

Essential characteristics for separators in valve-regulated lead–acid batteries

K. McGregor^{a,*}, H. Ozgun^a, A.J. Urban^a, G.C. Zguris^b

^aCSIRO Energy Technology, P.O. Box 312, Clayton South, Vic. 3169, Australia

^bHollingsworth and Vose Co., 219 Townsend Road, West Groton, MA 01472-0168, USA

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Abstract

The absorptive separator plays an important role in the operation of valve-regulated lead–acid (VRLA) batteries. The composition and physical characteristics of recombinant-battery separator mats (RBSMs), also known as absorptive-glass mats (AGMs), directly affect three critical factors associated with the performance of VRLA batteries. The factors are: electrolyte supply, oxygen-transport, and constraint of positive active-material growth. This paper discusses the influence of the physical properties of RBSMs on the performance of VRLAs, explains how these properties are measured, and defines the characteristics of an ideal separator. Separators used presently in VRLAs meet some of these criteria, but development of advanced materials is required to improve battery life.

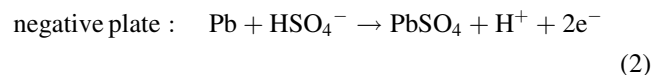
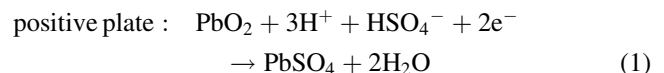
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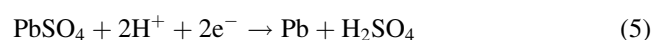
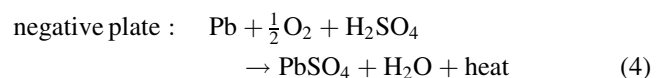
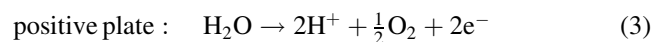
1. The separator in valve-regulated lead–acid (VRLA) batteries

Traditionally, the lead–acid battery has a flooded design in which the plates are immersed in excess sulfuric acid solution. A disadvantage of flooded cells is the loss of substantial quantities of water during charging. This must be replaced at regular intervals, or the cells will fail due to dry-out. Successful development of valve-regulated lead–acid (VRLA) designs based on absorptive-glass mat, that do not require addition of water and perform in a manner similar to that of a sealed nickel–cadmium cell, was achieved in the early 1970s. This was a significant innovation, and opened up new application areas for lead–acid batteries that included portable medical and electronic equipment, and power tools. In a VRLA battery, sulfuric acid is either stored within the pores of the plates and the separator (absorptive-glass microfiber mat (AGM), also known as recombinant-battery separator mat (RBSM)), or immobilized by gelling with silica. The RBSM design operates under a ‘starved-electrolyte’ condition, i.e., the cell is filled with only enough acid to coat the pores of the plates and partially saturate the separator. The basic

discharge reactions for flooded and VRLA technologies are the same, namely:



When the cell is charged, and the majority of PbSO₄ has been converted to Pb and PbO₂, the overcharge reactions begin. For flooded cells, these reactions produce hydrogen and oxygen gas, with subsequent loss of water. The advantage of VRLA designs is that an ‘internal oxygen cycle’ operates, which minimizes water loss. In this cycle, shown below, oxygen is evolved at the positive electrode during charging and transfers through ‘channels’ in the partially-saturated separator to the negative electrode. Oxygen partially discharges the negative-plate to a state where the hydrogen production is low. As the cell is on charge, the lead sulfate produced is immediately reduced to lead, and heat is generated [1]:



* Corresponding author. Tel.: +613-9545-8912; fax: +613-9562-8919.
E-mail address: kathie.mcgregor@csiro.au (K. McGregor).

The effective operation of the cycle for RBSM designs is dependent upon the microstructure of the separator, its degree of saturation, and the charge algorithm. One of the crucial barriers to the development and commercialization of the VRLA battery was the storage of sufficient electrolyte in the separator to give adequate discharge capacity, whilst maintaining enough open channels for the transport of oxygen. Other obstacles included the elimination of water loss during the life of the cell, and minimization of sulfation during prolonged storage in the discharged state. The inventors of VRLA technology, McClelland and Devitt [2], investigated a large number of materials for separators, including synthetic non-wovens,¹ a latex-bound diatomaceous earth, phenolic-treated cellulose, and other treated cellulose papers [3]. Cycle-life was strongly limited by water loss, and acid capacity was poor. Many combinations of materials were tried. A key breakthrough was the discovery that cells containing a layer of treated cellulose paper and a layer of Whatman GF83 filter paper (made from glass microfibers) showed much less water loss. This led to the use of glass microfibre papers in combination with other materials and finally, alone. Subsequently, McClelland and Devitt discovered that highly-porous AGMs were suitable separating media. Following this breakthrough, VRLAs became technically and commercially viable. A spiral-wound cell configuration was employed which, although challenging to manufacture, proved to be a vital element in the design of a long-lived cell. The first VRLAs produced by Gates Energy Products in the 1970s employed a high specific-surface-area (SSA) all-glass separator with a high content of fine-diameter, flame-blown microglass fibers. Such cells had good float and cycling properties and showed little or no water loss. Ultimately, they failed from grid-corrosion and growth of the positive-plates, the failure modes that usually limit the life of flooded cells.

1.1. Impact of separator on positive-plate performance

Another reason for the good performance of the Gates batteries was the high degree of force, or plate-group pressure, applied to the active-material by means of the spiral-wound cylindrical design. It is now well-known that plate-group pressure plays an essential role in constraining the expansion of the positive active-material during deep-discharge cycling and thus extends cycle-life [4–7]. Expansion of the positive active-material leads to a loss of contact between PbO₂ particles. Consequently, the active-material displays poor conductivity and there are difficulties in discharging the PbO₂. This phenomenon is commonly referred to as ‘premature capacity loss’ or PCL [4].

During manufacture, the cell group is compressed and inserted into the case. Thus, a given level of pressure is applied

to the plate-group. The maintenance of adequate plate-group pressure against the positive-plates relies upon the elasticity of the RBSM separator, and any physical changes in the material can reduce the plate-group pressure within the cell. The composition and physical attributes of the RBSM separator are of key significance, since these influence its elastic characteristics. In addition, the strength of the battery container can also affect plate-group pressure. For example, battery containers used in flat-plate batteries are generally constructed from soft material (e.g., polypropylene) that can deform and allow expansion of the plate-group which, thereby, reduces the pressure. Tubular-plate and spiral-wound designs have a significant advantage over flat-plate batteries with respect to some of the problems associated with the application of plate-group pressure, since the configuration of the plates ensures that positive active-material is tightly held. Such designs are, however, more costly to manufacture.

1.2. Impact of separator on negative-plate performance

A further type of capacity loss that limits VRLA battery life in both cycling and float applications is insufficient recharge of the negative-plate. This means that considerable difficulty can be encountered in bringing the negative-plate to a full state-of-charge, usually in the latter stages of life. The lack of adequate charge leads to plate sulfation, particularly in the lower regions of the plates, and results in significant capacity loss. This phenomenon is often manifested at high rates of operation. The problem represents a major technical challenge in the development of reliable, high-power VRLAs. It is imperative that this challenge be overcome so that high-power VRLAs can gain a foothold in the rapidly emerging markets for hybrid electric-vehicles and 36 V automotive battery systems.

Insufficient recharge of the negative-plate has been attributed to a number of causes [8] that include:

- highly efficient oxygen recombination that shifts the negative-plate potential to such low values that the plate cannot be fully charged;
- electrolyte-stratification, which may take place with separators with large average pore sizes;
- degradation of negative-plate expanders that reduces the SSA of the negative-plate;
- excessive self-discharge that impedes recharge of the negative-plate.

Notably, the first two points involve the separator and its physical structure to some extent, whilst the remainder are linked to expander stability and active-material purity. Several strategies to address these issues are being pursued in the research programme of the advanced lead–acid battery consortium, namely [8]:

- modification of separator microstructure to reduce oxygen-transport and prevent large shifts in the negative-electrode potential that hinder charge acceptance;

¹Fabrics consisting of assemblies of textile fibers (oriented in one direction or a non-random manner) held together by: (i) mechanical interlocking; (ii) fusing of thermoplastic fibers; (iii) bonding with rubber, starch, glue, casein, latex, cellulose derivative, or synthetic resin.

- development of improved charging algorithms that control water loss and enable the battery to achieve a full state-of-charge;
- development of expanders/additives with greater stability to allow more efficient charging of the negative-plate.

Since this paper focuses on separator characteristics, further discussion is centered around the approaches taken to modify separator properties. The overall aim is to reduce the rate of oxygen-transport. It has been reported that the diffusion coefficient for oxygen-transport in the gas phase ($\sim 0.2 \text{ cm s}^{-1}$) is significantly greater than that in sulfuric acid electrolyte ($9 \times 10^{-6} \text{ cm s}^{-1}$) [9]. This results in a mass-transport difference of close to a factor of 10 when oxygen solubilities are included (NB, the electrolyte film thicknesses in the pores of the positive and negative plates are estimated to be 0.01 and 0.1 μm , respectively). Hence, the principal mode of oxygen-transport in VRLA cells is via gas-phase diffusion from the positive-plate through unsaturated regions of the separator to the negative-plate.

