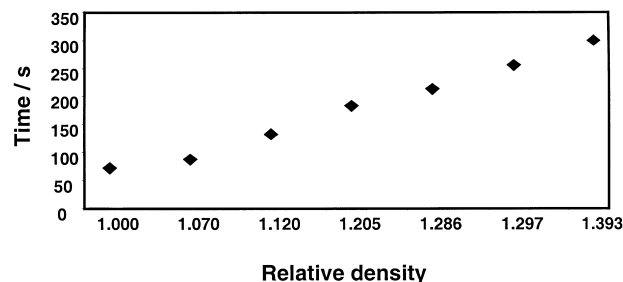

Fig. 4. Wicking time to 10 cm vs. relative density of sulfuric acid (separator: Hovosorb® II BG24017).

with an unsuitable surface treatment, problems can manifest themselves either while the material is still wettable or after the material has lost its hydrophilic nature.

The battery in Fig. 3 shows an example of a problem which can occur with improper surface treatment of the separator to make it hydrophilic. During testing with a commercial melt-blown separator, this battery generated foam which escaped through the vents. Due to the possibility of thermal runaway, the cycle test was stopped early.

3. Influence of sulfuric acid density on wicking

During filling a battery with sulfuric acid, as well as during charge–discharge service, there is a change in the relative density of the acid. This change can influence the concentration gradient of the electrolyte within the separator. The effect was examined by conducting visual wicking tests on various separators to determine the speed of fluid uptake to a height of 10 cm (Figs. 4 and 5) and 15 cm (Fig. 6) at various acid relative densities. The results showed that as the relative density was increased, the rate of wicking decreased. In one test, as the relative density was increased, the commercial melt-blown RBSM actually curled away from the acid (Fig. 7). This indicated that the acid did not wet the melt-blown material. By contrast, the AGM on the left in Fig. 7 wetted out and remained straight. To determine if the relative density of the acid changed as it wicked up the separator, a check was also made with a refractometer. The data suggested no change, but it should be noted that 15 cm is a small distance.

The impact of an increase in acid relative density on the wicking rate is shown in Figs. 4–6. The behaviour can
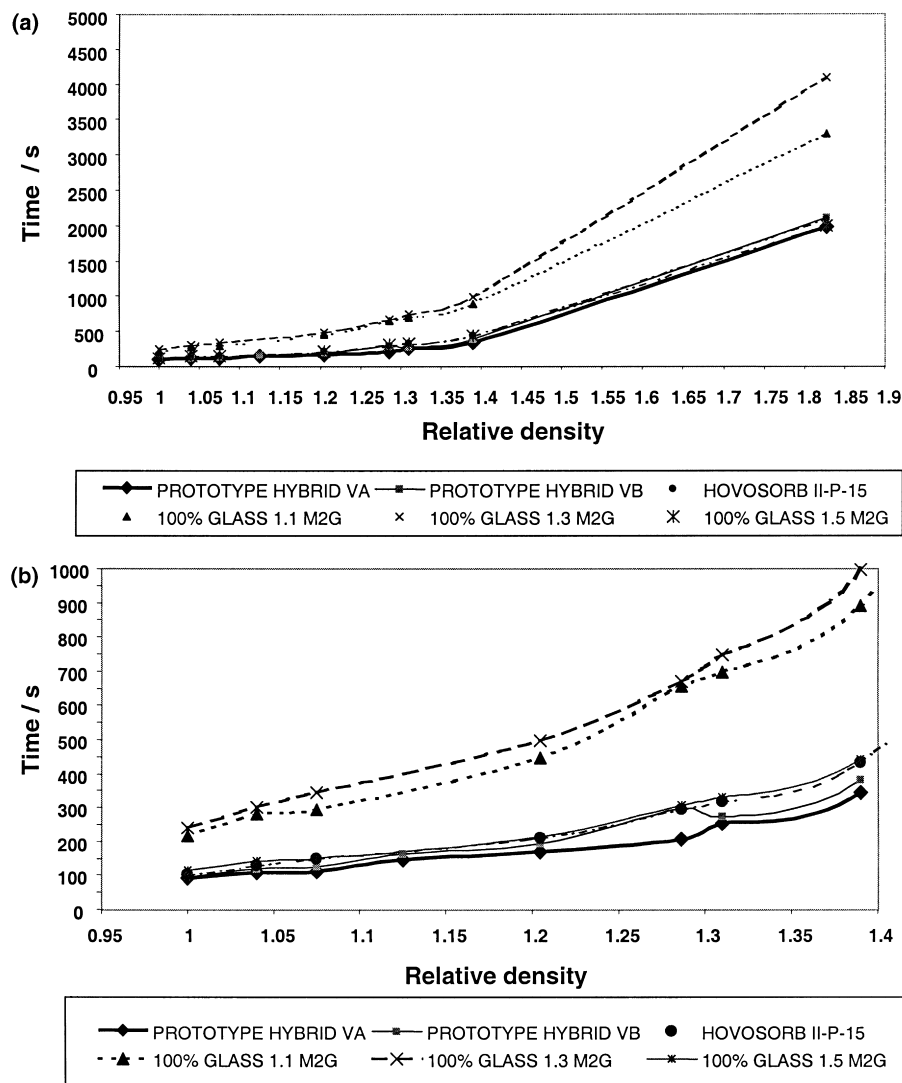

