



Gas transfer in saturated and partially saturated absorbent separators (AGM)

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Abstract

This paper will cover the mechanism of gas transfer from plate to plate in saturated and partially saturated separator systems.

The movement of a gas through liquid filled or partially filled capillaries can be applied to the way that gases moves through separators for valve-regulated lead–acid batteries (VRLA). Experimental data shows that high levels of saturation (>90%) inhibits easy gas movement.

This inhibition of the gas movement is overcome due to the build up of pressure at the separator/electrolyte interface causing bubbles of gas to pass through the separator. The separator has an influence over the saturation level and the pressure required to allow gas movement by overall pore structure in the *x*, *y* and *z* planes, composition, hydrophobic or hydrophilic nature and compressibility. The presence of surfactants can influence the formation of gas bubbles, either being an aid or a barrier to their formation.

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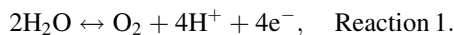
Keywords: Gas transfer; Saturation; Separator; VRLA; Compression; Sheet formation; AGM; Batteries; Lead

1. Oxygen cycle

1.1. Main reactions

The VRLA battery is based on the internal oxygen cycle. The fundamentals of this cycle are described briefly below. The reactions as shown are for the charging reactions and are reversed during discharge.

During float charge the current decomposes water and oxygen is evolved on the positive plate according to the reaction:



The oxygen diffuses via the gas phase through the unfilled pores of the absorbent glass mat (AGM) to the negative plate, and reacts there with the formation of lead oxide, lead sulphate and water:



This is a slow, rate-determining step due to the low O_2 concentration, limited by diffusion and the unfavourable kinetics of the gas–solid reaction.



The float current passing through the cell then reduces on the negative electrode, thus, the lead sulphate is converted

back to lead and sulphuric acid so that a closed cycle (oxygen recombination cycle) is obtained. Due to the oxygen recombination reaction very little hydrogen evolution occurs on the negative plate.



Balancing of all of these reactions results in no net change to the cell chemistry; the only effect is the conversion of electrical energy to heat via enthalpic contributions from reactions 2 and 3.

The overall reaction for the oxygen recombination cycle is hence:



1.2. Side reactions

The cycle is not without its side reactions/side effects which lead to the reduction in capacity during the service life of the battery or cell.

At the positive plate the Pb grid corrodes to PbO_2 . The corrosion rate increases with temperature (doubling approximately every 10 °C), float voltage and acid concentration. The corrosion attack may be an area type attack or a grain boundary attack or a combination of both. The corrosion product, lead dioxide, requires a 37% higher volume than the lead source material. This volume expansion induces mechanical forces in the grid, which will become deformed

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and stretched. At the negative plate hydrogen evolves and corrosion of the grid and conducting elements take place as a result of the oxygen recombination reaction and the presence of inorganic sulphate salts in the electrolyte.

Heat is generated internally during charge and discharge. Heat stagnation can cause thermal runaway, which sees an increase in the current and temperature leading to the destruction of the battery.

These secondary reactions lead to water loss, which under normal conditions only reduces the capacity during service life slightly.

Excessive water loss by one or more of the above mechanisms can cause the premature failure of a VRLA battery by a process called dry-out. Dry-out results in reduced electrolyte volume and capacity loss.

1.3. Oxygen transfer

In the oxygen cycle, oxygen generated during charge and overcharge at the positive plate can transport from the positive plate to the surface of the negative plate through the separator.

At the positive plate the oxygen bubbles produced at the interface of the positive plate either burst allowing the oxygen to diffuse through the separator or to migrate upwards and over the separator to the negative plate. The passage of choice is the one with the least constraint be this the shortest or easiest path to follow, which is through the separator.

At the negative plate the oxygen penetrates a thin electrolyte film at the plate surface and is reduced as described in [Section 1.1](#).

This paper will look at the transport of oxygen through the separator from the positive to negative plate looking at diffusion and how this can be affected by the nature of the AGM with particular interest in saturation, pore size, sheet formation, compression, gas pressure, temperature, viscosity, contact angle, and molecular weight which all have an influence on diffusion.

2. What affects the transfer of oxygen through the separator?

When looking at the movement of gas through a separator returning to first principles can explain the different phases present and how they interact within the system. However, actual test cells do not always agree with theoretical results.

2.1. Diffusion

Diffusion occurs by a variety of different means:

- *Knudsen diffusion* occurs when the mean free path is significant relative to the pore size and is a wall interaction.