One study has suggested [10] that the apparent oxygen diffusion coefficient in VRLA cells is influenced by both the separator saturation level and the tortuosity of the material itself. The most rapid rate of oxygen-transport is reported for saturation levels of less than 80%; levels above 90% saturation, the separator behaves as if it were flooded. Even at a given saturation level, oxygen-transport can vary considerably between materials due to differences in the paper-making processes from one manufacturer to another. Accordingly, one strategy to hinder operation of the internal oxygen cycle concerns reducing the overall pore-size distribution of the separator and hence, increase the tortuosity of the path for gas-phase diffusion. This approach may, however, increase water loss and grid-corrosion. Notably, Panasonic have recently developed a high-power VRLA battery that employs two different separators, one made from hydrophilic synthetic fibers and the other from fine glass fibers [11]. The battery is reported to give excellent deep-discharge cycle life, without capacity loss at the negative-plate or the need for excessive overcharge. This has been attributed to inhibition of the oxygen cycle by the synthetic separator.

A second strategy is based upon maintaining an adequate and uniform electrolyte film thickness in the pores of the negative-plate. When a VRLA cell is filled with electrolyte, the pores of the plates are coated with only a thin film of sulfuric acid. It is thought that the rate-determining step in the oxygen-transport process is diffusion through the electrolyte film in the pores so that oxygen can react with the sponge lead of the negative-plate [10]. The film thickness at the negative-plate is estimated to be in the order of 0.1 μm in a typical VRLA cell, but can vary significantly (even from one area of a negative-plate to another) with changes in the mass balance (acid-to-oxide ratio) or other factors that affect electrolyte distribution. It has, therefore, been proposed [12] that the separator material which directly faces the negative-plate should have a more open pore structure than that which faces

the positive-plate, in order to ‘flood’ the surface of the negative pores. This approach should inhibit the efficacy of the internal oxygen cycle, and might be achieved by employing a separator composed of two layers. One layer would contain predominantly fine fibers to give a high SSA material with fine pores, while the other would be a mixture of coarse and fine fibers to give a low SSA material with more open pores. Such a strategy may, however, increase water loss and grid-corrosion. A recent study [13] has also shown that other important characteristics for VRLAs, such as wicking, average pore-size and ability to resist stratification are improved by adopting a multi-layered separator design.

2. Physical properties of separators

As indicated earlier, separators for VRLAs require a complex mix of properties, since these influence three critical factors associated with VRLA battery performance, namely, electrolyte supply, oxygen transport and constraint of active-material growth. Ideally, a separator should:

- act as an electrical insulator;
- possess sufficient strength for processing;
- sustain a high level of pressure at the positive-plate;
- conform to the surface of the plates at the required level of force;
- provide a sufficient supply of electrolyte to the plates;
- prevent acid-stratification;
- allow effective oxygen-transport to the negative-plate.

There are many physical properties that can be used to characterize separator mats. For simplicity, these parameters are grouped in Fig. 1 in terms of their possible influence on the performance criteria for separators in a VRLA cell. The key physical properties which provide information about the mechanical characteristics of separator mats are: composition, structure, resilience (elasticity or compressive behavior), tensile strength, elongation and density (porosity). The capability of separators to fulfil functions associated with oxygen-transport and electrolyte supply can be evaluated from studies of parameters, such as porosity, SSA, pore-size distribution, wicking/acid absorption, and analysis of acid leachate.

Separators that have poor mechanical properties may tear or puncture during the manufacturing of cells. This would allow dendritic growth and inter-plate shorts to occur, and, thereby, would curtail the life of the cell. Moreover, such mats may not constrain adequately the growth of the positive active-material that arises during deep-discharge cycling. During such cycling, there is a tendency for the positive-plates to swell and expand, which can lead to loss of inter-particle connectivity and ultimately, PCL. This is a particular problem faced by thin-plate VRLA designs. Separators must also conform well to the uneven surfaces of the plates. Rigid materials can lose contact with the plates as the active material expands and contracts during cycling, which also

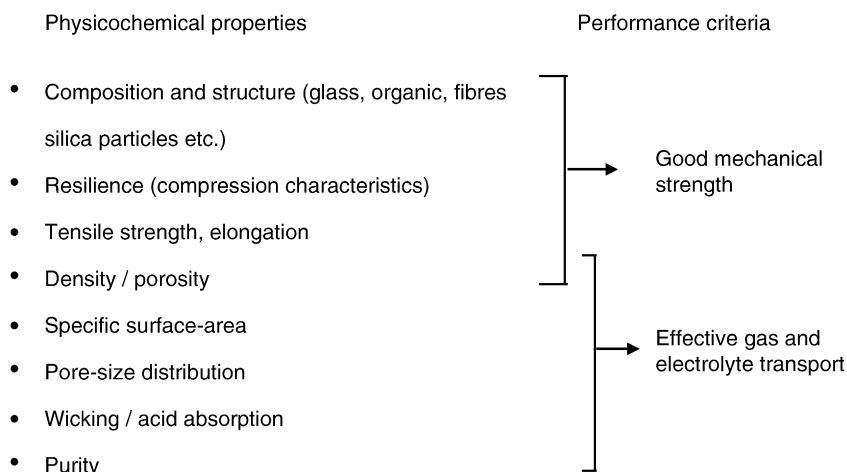


Fig. 1. Correlation of physical properties with performance parameters for separators in VRLA cells.

leads to capacity loss. Moreover, if the plate-separator contact is not uniform, the cell resistance will increase. This may raise the cell float voltage, and enhance the rate of water loss.

A ready supply of electrolyte must be supplied to the plates by the separator, or cells will deliver poor capacities. This is particularly important for cells discharged at low rates, where the active-material utilization is high, and more acid is required than is available in the pores of the plates. Separators must also resist the effects of acid-stratification in deep-cycling applications of batteries, i.e., the development of a non-uniform acid concentration in the cell. This will lead to poor active-material utilization in some regions, and hence, capacity loss.

Finally, there should be sufficient unsaturated voids in the separator to allow effective transport of oxygen to the negative-plate, i.e., at a suitable rate that allows the negative-plate to be brought to a full state-of-charge. The charging method, separator structure and electrolyte saturation level contribute significantly to the efficacy of oxygen-transport. Inefficient operation of the oxygen cycle leads to long charging times, grid-corrosion, and water loss. On the other hand, as mentioned earlier, when oxygen recombination is highly efficient (i.e., >95%), the potential of the negative-plate is shifted to such an extent that it cannot be charged sufficiently, and a steady 'walk-down' in negative-plate capacity occurs.

In summary, a separator should possess good mechanical strength and should permit the effective diffusion of gas and electrolyte. The aim of this paper is to provide a better understanding of the link between the physical properties of RBSM separators and the performance of VRLAs, and to define the requirements for an ideal separator.

3. Separator composition

Traditionally, RBSM separators are produced from blends of all-glass microfibers of varying diameter by means of a specialized paper-making machine (e.g., Rotoformer, Foudrinier) [14,15]. Fiber diameters are typically in the order of

<1 μm (fine) and 3 to >10 μm (coarse). A percentage of even thicker, chopped strand glass-fibers is also sometimes used to enhance the stiffness and wet crush resistance of the separator [16]. The blending ratio of the fibers is particularly important, since the desired physical properties of the mat must be balanced against the cost. For example, mats that contain a high proportion of the more expensive fine fibers have a large internal SSA, small pore-size distribution, and higher tensile strength. Incorporation of less expensive, coarse fibers decreases the tensile strength, and reduces both the SSA and the resilience of the mat when compressed in the battery. Some of the benefits of the use of finer glass fibers can be traced to Griffith's theory of the fracture mechanics of glass [17]. Griffith showed that very thin fibers of glass have much higher tensile strength because they have less flaws. The finished product, which is supplied in the form of a roll, is a voluminous, wet-laid,² non-woven mat with high porosity (~95%).

Separators composed of all-glass fibers have a number of important attributes. Microglass fibers have good chemical stability in the presence of acid, and high resistance to oxidation over a wide temperature range. On the other hand, separator materials must be readily wettable by electrolyte in order to perform effectively. The contact angle of glass fibers with sulfuric acid is zero and under this condition, the acid wets the fiber completely and spreads freely over its surface [18]. The wettability of all-glass separators, therefore, is excellent and depends only on the viscosity of the acid and the surface roughness of the fibers. Increased viscosity and fiber roughness serve to reduce separator wettability. Glass-fiber separators have a distinct advantage over materials composed of, for example, organic fibers where the contact angle with sulfuric acid is greater than zero. In such cases, the liquid is relatively non-spreading and will not wet the material properly. Organic materials can be treated with

² Wet laying is the process of forming a web by dispersing fibers in an aqueous medium, and then collecting them on a screen or perforated drum. Such materials are referred to as 'wet-laid non-wovens'.

surfactants to enhance their wettability in acid, but the change may not be permanent. Thus, properties, such as good chemical stability and permanent wettability, together with low cost, give microglass fibers an advantage over most materials.