Fig. 5. (a) Wicking time to 10 cm vs. acid relative density for various separators; (b) expanded view of (a) for range of acid relative densities as used in batteries.
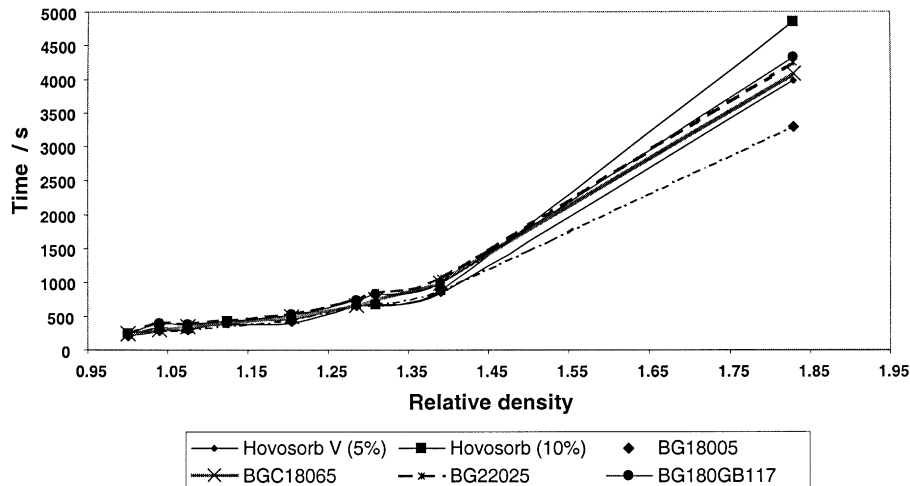
Fig. 6. Wicking time to 15 cm vs. acid relative density for various separators.

exert an influence on both filling and battery performance. The fact that VRLA batteries use acid with a higher relative density, together with the fact that the filling is a costlier process, may be partly explained by this data.

Sodium sulfate is added to most VRLA batteries to control dendrite growth. A brief study was made of the influence of various levels of sodium sulfate in sulfuric acid at a relative density of 1.286. The results indicate (Table 1) that sodium sulfate does not influence the rate of
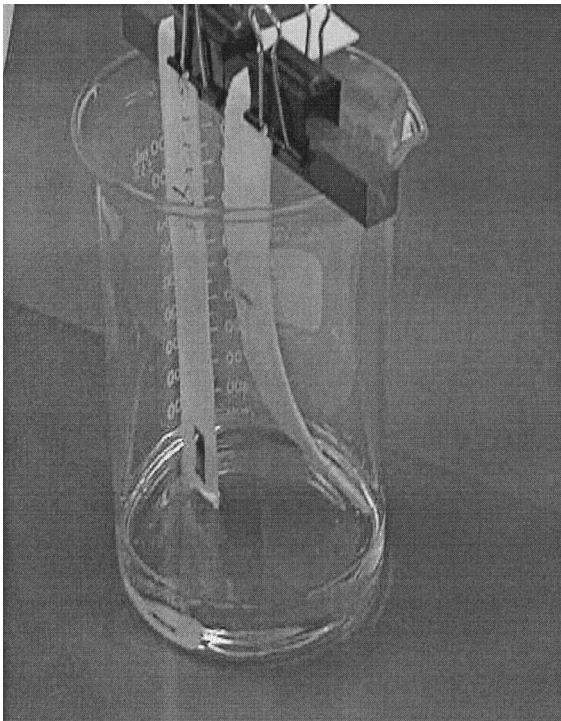
wicking, except for a slight decrease in rate at an addition of 5 wt.%.