- *Fick's diffusion* is a molecule to molecule interaction.
- *Transition diffusion* is a combination of Knudsen and Fickian diffusion.
- *Surface diffusion* occurs when the solutes adsorb onto the surface of the pores and jump from one adsorption site to another.
- *Hydrodynamic flow* (Poiseuille's law) occurs when there is a difference in total pressure across the porous solid.

The movement of oxygen through the separator by diffusion is influenced by several factors that increase or decrease the transfer rate. In the assumed pore structure of an AGM the movement by diffusion takes into account the porosity, pressure, temperature and molecular weight. The separator tortuosity may be a factor, depending on the separator composition and porosity.

2.1.1. Porosity

Porosity is the ratio of the volume of a substance's pores or interstices to the total volume of its mass, expressed as a percentage. The porosity of a substance can be changed by filling the pores or altering the base nature of the material. This section will discuss such changes.

2.1.1.1. Level of saturation. With high levels of saturation, gas cannot enter the pores which are filled with electrolyte unless a force is applied.

With lower levels of saturation, gas can move freely through a porous structure. This was demonstrated by the work on AGM conducted by Culpin and Hayman [1] and Ball et al. [2] where their measurements showed that the rate of oxygen diffusion is significantly dependent on the level of saturation with sulphuric acid ([Fig. 1A](#)). Two limiting cases were found. At low levels of saturation (<60%) the diffusion rate is comparable to gaseous diffusion whilst at higher saturation's (>90%) the diffusion rates are several magnitudes lower and are equivalent to gaseous diffusion through a liquid. Effectively below 60% saturation the separator behaves as if there was no liquid present and above 90% saturation the separator behaves as if it were completely saturated with liquid. The measured diffusion rates followed the theoretical values expected from the Laplace equation for the diffusion of gases through liquid filled capillaries. Their general approach/conclusions relate to the basic physics of porous media.

The introduction of a surfactant gave a conclusion that the rate of diffusion through the separator under test was reduced ([Fig. 1A](#)). Further discussion on this point, under [Section 2.4](#), reviews both anionic and non-ionic surfactants—both yield different outcomes which is an extension to the previous findings.

These tests were conducted in the uncompressed state and in a horizontal plane, which would encourage the electrolyte at the various levels of saturation to move to the lower surface. A wet laid separator has two surfaces a wire side and a felt side. Of importance is the gradient through the