Microglass-fiber separators also have some disadvantages. Such separators are composed typically of 95% air and 5% solid glass fibers. Such materials are held together mainly by the frictional forces of the glass fibers, and once wetted the coefficient of friction is lowered. Consequently, microglass-fiber mats undergo relaxation/contraction once they have absorbed sulfuric acid, and become compacted by plate expansion. Both these features act to reduce the plate-group pressure, commonly referred to as compression,³ which is essential for good battery life [4–7]. Thus, it is particularly important that any loss of plate-group pressure due to separator relaxation is minimized. Furthermore, the tendency nowadays is to employ a smaller percentage of fine glass fibers to reduce the cost of RBSM. Consequently, standard glass mats used in many VRLAs generally contain more coarse fibers, which gives a low-SSA material with less resilience and, therefore, less ability to maintain adequate plate-group pressure. In some quarters of the battery community, it is thought that there has been a decline in the performance of VRLAs that has been caused partly by the requirement of more demanding duties from batteries, and partly by changes in separator composition and structure [19]. Consequently, attention has turned to improving the properties of RBSM, preferably with minimal increase in cost.

Improvements are being sought by separator manufacturers through the incorporation of: (i) various proportions of organic fibers, such as polyesters, polyethylene and polypropylene; (ii) significant proportions of fine-particle silica; (iii) both (i) and (ii); (iv) increased fine-fiber content; (v) increased density. Nevertheless, most of the materials are still based on glass fibers. On the other hand, composite materials, such as glass-advanced polyester fiber hybrids, have emerged as real alternatives to all-glass mats, and offer superior tensile strength and resilience [20,21]. Moreover, even when such materials are ‘fully-saturated’, the presence of a small content of hydrophobic fibers creates unfilled pores and assists the transport of oxygen. All-organic, non-woven RBSMs (e.g., melt-blown⁴ polypropylene materials)

³Historically, the term ‘compression’ has been used when referring to the mechanical pressure between the adjacent plates and separators in a plate-group. This is because the standard type of separator (micro-glass-fiber) is a elastic material which becomes compressed under load, a certain percentage compression translates approximately to a certain pressure on the plates and separators. More recently, researchers have begun expressing the magnitude of plate-separator pressures in standard units of pressure (e.g., kPa). Reference to pressure (rather than percentage compression) allows easier and more accurate quantification of the forces experienced by the plate-group.

⁴Melt-blowing is a method of forming fabric from thermoplastic resins; the resin is melted, extruded and air-blown with fast-moving air that stretches or attenuates the fibers, which are then condensed and collected. Such materials are known as melt-blown non-wovens.

have also been used, but there are concerns with the decreased high-temperature stability of such materials and in some instances, the poor wicking and drainage properties. A ceramic tile, made from inorganic material, exhibits excellent compression-resistance, but problems with loss of contact with the plates are encountered due to its complete rigidity and inability to conform to the surface of the plate [22]. Furthermore, ceramic materials are extremely costly. A wettable organic material based on microporous polyethylene, termed the ‘acid-jellying separator’ (AJS), has also been developed [7]. This material is more rigid than microglass-fiber mat, yet is able to mould to the surface of the plates. The cycle-life of cells assembled with AJS appear to be promising, but comparison with a state-of-the-art RBSM, suitable for deep-cycling, has not been reported. In the near-term, it is unlikely that this material will find widespread use due to the high cost and low-porosity of the material, and to difficulties in scaling-up the manufacturing process.

4. Resilience

Expansion of the positive active-material is inherent in plate charge–discharge and if unchecked, results in capacity loss. Cells subjected to deep-discharge at high rates are particularly prone to this mode of failure. The ability of the separator to maintain an adequate force against the plates (i.e., the plate-group pressure) is important in achieving good cycle-life. In an RBSM cell, the pressure is provided by subjecting the plate-group to an external force prior to insertion into the container [6]. This reduces the thickness of the RBSM between the plates and sets up a force which is directed against the plates and the cell container. Measurements of the pressure and how the separator yields to this pressure (i.e., its thickness) evaluate the capability of the separator to maintain a certain plate-group pressure, and its resilience (i.e., the ability to resume its original shape after compression or extension).

The behavior of RBSM materials when subjected to a certain force or pressure is often described as ‘spring-like’. Strictly speaking, this is not correct. Spring-like materials are linearly elastic and their behavior can be described by Hooke’s Law, where the magnitude of the force, $F(x)$, is a linear (reversible) function of the change in thickness of the material, x , [23]. RBSM separators, however, show a combination of plastic-deformation and elastic characteristics when subjected to a given force. That is, their compression-extension behavior is not reversible, as is expected from a purely elastic material. One way of describing the properties of such materials is to use the terms stress, strain and the compression modulus [24]. The volume stress, ΔP , is defined as the ratio of the magnitude of the normal force, F , to the area, A . This quantity $\Delta P = F/A$ is also called the ‘pressure’. The volume strain is equal to the change in volume, ΔV , divided by the original volume, V . Stress is proportional to the force that produces a deformation; strain is a measure of

the degree of deformation (or change in thickness), and the constant of proportionality is the bulk compression modulus, B , i.e.,

$$B = \frac{\text{volume stress}}{\text{volume strain}} = - \left(\frac{F/A}{\Delta V/V} \right) = - \frac{\Delta P}{\Delta V/V} \quad (6)$$

The force exerted by the separator is comprised of surface tension forces, friction forces and elastic forces of the fibers. If the material is released, it will expand by a certain amount, with a certain strain–stress (or thickness–pressure) behavior. Thus, although RBSM materials are not truly spring-like, when compressed they possess some stored energy, and this allows such separators to maintain pressure against the plates.

One problem is that, over the years, many protocols have been used to assess the resilience or thickness–pressure behavior, and it is now well-known that the measured thickness of separator materials is highly dependent upon the method of testing and the area of the pressure foot (anvil) which is in contact with the separator test material. Nowadays, most separator manufacturers use a method for assessing the resilience of RBSM which is recommended by the Battery Council International (BCI) Technical Subcommittee on Separators [25]. The BCI test measures the thickness of the separator under various loads that are added to the anvil stem of a micrometer. The diameter of the anvil is 29 mm. The thickness determined under a load (compression) of 10.34 kPa is the so-called BCI thickness, and the separator is considered to be at zero compression at this point. In the standard BCI test, increasing loads are applied to a separator and a minimum amount of time (30 s) is allowed for the separator to achieve a constant thickness (compression). The loads are removed entirely after the application of each given pressure, and the thickness is determined again (recovery). In this way, alternating compression and recovery measurements are made. The data are

used to plot compression and recovery curves for the separator. Measurements are made for a given RBSM, both dry and acid-saturated. During the acid-saturation step, the separator is not compressed, and the amount of acid added is representative of saturation levels inside a battery (six to seven times the weight of the dry separator). Compression and recovery curves for a typical all-glass RBSM are shown in Fig. 2, and the values of separator thickness at increasing applied pressure are given in Table 1. The dashed line in Fig. 2 indicates the alternation between compression and recovery measurements.

The curves in Fig. 2 show that the thickness of the dry separator (dry compression) decreases under increasing loads. A further drop in thickness is observed upon partial saturation of the separator with acid (wet compression); this is presumably caused by adhesion between the acid-soaked fibers due the effects of surface tension and a change in the coefficient of friction amongst the fibers. It is also seen that, for a given separator thickness, an acid-saturated separator will apply less force to the plates than a dry separator. Consequently, when acid is added to a dry plate-group, where the inter-plate spacing is fixed, there is a fall in plate-group pressure. Following saturation, the plate-group pressure remaining inside the battery is critical. If it is too low, then the battery cycle-life will be curtailed. Recent research conducted in the ALABC programme suggests that the wet plate-group pressure needs to be maintained at a level of 40 kPa or greater [26].

Although the BCI test provides some useful information regarding the compression characteristics of separators, there are a number of limitations with this approach:

- only a single run is performed in the dry and acid-saturated states, and thus no information is obtained regarding any further ‘packing-down’ of the separator;

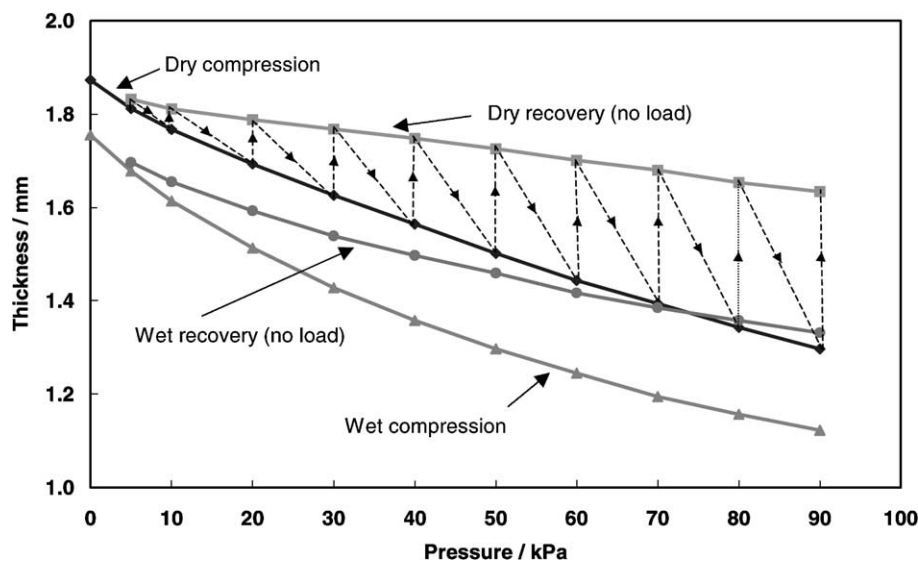


Fig. 2. BCI compression vs. applied pressure for typical all-glass separator. Dashed line indicates alternation between compression and recovery measurements.