4. Separator wicking in the *z*-direction

Most wicking tests determine the absorbency of the separator in the *x*–*y* plane of the material. Using an M/K Systems absorbency testing system (GATS, Fig. 8), the influence of absorbency in the *z*-direction can be better understood. (Note: the tester can also be used in the *x*–*y* plane with attachments.) The instrument is a highly sensitive demand wettability device. An electronic balance with three-decimal (0.001 g) sensitivity is the heart of the system. A reservoir containing the test liquid is placed on the balance. The reservoir is attached to the test plate on which the sample of separator rests. Flow from the reservoir to the sample is initiated by two different methods, depending on the type of test plate that is being used. To offset the effects of gravity, there is a vertical levelling mechanism which lowers the test plate at the same rate as that of the fall in the level of the fluid in the reservoir. This provides a true picture of the actual absorptive demands of the material under test. The data is collected, downloaded to a computer, and displayed or printed out as a graph.

Fig. 7. Test set-up to determine wicking time as a function of acid relative density.

Table 1
Influence of sodium sulfate on wicking according to Japanese Industrial Standard

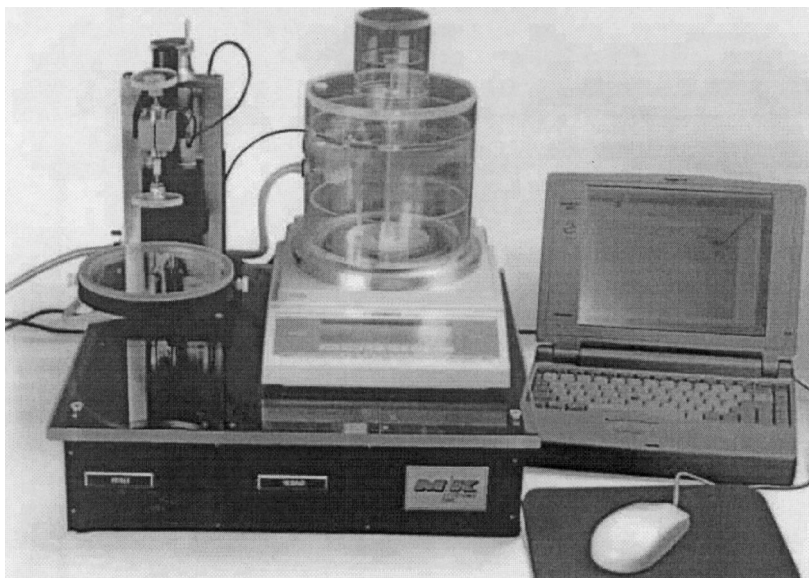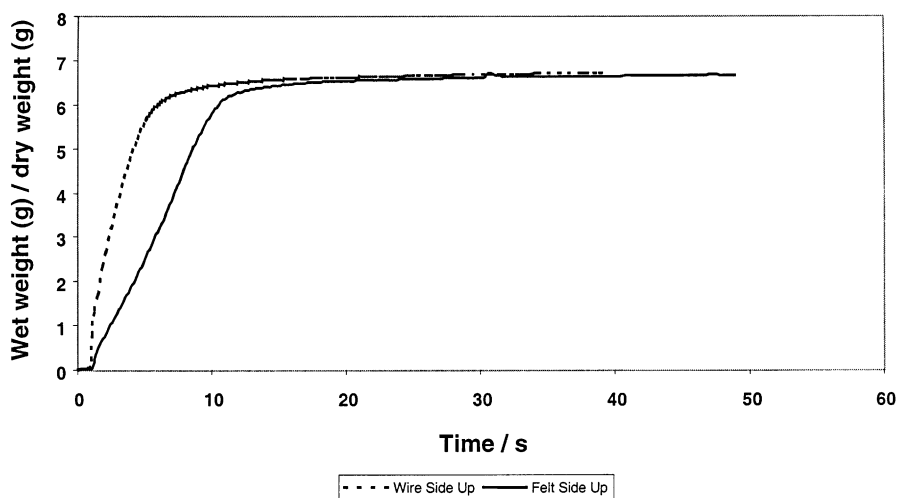| Saturating fluid	Time for wicking to 10 cm (s)
Plain water	105
Plain 1.286 relative density acid	254
+ 1 wt.% sodium sulfate	254
+ 2 wt.% sodium sulfate	254
+ 3 wt.% sodium sulfate	255
+ 5 wt.% sodium sulfate	286

Fig. 8. M/K Systems absorbency tester.