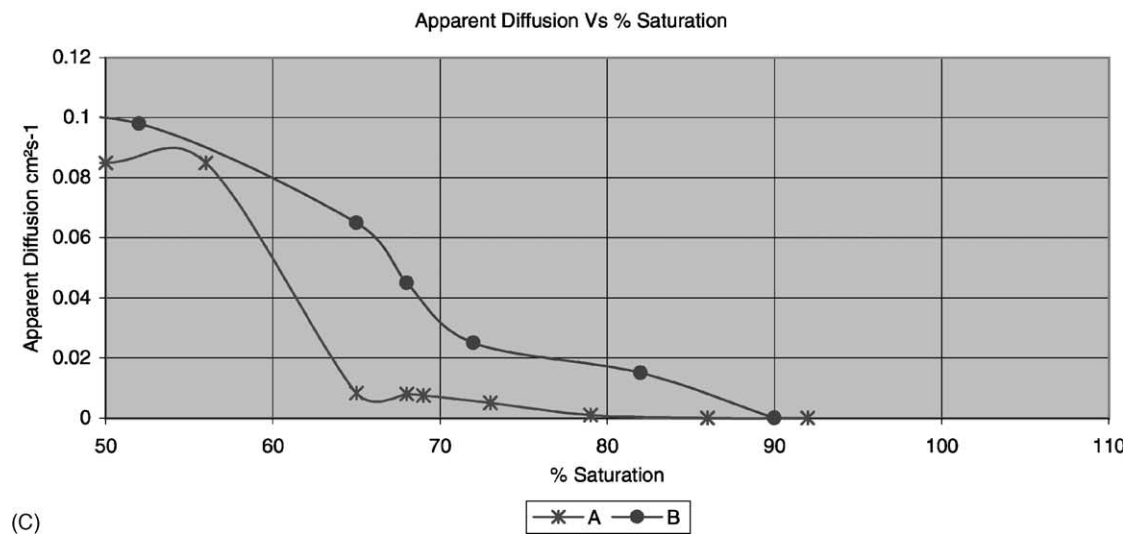
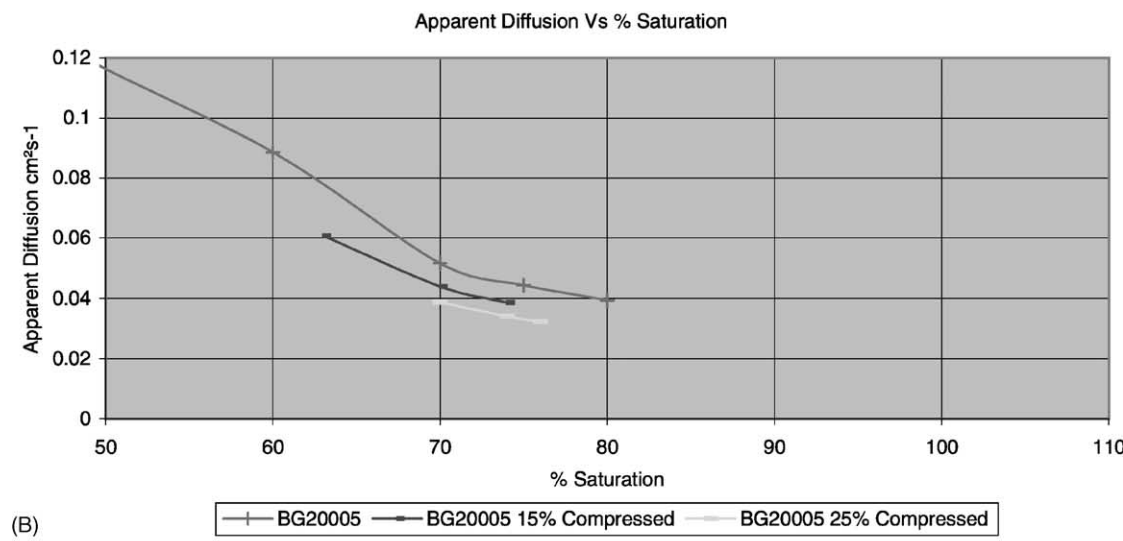
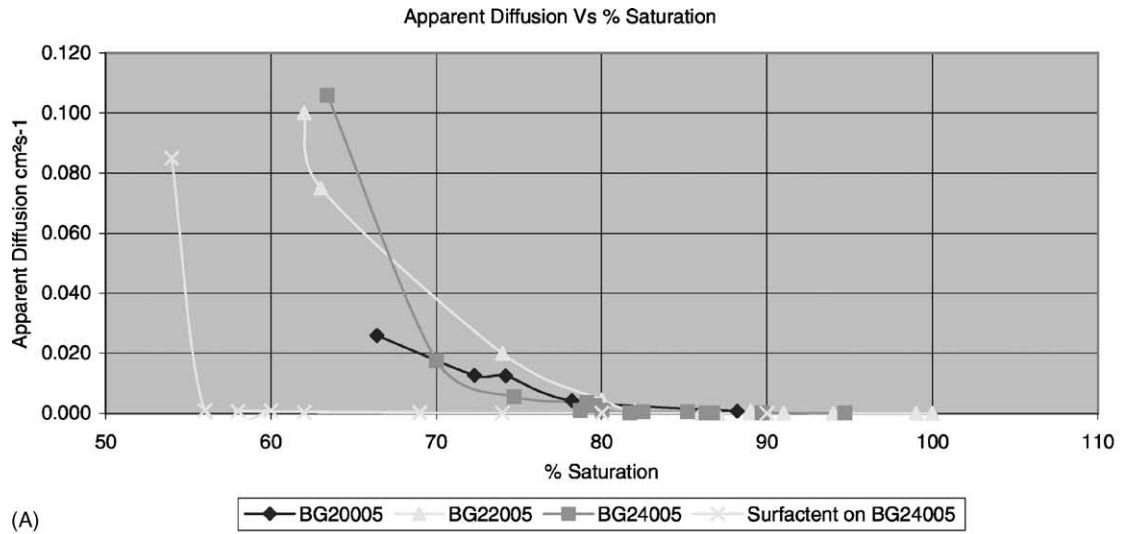


Fig. 1. Saturation level change with grammage and surfactant, compression and furnish.

separator, which is inherent in the manufacturing of a wet laid AGM. The separator may appear fully saturated but in reality it has not totally filled as the finer pores on the wire side are preferentially filled, blocking the pores to the movement of oxygen. This explains why the gas transfer is cut off below the 100% saturation level.