Table 1
Physical properties of a typical all-glass RBSM separator

Property	140 All-glass
Composition	Glass, fine fiber and chopped strand
Grammage (g m^{-2})	256
Density, 10 kPa (gsm mm^{-1})	140
Thickness ^a , dry, 10 kPa (mm)	1.82
Thickness ^b , dry, 10 kPa (mm)	1.42
Thickness ^a , dry, 20 kPa (mm)	1.59
Thickness ^b , dry, 20 kPa (mm)	1.38
Thickness ^a , dry, 50 kPa (mm)	1.45
Thickness ^b , dry, 50 kPa (mm)	1.26
Thickness ^b , dry, 60 kPa (mm)	1.23
Thickness ^b , wet, 10 kPa (mm)	1.19
Thickness ^b , wet, 20 kPa (mm)	1.18
Thickness ^b , wet, 50 kPa (mm)	1.13
Thickness ^b , wet, 60 kPa (mm)	1.10
MD tensile (kN m^{-1})	1.33
CD tensile (kN m^{-1})	0.89
MD elongation (%)	4.2
CD elongation (%)	5.7
BET (N_2) SSA ($\text{m}^2 \text{g}^{-1}$)	2.1
Volume porosity	94.4
Min. pore diameter ^c (μm)	1.8
Max. pore diameter ^c (μm)	10
Mean flow pore diameter ^c (μm)	2.9
Pore-size distribution	See Fig. 6a
Acid absorption ability (Acid ^d in grams per gram separator)	5.56 (60 kPa) 5.33 (80 kPa)
Electrical resistance ($\text{m}\Omega \text{cm}^2$)	11.0

^a BCI test.

^b Piston-cell, steady-state measurement.

^c Coulter analysis, average of four analyses.

^d Relative density: 1.300.

- the method is not representative of actual cell conditions (e.g., arrangement of plates and separators), and it is known that the separator thickness obtained for the same nominal force differs according to the area of the pressure foot;
- information about the long-term compaction behavior of the separator is not obtained.

To address these limitations, CSIRO has developed innovative protocols for the evaluation of separator performance. The work has been undertaken during a series of ALABC projects [6]. A novel device for the measurement of separator thickness under a range of applied pressures was designed and built by CSIRO (Fig. 3). This device, termed the ‘piston-cell’ consists of a perspex case in which a piston, driven by gas-pressure, is used to apply given levels of plate-group pressure to the separator material under test. Purpose-written software controls automatically the pressure which is applied, and records the cell voltage, current, charge–discharge capacity, and plate-group thickness. The software also allows the piston-cell to be used to determine the effects of cycling a VRLA cell at constant plate-group pressure (monitoring thickness) or at constant plate-group thickness (monitoring pressure).

The compression characteristics (thickness–pressure tests) of the candidate materials are measured in piston-cells by applying pressures of 10–80 kPa, in increments of 5 kPa, to ‘plate-groups’ which consist of eight separators interspersed with sheets of polyvinyl chloride. In the first set of measurements, the separators are dry. The thickness at each pressure is recorded after 30 s, provided that the rate of change of thickness is $\leq 4\% \text{min}^{-1}$. Otherwise, the pressure is maintained until this ‘cut-off’ target is obtained. Four repeats of the test are performed to give a total of five runs. Next, whilst under vacuum and subjected to a plate-group pressure of 80 kPa, the separators are saturated by filling the cell with acid (1.300 relative density). After 1 h, the excess acid is decanted. The compression characteristics of the wet separators are then evaluated by the same procedure. Several dry and wet runs are conducted, until there is little difference in thickness between subsequent runs, i.e., the materials have reached a ‘steady-state’ thickness.

Thickness–pressure plots for a typical all-glass material are presented in Fig. 4, whilst values for separator thickness at increasing applied pressure are listed in Table 1. At pressures up to ~ 70 kPa, there is an appreciable decrease

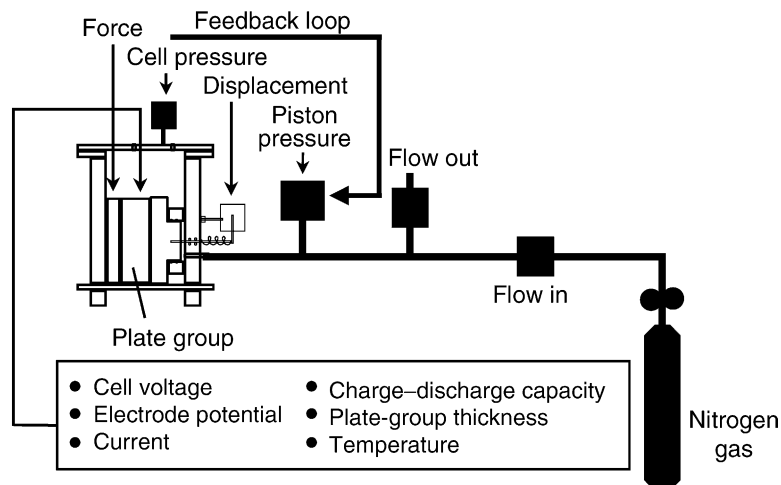


Fig. 3. CSIRO piston-cell for evaluation of separator performance.

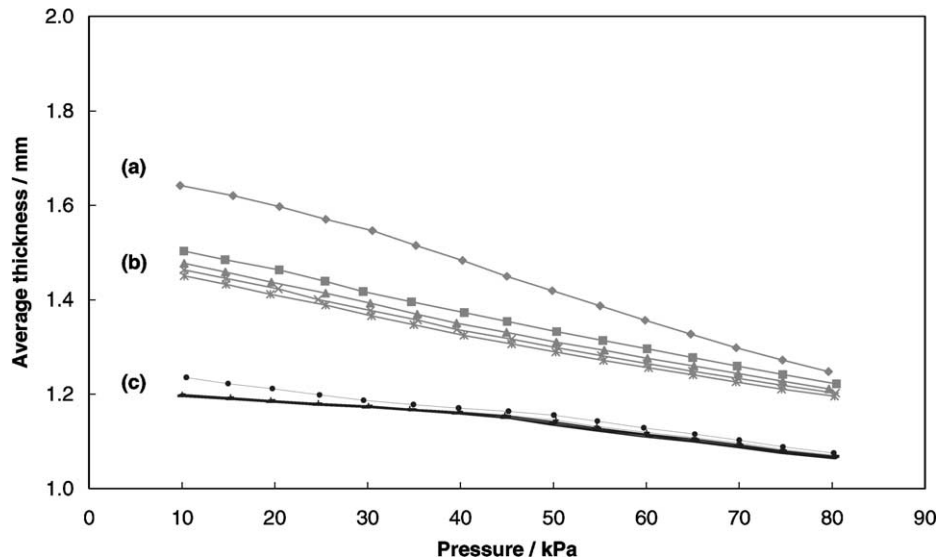


Fig. 4. Average thickness of typical all-glass separator (based on data for eight sheets of material) as function of applied pressure for the following conditions: (a) dry, first run through pressure range; (b) dry, second (upper plot) and subsequent runs; (c) saturated with sulfuric acid (relative density: 1.300).

in the average dry thickness between the first and second dry runs (plots (a) and (b), Fig. 4), i.e., there is some ‘packing-down’. Upon saturation, a further fall in thickness is observed at all pressures (plot (c), Fig. 4). Both the BCI and piston-cell tests show similar trends (Figs. 2 and 4), and demonstrate that a typical all-glass separator will exert less force on the plate in the wet state than in the dry state. The values obtained from the piston-cell tests are somewhat lower than those measured in the BCI tests (Table 1). Since the configuration of the piston-cell simulates more accurately

that of a working VRLA cell, it is likely that these values are more meaningful to battery manufacturers.