Fig. 9. *z*-Direction wicking, based on what side the water is introduced to a sample of BG24017. Pressure on sample is 0.3 kPa.
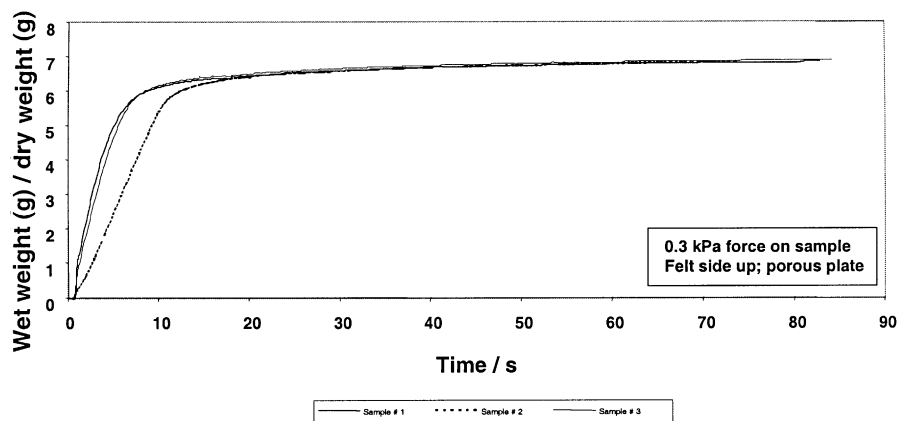

Fig. 10. Illustration of the repeatability of the GATS tester. *z*-Directional wicking. Three tests on the same material.
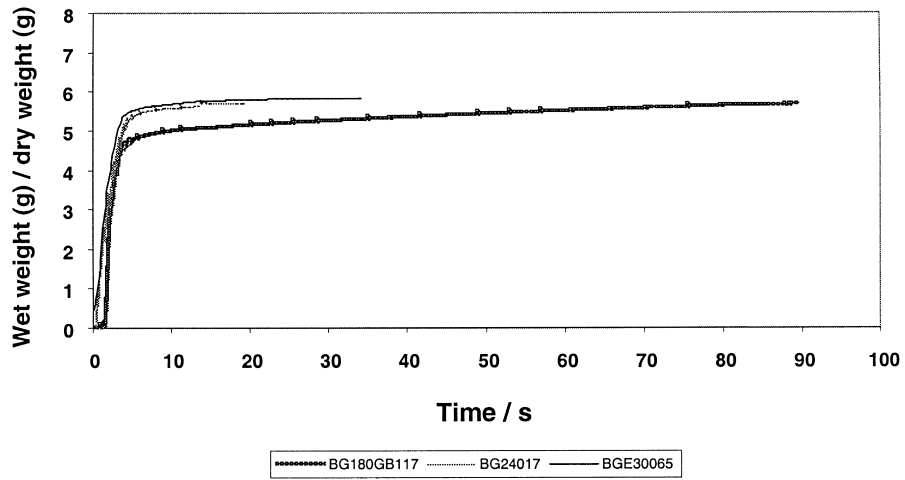
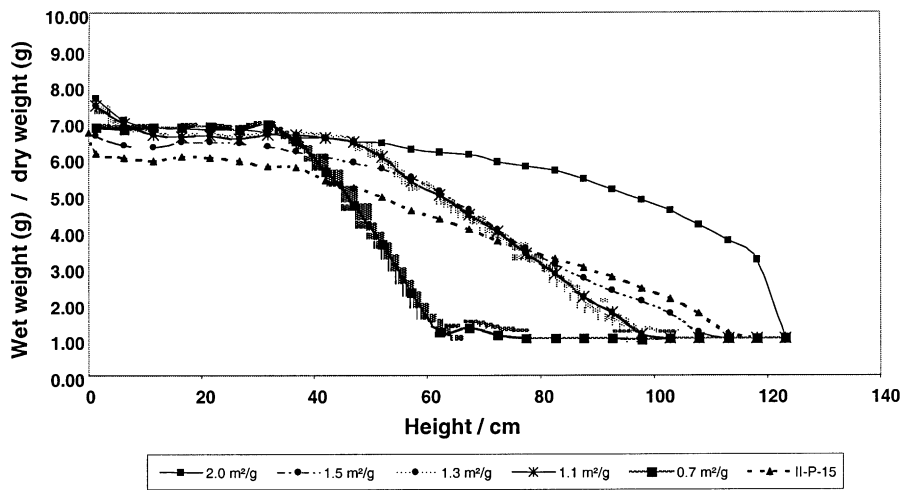Fig. 11. *z*-Directional wicking (felt side up) for three grades of separator. Pressure on samples is 5.3 kPa.