Culpin and Hayman conducted further studies with compressed separators (Fig. 1B). The same observation where seen with 15 and 25% compression from the original 10 kPa thickness, i.e. the separator appears fully saturated before the 100% saturation point. This is understandable, as the separator is never fully saturated only being filled to the same point, e.g. 90% saturation. If you take a separator at 10 kPa with 90% saturation and compress it by 15–25% the saturation level will increase as the thickness reduces, similarly if you take a compressed separator and uncompress it the saturation level will reduce, so the observation that the oxygen flow is the same at the same saturation level irrespective of compression is easily explained. What will change would be the force required to move the oxygen through the more compressed sample.

In addition, Ball et al. compared separators with different surface areas (Fig. 1C) with the conclusion that as the saturation level increases the gas paths get blocked at a lower level of saturation with a more open separator—a more open separator has a lower surface area and has a larger effective pore size distribution leading to easier filling with electrolyte which would explain these observations and are discussed in more detail under Section 2.1.1.2.

The following trends can be determined from these different studies (Fig. 1). As the grammage increases the slope of the diffusion curve becomes shallower, as the furnish become finer the diffusion curve shallower, as the compression increases the curve becomes shallower. These all point in the same direction, i.e. the thicker the separator the longer the path for the gas to transfer across from one side to the other, thus, slowing diffusion, the more fine fibre in the furnish the smaller the apparent pores so the slower the rate of diffusion and in the case of compression, the addition of compression reduces the larger pores introducing more layers into the apparent pore structure slowing the transfer.

The presence of a surfactant can significantly impact the property of the separator increasing the diffusion rate. The introduction of unwettable fibre has the same influence enabling a full-saturated system to recombine.

There is a need for a method by which a separator can be compressed and wetted in a similar manner as in the cell, i.e. vertical, vacuum or gravity filled, with competing porous material on both sides.

2.1.1.2. How the electrolyte fills the separator. Separators when saturated or partially saturated have been likened to a bundle of capillaries with different diameters. This gives a basic mathematical model as to the speed and height a fluid will wick in a separator.

The velocity of wetting is described by the Washburn equation—this shows that as the radius of the capillary increases the speed of filling increases. If this is related to a separator the speed of filling of a coarse pore separator is higher than a fine pore separator (Eq. (1)).

$$V = \frac{2r\gamma \cos \theta}{8\eta h} - \frac{r^2 \rho g}{8\eta} \quad (1)$$

The height to which a separator fills is inversely proportional to the radius of the capillary thus the finer the separator pores the higher the wicking head will rise (Eq. (2)).

$$h_m = \frac{2\gamma \cos \theta}{\rho\gamma r} \quad (2)$$

This Laplace equation gives us the relationship between large and small capillaries or pores which shows that the smaller pores will fill in preference to the larger pores (Eq. (3)).

$$\Delta P = \frac{2\gamma \cos \theta}{r} \quad (3)$$

In reality the wetting fluid enters the larger pores or caverns first, the fluid is drawn into the smaller pores, which take longer to fill but will fill in preference to the large pores due to the increased sucking power. Smaller pores preferentially fill, take longer to fill and are harder to empty. Thus, a separator with a fine pore structure takes longer to adsorb electrolyte and will be harder to free of electrolyte. In a fibrous web the pores are made up of the crossovers of the different fibres. The wetting fluid will migrate to the point of least resistance, which are the smaller junctions (pores) where the pressure of the film is the lowest.

The introduction of plates next to separator changes this balance further. The positive paste has a far smaller mean pore size when compared with an AGM, causing electrolyte to migrate to the smaller pores of the paste from the separator. In an ideal case the negative paste has mean pores of similar size to that of an AGM allowing free transport of electrolyte between the separator and negative paste. If the AGM has too smaller mean pore diameter the acid migrates to the separator. If the pore structure is too large the acid floods the negative paste. So the mean pore size balance within the system is important.

The speed of wetting and the potential for swelling or contraction of fibres on wetting should not be overlooked and the Washburn equation can be modified to take such effects into consideration [3] (Eq. (4)).

$$I = \frac{(\sigma r \cos \theta)^{0.5}}{2\eta} (t - t_w)^{0.5} - k\Delta Z \quad (4)$$

where t_w is wetting time and ΔZ the swelling.