To enable comparison of the performance of different RBSM materials, the thickness–pressure plots are normalized to their steady-state thicknesses at 10 kPa in the dry state. The results for an inorganic-ceramic (RBSM A), a glass–silica (RBSM B) and a typical all-glass separator (RBSM C) are displayed in Fig. 5. The RBSM A and B separators are developmental materials. Such normalization means that the greater the displacement of the curve below

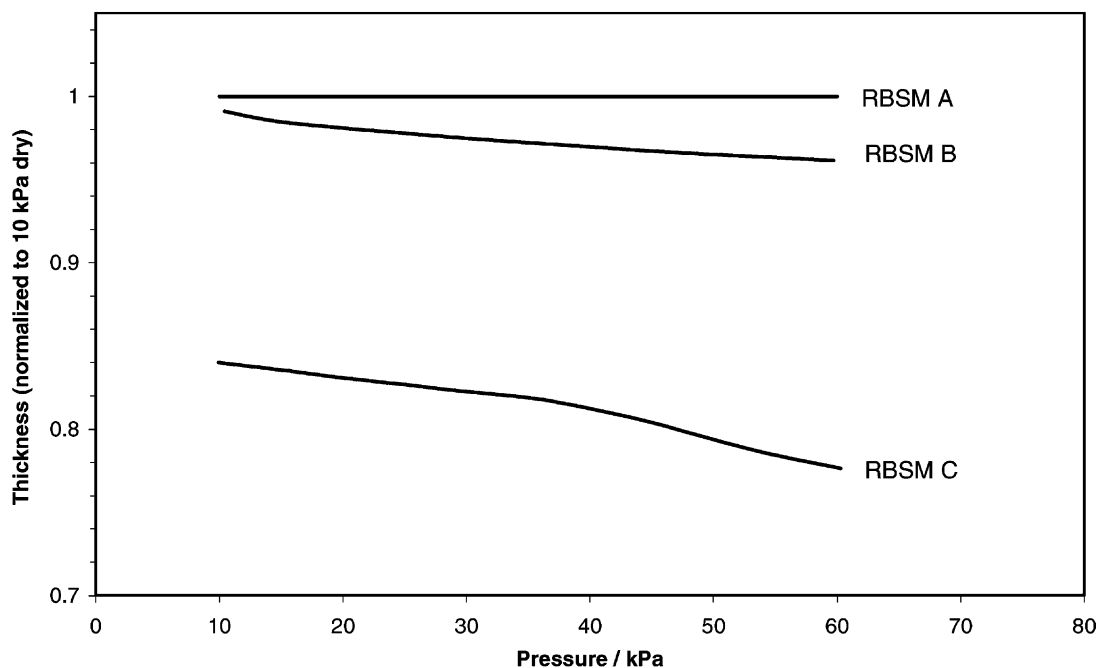


Fig. 5. Thickness–pressure behaviour of different separator materials when saturated with acid. Each line represents the steady-state behavior. RBSM A: developmental inorganic-ceramic material; RBSM B: developmental glass–silica material; RBSM C: typical all-glass material.

that for a rigid material (for which thickness is unaffected by wetting with acid), the greater is the separator compaction upon wetting. In this way, the data in Fig. 5 provide a relative indication of the extent to which a material packs down when saturated with acid. The ability to retain close to the original (dry) thickness (force) is an important property for separator materials since it exerts a strong influence on the accuracy to which the plate-group pressure of a cell can be set. The extent to which the materials yield to increased applied pressure, i.e., the ‘compressibility’, is given by the slope of the plots in Fig. 5.

The RBSM A separator is a completely rigid material. It does not yield to applied pressure, nor is it affected by wetting. It exhibits excellent compression-resistance but, as mentioned earlier, its rigidity may lead to loss of contact with the plates and an inability to conform to the surface of the plate upon charge–discharge cycling. The RBSM B separator is more affected by wetting than RBSM A, but far less than RBSM C. Its thickness–pressure plot shows only a small vertical displacement from that for a rigid material. This is a desirable characteristic. The RBSM C separator undergoes an appreciable degree of compaction upon wetting, and it is therefore considerably more difficult to set and maintain an accurate plate-group pressure with this material. It also has a slightly larger thickness–pressure slope, which demonstrates that for the same change in pressure experienced by, for example, RBSM B, a greater change in thickness will be produced in RBSM C.

The piston-cell tests are performed over a period of up to several hours, whilst the BCI tests occupy a shorter interval (15 min). Information on the long-term durability of RBSM

materials is also important, as it is necessary to establish the extent to which materials can retain a given thickness over extended periods (e.g., months). Such information can provide a useful estimate of the plate-group pressure within a cell at some later time in service. CSIRO has devised a test to assess mechanical durability under conditions that simulate, to some extent, those in a VRLA cell. In this so-called ‘constant-load’ test, ten sheets of separator are placed in a leak-proof bag and saturated with acid. The separator ‘stack’ is placed between perspex spacers, and a load corresponding to, for example, 40 kPa is placed on the stack. The thickness of the stack is measured initially, and then every few days thereafter. The test can also be performed using the piston-cell, where data are logged every few minutes. To enable comparison between materials of different thickness, the data are reported as the ratio of the measured to the initial thickness.

Results for RBSMs A to C are shown in Fig. 6. RBSMs B and C experience a fall in thickness during the first 3 days. The rate of fall of thickness is greatest for RBSM C and ultimately, this material suffered the largest loss of thickness. Most importantly, though, RBSM B approached its final thickness in a relatively short time (<10 days). For RBSM C, such a state was not attained until around 60 days. Based upon evidence obtained from both the short-term and long-term thickness–pressure studies, it can be concluded that RBSM B gives the best performance because it retains a greater degree of thickness upon wetting, and achieves constant thickness more rapidly. The resilience characteristics suggest that this material is suited for use in VRLA applications where maintenance of adequate plate-group pressure is critical for good performance (e.g., high-rate, deep-cycle).

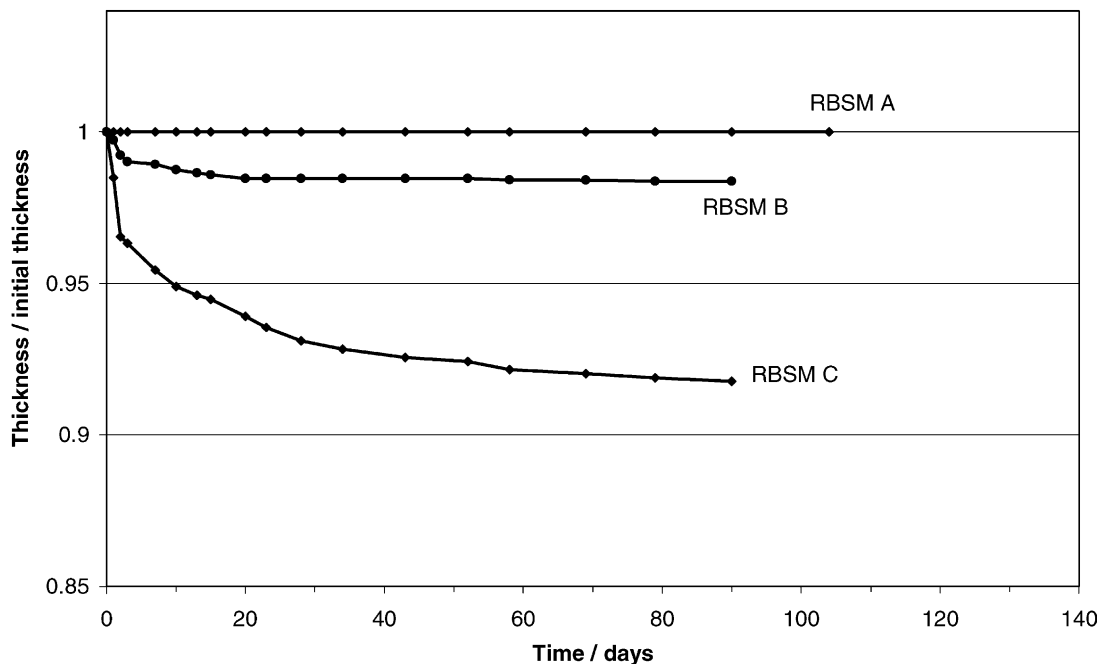


Fig. 6. Ratio of separator thickness to initial thickness (acid-saturated) as function of time at constant load of 40 kPa for different separator materials. RBSM A: developmental inorganic-ceramic material; RBSM B: developmental glass-silica material; RBSM C: typical all-glass material.

5. Tensile strength and elongation

The properties of tensile strength and elongation provide a measure of the ‘robustness’ of RBSM materials in the manufacture of VRLA batteries. Tensile strength refers to the maximum tensile stress sustained by a test sample prior to rupture, and is reported as the force per unit width of the sample. Elongation is the maximum tensile strain developed in a test sample prior to rupture. It is expressed as the percentage increase in length of the sample relative to the original length. Greater tensile strength allows for faster processing during battery assembly and thus lowers manufacturing costs. Tensile and elongation characteristics can be very sensitive to storage conditions (e.g., temperature, relative humidity) and will usually degrade with time. Fiber orientation is not completely random, and thus, tensile and elongation properties in the direction in which the mat is manufactured (the ‘machine direction’, MD) are usually higher than those across the width of the mat (‘cross direction’, CD).

Values of the MD and CD tensile strengths generally lie within the range 0.875–1.75 kN m⁻¹, while elongation varies from 0.5 to 10%. For example, the MD and CD tensile strengths for a typical all-glass RBSM are 1.33 and 0.89 kN m⁻¹, respectively, whilst the MD and CD elongations are 4.2 and 5.7%, respectively (Table 1; NB, this particular material was manufactured using advanced E-vanite fibers, which produce higher elongation. Most glass fibers give very low elongation). Tensile strength can be influenced by the fiber composition, SSA of the mat, and the manufacturing methods of both the glass fiber and the separator. Composite materials, such as glass–organic fiber hybrids typically give much higher values of tensile strength than all-glass separators, and high-SSA materials show greater strength than low-SSA counterparts.