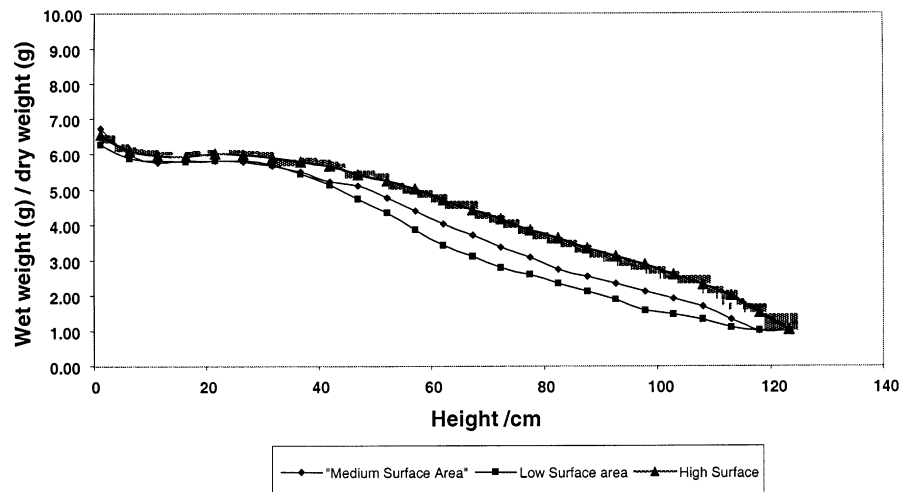Fig. 12. Effect of separator surface area ($m^2 \ g^{-1}$) on wicking height.

Fig. 13. Wicking performance of hybrid separators.

With the GATS, fluid can be introduced at a single point or via a porous plate. A porous plate is a good representation of how the plate may wet the separator.

The following observations have been made from studies with the GATS. Depending on which side the separator had touched the fluid, the speed of absorption of the fluid can be different. Results suggest that the felt side (nonforming side) tended to wick the fluid up to twice as fast as when introducing the fluid from the other side (forming side, Fig. 9.). Nevertheless, in both cases the total amount of fluid is eventually the same. Remembering that the rate of vertical wicking decreases as the acid relative density increases (see Section 3), this difference, if it simulates the conditions in the battery, suggests that a change in the placement of the separator is important with respect to factors such as high-rate performance. The data presented in Fig. 10 show that testing does result in some difference in repeat measurements and that there is a change in the capture rate of data so that it becomes difficult to average different test runs. This small error in reproducibility can be overcome by refinement of the test protocol.

Results obtained in the *z*-direction with the GATS support those obtained from tower wicking tests with long strips. The performance of three different materials is compared in Fig. 11. The data is in agreement with previous work in that the height of wicking is dependent on the structure of the material. The greater the surface area of the material, the higher the fluid will wick up the tower. Larger pores give up water more easily, and also provide for a faster wick height, but at lower saturation levels. This highlights one problem with using visual measurement techniques to determine wicking, namely, two materials can require the same time but have totally different saturation levels. Tower wicking tests based to 120 cm are given in Figs. 12 and 13. The data demonstrate the dependency of the saturation level on surface area (pore structure). In Fig. 11, the all-glass sheet wicked the fastest, while the hybrid separator, Hovosorb II-P-15, wicked the slowest. After suitable time, all the separators wicked the same relative volume of fluid. The data in Fig. 13 show that the surface area is also important with hybrid separators. These newer types of mainly microglass separators offer improved puncture and tear-strength properties. These help the battery manufacturer to reduce internal shorting and battery assembly-line problems. The unique structure also provides a retention of the strength properties when saturated with acid, and this prevents the movement of pellets or lumps of paste that otherwise would create shorts between the plates.

5. Summary

The separator is a key component in a VRLA battery. The fluid absorption properties of a separator are an important design consideration. A separator that does not have good hydrophilic properties can cause battery problems. Data suggest that the rate of absorption is influenced by the method used to wrap the plates. In addition, the change in wick speed with change in acid relative density may provide some better understanding of how to increase the service lives of VRLA batteries.

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