In reality a fibrous separator is not a series of pores but fibres layers which give the appearance of pores as the fibre and layers cross over each other. The fibrous structure has an x , y and z component that can significantly change the apparent pore size in each plane (Figs. 2 and 3).

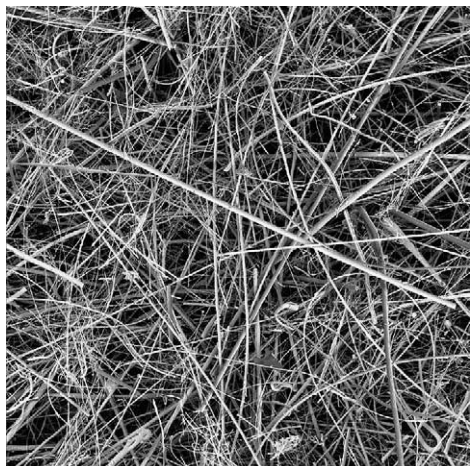


Fig. 2. SEM pictures of xy plane of AGM separator.

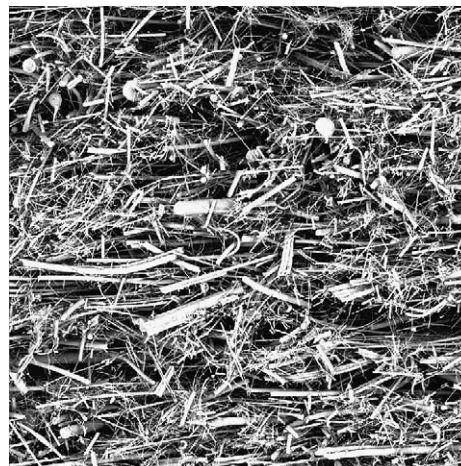


Fig. 3. SEM pictures of yz plane of AGM separator.

The separator shows a tendency for a more open pore structure in the xy plane than the z plane (Fig. 4). This can be explained by the way the sheet is laid during manufacture where by a layered structure is produced by drainage over a wire mesh. In the plane the gradient of fibre layering also gives different pore sizes through the sheet. The degree of layering can be changed as well as the distribution of large and small fibres leading to a different packing density. This can explain some of the observed differences seen with respect to saturation levels of a fibrous media.

2.1.1.3. Gradient through the sheet. The basic forming process of a wet laid fibrous web consists of a composite of three hydrodynamic processes—drainage, oriented shear and turbulence. Of importance here is the compaction of the sheet during formation, the directionality and the flocculation of the fibres, which can lead to significant differences in the formed sheet.

During the drainage process the fibre is dewatering consolidating the mat. The mechanism by which the sheet drains is by filtration and some thickening (Fig. 5).

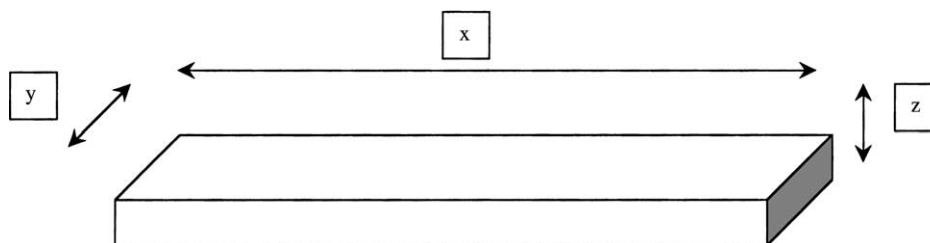


Fig. 4. Diagram representing planes.

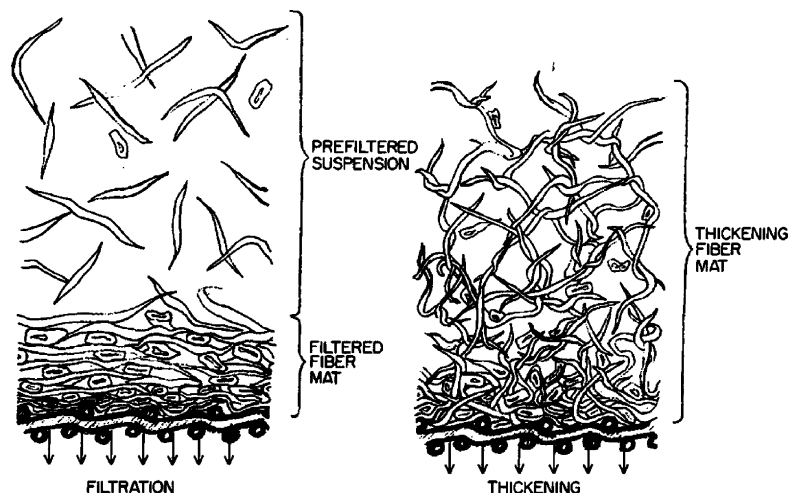


Fig. 5. Filtration and thickening process.