6. Specific-surface-area and porosity/density

For an RBSM composed of glass fibers only, the SSA is influenced by the proportions of coarse and fine fibers. For materials of equal dry density, there is an increase in SSA with increasing content of fine fibers and thus, a decrease in the mean pore-size. The latter will restrict the transport of electrolyte and oxygen in VRLAs, particularly at high charge and discharge rates. On the other hand, the use of high-SSA separators (~2–2.5 m² g⁻¹) minimizes acid-stratification in deep-cycling applications of batteries. This is defined as the tendency for electrolyte of higher relative density to accumulate in the lower regions of the cell. For VRLA cells, a second form of stratification is also possible where the volume distribution of electrolyte is affected. For example, changes in the capillary properties of the separator can cause drainage of the electrolyte from the upper portions of the cell, and the resulting effects on cell performance are similar to those associated with a lowering of electrolyte

density. It has also been reported [27] that an increase in SSA can improve the resilience of RBSM. For a given weight of material, a greater content of fine fibers (i.e., higher SSA) offers improved elasticity.

Materials with low SSA (~0.8–1 m² g⁻¹) contain a higher proportion of coarse fibers and a more open pore-structure (Section 7). These materials will release acid held within the pores more easily than materials with high SSA that have a smaller pore structure. Moreover, low-SSA materials show less electrical resistance in the saturated state, which may result in better high-rate performance (e.g., cold-cranking rates) from cells. For RBSM materials, values of electrical resistance are typically around 50–70 mΩ cm⁻². These measurements are performed in the flooded state using the BCI Battery Separator Test Method I (ohmic resistance) [25], since there is presently no approved BCI test to determine the electrical resistance of partially-saturated RBSM.

The volume porosity of the separator in VRLAs is critical. If the porosity is insufficient, then less acid is absorbed in the RBSM, and low-rate capacities are poor. To provide a sufficient supply of acid to the plates, materials with volume porosities of no less than 90% should be used; 94–95% is desirable. Adequate acid in the separator will also assist heat dissipation within the battery, and ameliorate the effects of any temperature rise. The lower acid content in the RBSM battery, compared with that for flooded or gelled batteries, is a disadvantage of this technology, and thus low-porosity separators should not be considered. It is possible, though, to increase the acid content of RBSM designs by allowing a greater ‘fringe’ area of separator, increasing the inter-plate spacing or filling the head space with additional separator material.

As with SSA, porosity/density influences the pore-size distribution in RBSM and hence, the effectiveness of gas and electrolyte transport. Consequently, materials with higher density (and, thus, lower porosity) are expected to show a finer pore structure and greater resistance to acid-stratification, but to wick more slowly (Section 8).

7. Pore-size distribution

The fluid-transfer properties of a VRLA cell, assembled with 100% microglass separator mat, depend on the nature of the electrolyte (density, viscosity), the composition, density, pore structure and degree of saturation of the separator, and the pore structure of the positive and negative active-materials. Work by Culpin and Hayman [10] has shown that the movement of fluid at the interface between the battery plates and glass mat separator follows the Laplace equation:

$$\Delta P_{\text{fluid}} = 2\gamma \cos \theta r^{-1} \quad (7)$$

where ΔP_{fluid} is the pressure difference across the fluid–fluid interface; r the average diameter of the capillaries (pores) in the system; γ the gas–liquid interfacial tension

(surface tension); θ the solid–liquid contact angle. For two different-sized capillary tubes connected to one another, fluid will move spontaneously from the wider to the narrower capillary due to the larger pressure difference across the interface in the latter capillary. This relationship holds as long as the liquid is not forced into the porous structure, or the structure is not immersed in the liquid. The situation is more complex in porous media, such as microglass mat and battery active-materials, since each has a range of pore sizes. The Laplace equation, however, is still valid. To ensure a high degree of electrolyte saturation in the plates, the mean pore-size of the separator should be greater than that of the active-materials (note, the average pore sizes for healthy positive and negative active-materials are, from experience, <1 and $5\text{--}6\ \mu\text{m}$, respectively). This will also provide maximum capacity for the cell. Moreover, if this is true, then the degree of saturation in the separator will be less than that in the plates, which will assist oxygen-transport from the positive to negative-plates. If the pore structure of the separator is too large (mean pore-size $>30\ \mu\text{m}$), then the risk of dendritic growth and the subsequent formation of short-circuits increases. For these reasons, a knowledge of the pore-size distribution of the separator in VRLA batteries is important.

There are three tests recommended by the BCI for the determination of the pore-size of RBSM [25], namely: (i) Procedure VA: Bubble Point Method; (ii) Procedure VB: Liquid Porometer Method; (iii) Procedure VC: Mercury Intrusion Method. Procedure VA measures the maximum pore diameter, whilst Procedures VB and VC determine the pore-size distribution and pore characteristics, respectively. Procedure VB is the widely used in the paper industry for the determination of pore-size. In this procedure, a CoulterTM or Porous Material Inc. (PMI) Porometer, or similar equipment, is used to measure the bulk pore-size characteristics of the RBSM materials in terms of number distribution and fluid-flow distribution. Several samples of the test material are subjected to measurement to gauge the degree of variability in the pore distribution. Pore distribution by ‘number’ simply describes the number of pores in each instrumental size range per unit area. Pore distribution by ‘flow’ weights the number distribution by the corresponding laminar fluid-flow rate for each range of pore-size. In so doing, this interpretation of the pore-size data attaches greater importance to those pores which contribute more to the flow through the separator by a liquid or gaseous fluid, and it therefore provides information on the permeability of the material. This difference is shown schematically in Fig. 7. For example, for a sheet of separator with a single hole (pore) $10\ \mu\text{m}$ in diameter, the porometer measurement would show a narrow peak, centered at $10\ \mu\text{m}$, that would rise up to exactly 100% for both the differential number and differential flow representations (Fig. 7a). If the separator had one hole of $5\ \mu\text{m}$ and another of $10\ \mu\text{m}$, the two differential number peaks would each be 50% high (Fig. 7b), while the corresponding

differential flow distribution peaks would rise to 20% at $5\ \mu\text{m}$ and 80% at $10\ \mu\text{m}$, since flow is roughly proportional to hole area (Fig. 7c). The plots for differential number or flow versus pore-size illustrate the distribution of pore diameters, whilst the plots of cumulative number or flow illustrate the cumulative contribution of the pore diameters to the porosity of the sample. The pore-size distribution plots obtained by Coulter analysis for four samples of a high-SSA, all-glass RBSM are shown in Fig. 8. In the differential flow plot (solid lines, Fig. 8a), the majority of the pore diameters lie within the range $1\text{--}7\ \mu\text{m}$, and there is only a small variation in distribution between the samples. This shows that the material is quite homogenous. The median pore diameter (i.e., the value at which 50% of pores have larger diameter, and 50% have smaller) is $\sim 2.5\ \mu\text{m}$. The plots for pore-distribution by number (Fig. 8b) and the corresponding median pore diameter are similar to those obtained from pore-distribution by flow. The distribution, however, is slightly narrower, since the larger pores are not ‘weighted’ according to the laminar fluid-flow rate. The minimum and maximum pore diameters are 1.8 and $10\ \mu\text{m}$, respectively, and lie within the pore range normally found for RBSM ($2\text{--}5\ \mu\text{m}$ within the separator plane, and $10\text{--}20\ \mu\text{m}$ perpendicular to this plane) [10]. Typically, most fibrous RBSM materials have an anisotropic distribution of pores through the separator, that is, the pores that lie within the plane of the separator are smaller than those that lie perpendicular to this plane. The pore structure of the material discussed here is relatively fine, which will hinder acid-stratification.

As mentioned in Section 1.2, a fine and tortuous pore structure may also hamper the efficiency of oxygen-transport during charging. This would improve the charge maintenance of the negative-plate. The influence of separator pore structure on oxygen-transport, however, is yet to be defined. Recent ALABC studies have demonstrated that there is a strong linear correlation between the rate of oxygen-transport and the degree of saturation of the separator, viz., lower saturation levels enhance oxygen-transport [28]. Moreover, it has been reported that oxygen-transport through non-wetted pores in microporous polypropylene membranes is substantially more rapid than through partially-wetted pores [29]. Therefore, careful management of the saturation level of the separator and maintaining a uniform electrolyte film thickness in the pores of the negative-plate may be the prime factors in controlling oxygen-transport through RBSM materials.