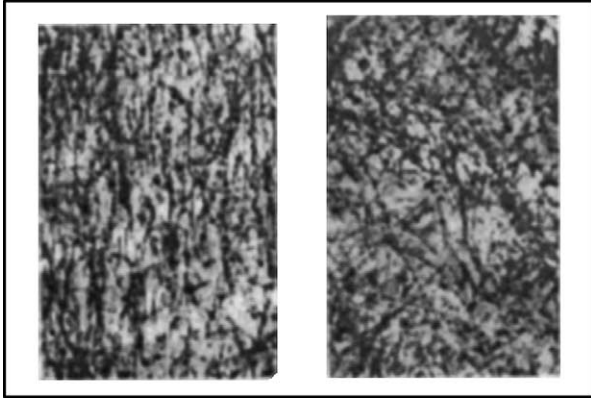


Fig. 6. Machine direction and cross machine direction orientation.

This leads to a gradient through the mat, which becomes relevant when you look at the levels of saturation across the sheet.

The orientation shear gives directionality to the sheet. As the fibre arrives at the wire the machine direction and cross directionality of the sheet can be adjusted leading to changes in the fibre orientation as the sheet is drained (Fig. 6).

Turbulence causes the fibre networks to break down which when controlled can reduce flocculation giving better distribution of fibres in the mat (Fig. 7).

Fibre diameter and length are also important factors when it comes to the layering of the sheet, giving rise to different packing densities.

Several packing theories exist describing how packing space can be represented statistically (Solomon [4], Frank [5], Hall [6], Cowan [7]) these take the basic idea that a three-dimensional space can be filled completely with regular tetrahedral, cubes and truncated octahedra.

Fibrous media have a lognormal pore radius distribution. The size of radii detected depends on the method of detection—normally conversion of measurements of fluid flow into equivalent flow through cylindrical capillaries. A multi-planar model of paper with layers of capillaries of distributed radii better describes the characteristic of a fibrous sheet giving rise to a mean effective radius averaged over m layers $r_{\text{eff}}(m, k)$ [8]. This can be used to describe different flow regimes Laminar or Poiseuille $k = 4$.

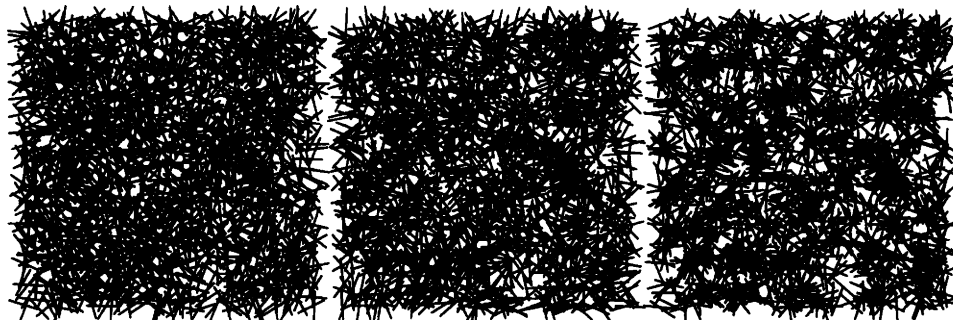


Fig. 7. Flocculation reduced by controlled turbulence.

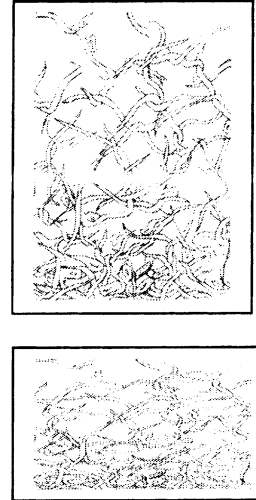


Fig. 8. Compression—fewer large pores.

Molecular or Knudsen $k = 3$ turbulent $k = 2$ capillary $k = 0.5$ (Eq. (5))

$$r_{\text{eff}}(m, k) = \left(\frac{m}{\sum_{i=1}^m r_i^{-k}} \right)^{1/k} \quad (5)$$

Due to the stochastic structure of the sheet to achieve a higher mean pore size the sheet must have a greater spread of pore sizes. Similarly with a smaller mean pore size the sheet will have a smaller spread of pore sizes. So with careful fibre selection and the use of the correct amount of compression an optimum pore structure can be achieved.

In a non-fibrous, non-layered separator made out of, for example, polyethylene the pore structure is defined during manufacture so under compression or wetting does not change, as it is fixed.

2.1.1.4. Compression. As the fibrous mat is compressed the numbers of layers that are utilised to measure the effective pore size increases as the layers come closer in contact, reducing the larger opening within the separator. Thus, the observation that the larger pores are reduced with no effect on the smaller pore size and a slight reduction in the mean (Fig. 8).

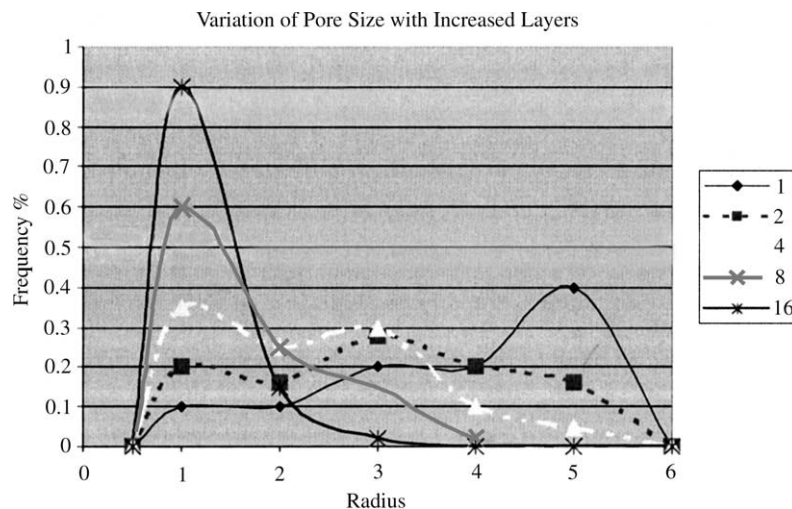


Fig. 9. Variation of pore size with increased layers.

Experiments conducted on individual layers being built up onto each other shows a distribution approximating to a logarithmic Gauss curve. Statistical treatment has been made, considering a separator sheet consisting of a number of layers with an arbitrary hole size distribution. Calculating the probability of finding a hole of a certain size at a given place, the hole size distribution for multiple sheets can be found. The calculation shows that with increasing layers a logarithmic Gauss distribution is approximated to whatever the hole size distribution of the single layer is like. Taking an arbitrary distribution with a maximum radius of 5 supposed for a single layer shows a shift to the left and a move to a logarithmic Gauss distribution as more layers are added [9] (Fig. 9).

Thus, an uncompressed AGM will have fewer layers used to define the pore structure whilst the compressed separator will have significantly more layers introduced defining the apparent pore size.

Compression makes the separator more uniform as the felt side will compress more than the wire side layers. Thus, the spread of electrolyte through the separator and the channels for gas transfer would be more evenly spread through the sheet. With an incompressible separator system the pore structure does not change and will be defined during manufacture, unlike that in an AGM which has an assumed pore structure which can change with saturation, gas transfer, furnish and compression. Any tests for wicking and gas transport must be conducted in the compressed state for an AGM, which is more representative of the system of installation.

2.2. Gas pressure

In an open/closed system the level of pore saturation determines how much of the gas movement is through and how much is over the separator.

Cells with saturation levels $\sim 98\%$ had high recombination efficiencies ($>90\%$) which are not sustainable at the very low diffusion rates measured at these saturation levels. The argument was proposed that in such a highly saturated system the oxygen evolved at the positive plate gives rise to an increased pressure at the separator/electrode interface which builds up until it exceeds the critical pressure to force gas through the separator. At this stage a pressure-induced transfer of oxygen across the separator commences with higher recombination rates. This concept was supported by Khomskaya [10] who emphasized the significance of gas pressure in the space between the electrodes' as this enhanced oxygen reduction rates in recombination cells. The pressure required, to achieve gas transport, increases greatly with smaller pores becoming laminar and compressible.