Another issue that has aroused interest concerns the desirability of an anisotropic or isotropic pore-size distribution for VRLA separators. As mentioned earlier, most fibrous microglass-based materials have an anisotropic distribution of pore-sizes. This is a consequence of the wet-laid manufacturing process. The small pores within the separator plane enhance wicking and inhibit stratification, whilst the larger pores perpendicular to this plane contribute to low electrical resistance and allow suitable rates of oxygen-transport. The ideal pore-size distribution for RBSM separa-

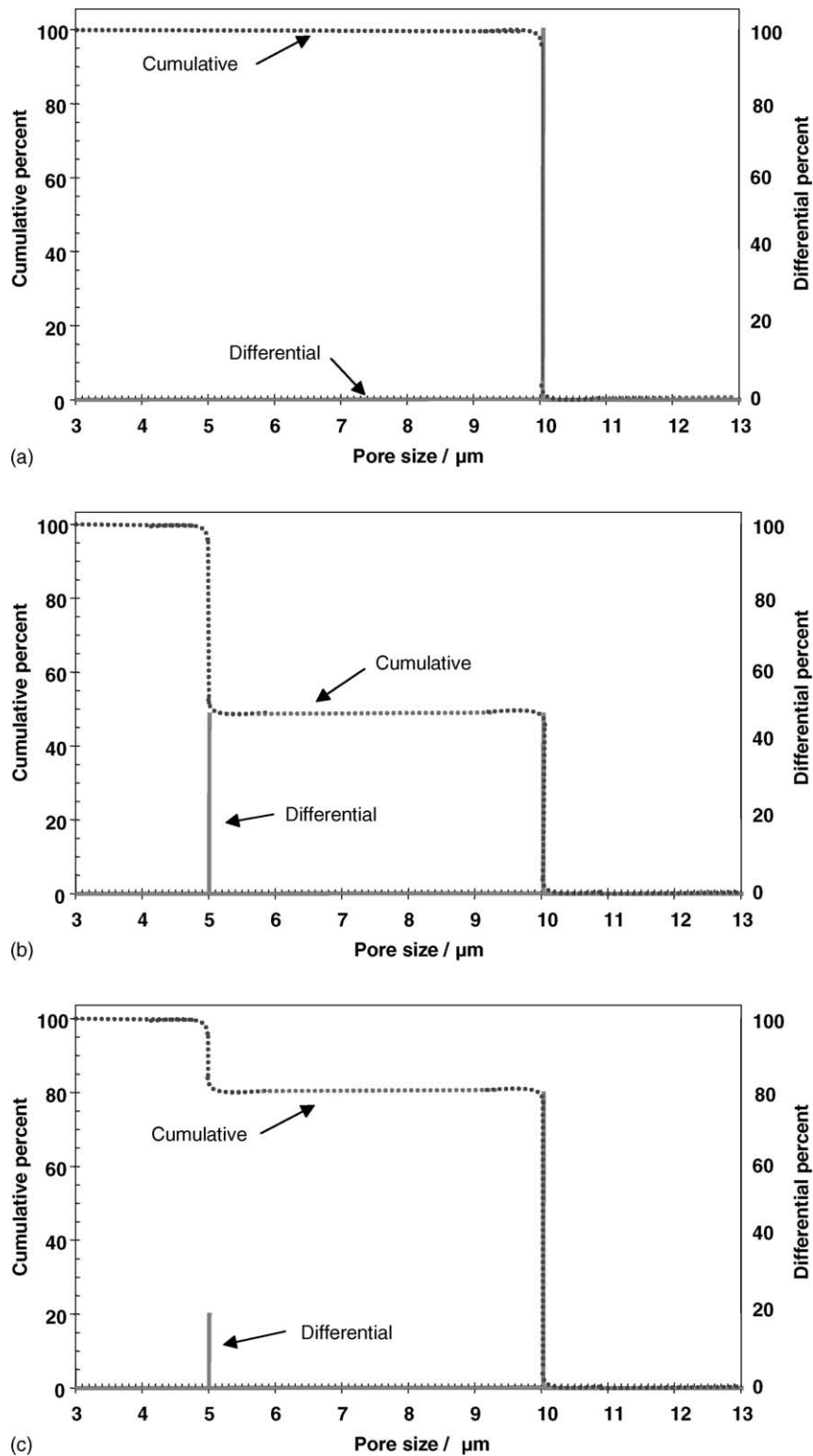


Fig. 7. Schematics of pore distribution: (a) by flow and number for sample with 10 μm pore; (b) by number for sample with 5 and 10 μm pores; (c) by flow for sample with 5 and 10 μm pores.

tors in various applications, however, has not yet been established. A range of views on this subject exist within the battery community [30]. For example, it is claimed that the ideal pore-size distribution is:

- (i) pores within the separator (x - y) plane, 2–4 μm ; pores perpendicular to this plane, 10–30 μm ;
- (ii) pores within the separator (x - y) plane, 1–2 μm ; pores perpendicular to this plane, ≤ 1 μm ;

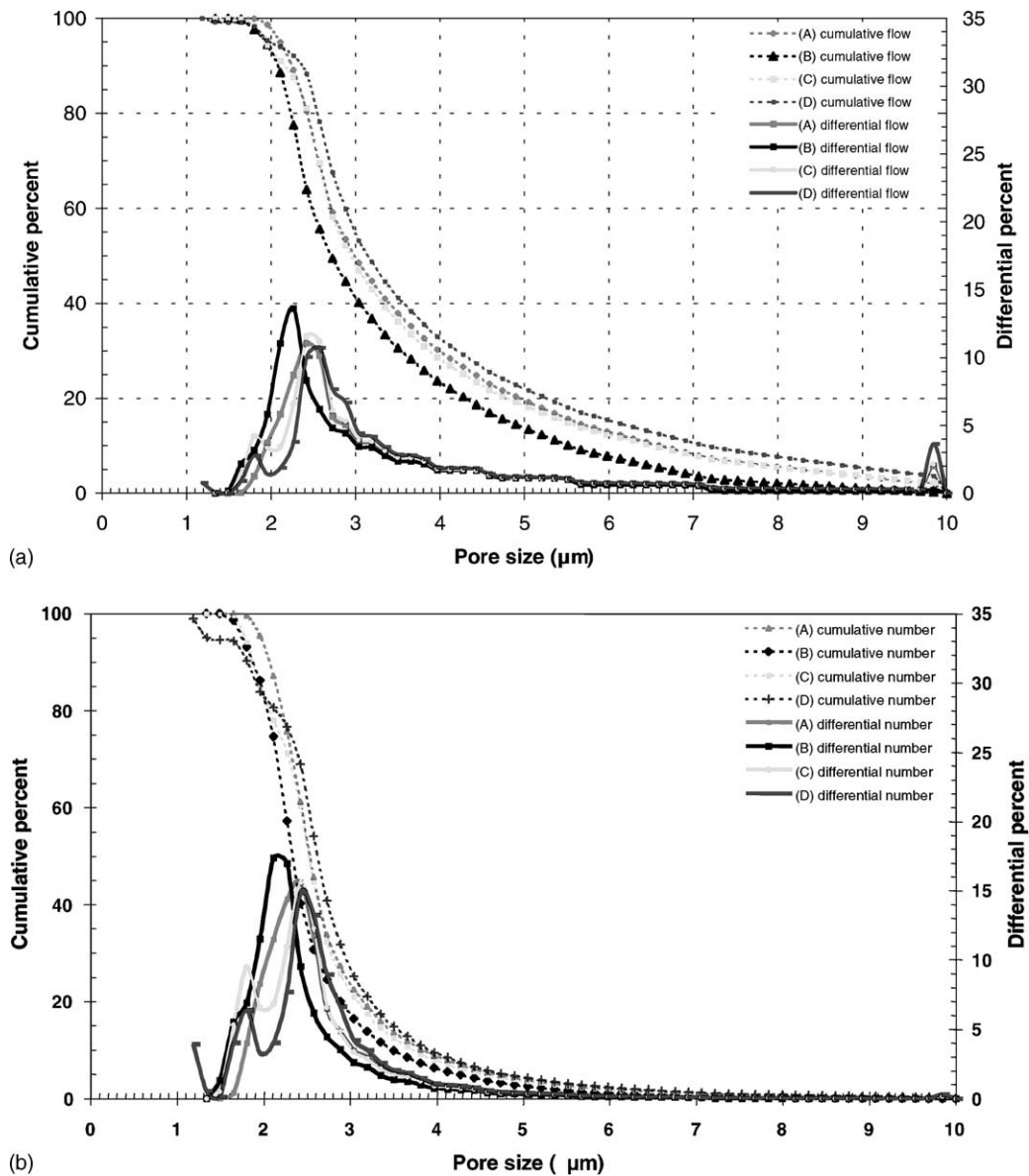


Fig. 8. Pore distribution by (a) flow and (b) number (Coulter analysis) for typical all-glass RBSM.

(iii) mean pore diameter within all planes, 1–15 μm, uniform distribution.

The first view is typical of the distribution found for microglass-based materials used presently, in many VRLAs. The second and third suggestions recommend pore-size distributions which are more uniform, i.e., the pore-sizes within and perpendicular to the separator plane are similar. It is thought that an isotropic or uniform distribution will create a more tortuous pore structure, particularly if the mean pore-size of the separator is small, and will therefore, reduce the efficacy of the transport of oxygen. Interestingly, non-fibrous separators, such as those manufactured from microporous polyethylene, for example, generally have an isotropic pore-size distribution. Accordingly, it has been proposed that a microporous sheet placed either between layers of glass mat

[12,13], or directly against the negative-plate [11] may hinder the operation of the internal oxygen cycle. Such an outcome would suit batteries for high-power applications, where charge maintenance of the negative-plate is problematic. There is still, however, some debate regarding the merits of this approach, and further studies are being conducted using both glass and non-glass materials with a variety of pore-size distributions in the ALABC research programme.

8. Wicking/acid absorption

Effective wicking is one of the critical properties of RBSM materials. In a VRLA battery, the separator must support a column of acid from top to bottom of the plate without any variation in saturation or concentration, and

permit electrolyte movement between the separator and plates. This function is usually assessed by wicking tests. Absorbent materials, such as RBSM have quite complex porous structures; there are pores (capillaries) of different sizes and shapes, and these are inter-connected in a three-dimensional network [18]. When electrolyte migrates through these pores, it follows a tortuous path, rather than a straight path as in an ideal capillary tube. Moreover, the electrolyte located in partially-saturated regions will experience, due to surface tension effects, varying forces from different pores. In a VRLA battery, the pores within the separator plane control the vertical wicking rate of acid. A larger pore structure within the separator plane will wick faster, but not as high. A finer pore structure will support a greater fluid height, but will wick more slowly. Moreover, a finer pore structure inhibits acid-stratification.

The BCI International Technical Sub-committee on Separators has reported that the wetting or wicking tests presently used by the separator industry are inadequate [25]. Acid wetting, wicking and drainage remain, however, critical characteristics of RBSM and must be assessed. One

method commonly used in the industry to assess wicking is to place strips of separators between clear perspex blocks of known dimensions. Thin spacers (e.g., polypropylene) are inserted between the perspex blocks to provide a compression of typically 20% when the perspex blocks are clamped together. The base of the apparatus is immersed in the wicking liquid (usually water or acid of known concentration), and the height of the wicking front is measured as a function of time.

Plots of saturation versus MD wicking height in water for a variety of RBSM materials are shown in Fig. 9. Comparison of the plots illustrates the changes in wicking height, and in the saturation levels of the separators. The saturation levels are defined as a ratio of the wet-to-dry weights of the separator, rather than a percentage level. As a guide, the ratio for a separator in a VRLA battery has a value of around six to seven. The wicking height is dependent on the pore structure, the wettability, level of compression, and the compressed porosity of the separator [10,28]. An RBSM with a high SSA and a fine pore structure supports a higher fluid height than a low-SSA material of equal dry porosity

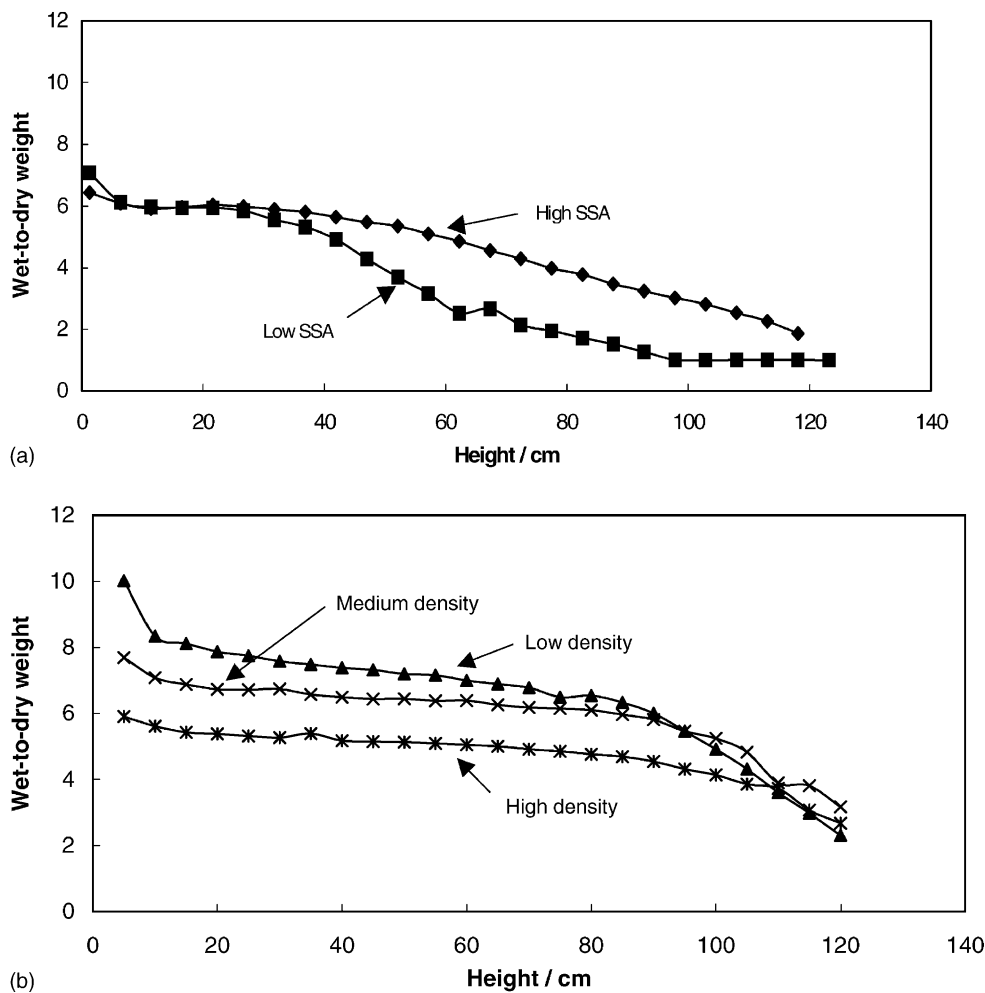


Fig. 9. Saturation vs. MD wicking height for RBSMs in water (20% compression, 24 h for (a) low and high SSA of equal dry density; (b) low, medium and high density of equal SSA.

(Fig. 9a). The saturation levels attained for the separators of equal SSA, but varying density are a reflection of the different porosities of the materials (Fig. 9b). For example, the low-density material, with a porosity of 94.4%, shows the greatest saturation level for wicking heights of up to 90 cm, whilst the high-density material, which has the lowest porosity (91.3%), displays the lowest saturation level for heights up to 35 cm. For plate heights of up to 35 cm, all separators in Fig. 9 show adequate wicking behavior for use in a VRLA battery, i.e., they are able to wick up to six to seven times their dry weight in acid.

One weakness of wicking tests is that they do not provide information on the ability of the separator to retain electrolyte, i.e., resist drainage. Since cells are often filled from the top of the container, this is an important measure. If electrolyte drains away from the upper regions of a fully-assembled cell, then acid starvation will limit capacity. There is little published information on drainage behavior. Culpin has shown [31] that the maximum drainage height for a typical glass-microfibre separator is greater than the wicking height. This is due to the irregular pore-structure of these materials, which contributes to problems with such capillary-rise hysteresis. For materials with cylindrical, parallel-sided capillaries, the wicking and drainage heights will be equal. Clearly, this is an area which requires further studies with a wide range of RBSM materials.

9. Towards an ideal separator

The ideal separator that suits all purposes does not exist. This is because different battery applications require diverse combinations of properties. There are a range of properties, however, that are considered generally desirable for most applications:

- acceptable tensile strength ($0.875\text{--}1.75\text{ kN m}^{-1}$) and elongation (0.5–10%) for processing;
- high porosity ($\sim 95\%$ uncompressed) to allow for effective acid filling and oxygen-transport;
- serve as an electronic insulator, but when partially saturated display low ionic resistivity ($50\text{--}70\text{ m}\Omega\text{ cm}^2$);
- readily wettable by sulfuric acid over the life of the battery;
- minimal shrinkage on wetting, sustain a high level of applied pressure at the positive-plate, and conform to the surface of the plates at the required level of force;
- resistance to attack by battery strength acid at high temperatures ($80\text{--}120\text{ }^\circ\text{C}$) and by oxidation at high potentials;
- high chemical purity, i.e., must not release metal or organic impurities, such as transition metals or chloride species;
- have a pore-size distribution ($1\text{--}20\text{ }\mu\text{m}$) which provides a sufficient supply of acid to the plates at the desired rate, but presents no risk of dendritic growth;
- have the ability to wick acid electrolyte to heights of up to 30 cm and minimize stratification and drainage.

Separators presently used in VRLAs meet some of these criteria. Most materials, however, are deficient in the area of resilience characteristics, viz., it is difficult to set and maintain adequate levels of plate-group pressure that constrain positive active-material growth. Although the incidence of premature failure of the positive-plate has been reduced, to some extent, by enhanced separator materials and manufacturing techniques, further improvements and developments are required to eliminate the problem entirely. Charge maintenance of the negative-plate is thought to be a major failure mode that limits life in VRLAs, in both cycling and float applications. It is considered that modification of separator properties, such as composition, multi-layer configuration, structure, pore-size distribution, etc. may be one method of impeding the efficiency of the internal oxygen cycle and improving the charge-acceptance. There is still considerable debate as to the ideal pore-size distribution for separator materials in various applications, and whether it should be anisotropic or isotropic in nature. These and other issues are being addressed in the ALABC research programme.

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