With a rise in the system pressure, the partial pressure of oxygen increases (the partial pressure of oxygen in air at 1 atm is 0.20 atm and at 10 atm it becomes 2.1 atm) leading to a proportional increase in the amount of oxygen that will dissolve into a fluid—Henry's Law.

The smaller pores and the increased pressure encouraging the oxygen to penetrate into the pores of the plate through the electrolyte boundary layer, facilitating the oxygen cycle.

2.3. Temperature

As temperature increases the viscosity of the electrolyte reduces leading to an increase in the oxygen diffusion—doubling from 20 to 60 °C—the flow of oxygen becomes easier as the temperature rises.

The solubility of oxygen decreases with the increase of temperature so the oxygen no longer remains dissolved in the electrolyte hindering transport in saturated systems but aiding transport in partially and unsaturated systems.

The surface tension of the electrolyte reduces and the influence of gravity to the movement of liquids takes a

more important roll leading to stratification and a transfer gradient.

Pavlov et al. [11] studied the effect of temperature on the efficiency of the oxygen cycle which showed that the efficiency of oxygen cycle decreases with temperature increase. This is due to the low solubility of oxygen, at raised temperatures, hindering the transport of oxygen through the electrolyte film covering the negative paste.

2.4. Viscosity

Viscosity is influenced by temperature but is also influenced by the presence of surfactant materials. Bubble size is important to the transport of oxygen through the separator.

The addition of anionic surfactants results in the accumulation of surfactants at the bubble surface, reducing the bubble diameter, due to the charge repulsion, hindering bubble coalescence. This can aid gas transfer where it is hindered increase the rate of transfer across the separator.

With non-ionic surfactants bubbles can aggregate, as the surfactants have no charge the rate of oxygen transfer is reduced as the bubbles get larger hindering transport across the separator.¹

2.5. Contact angles

The contact angle of glass with sulphuric acid is zero. The introduction of synthetic changes this angle and thus the wettability of the separator in question leading to areas that cannot be easily filled with electrolyte. Dependent on how the synthetic is introduced into the system, i.e. as a fibre or as a resin the local unwettable areas are significantly different from that of pure glass [12].

If the synthetic is applied as a resin the glass fibre surfaces at the point of cross over are coated with resin. As with any wetting fluid the resin moves to the point of least resistance thus the smaller pores are preferentially coated with unwettable areas. In the case of a synthetic fibre it is the synthetic fibre and not the glass that is unwettable so the smallest pores will not be the target of non wetting but the full spectrum of pore sizes, as we must remember the separator is a series of layers. The fibre is distributed randomly through the layers and thus has a random influence on the effective pore sizes, which they alter. The selection of modification can change the performance characteristics of the separator increasing or decreasing the efficiency of the oxygen cycle. This was shown well in the EALABC project where one form of modification helped and one hindered [13].

2.6. Molecular weight

The lighter the molecular weight the easier the gas is to transfer. Unless a major change in electrolyte chemistry

takes place it is unlikely that the molecular weight of oxygen can be reduced enough to make a significant change to the efficiency of transport.

3. Overview

Many factors influence the transfer of oxygen through a separator material. This paper highlights these items from the point of view of the separator, which has to be inert between the two active plates, but perform an essential task, which has seen it, called the third electrode. The transfer of oxygen from the positive plate to the negative plate occurs by the generation of oxygen at the positive plate. The oxygen produced forms bubbles, which burst allowing the oxygen to pass through the separator by diffusion through the electrolyte and the void spaces within the separator.

In the areas where the separator is flooded the transport of oxygen is by diffusion through the electrolyte, which is a slower route than through a gas filled void, as the oxygen has to dissolve into the electrolyte before it is moves on, thus rate limiting.

In the areas where the separator is partially wetted the electrolyte coats the surface of the fibres. The coated fibre then becomes a proton flow enhancer, which aids the flow of oxygen through the separator along the surface of the fibre.

In the areas where the separator is dry the glass is an insulator so the oxygen is transported through the void in the separator and not associated with the fibre. The diffusion is quick, as the flow is not hindered by the presence of the electrolyte. Unlike a separator that has a fixed pore structure an AGM has a structure that is in a constant state of change as more or less layers come into play to determine the apparent pore distribution as the fibres as wetted and or compressed during charge and discharge.

The ratio of the structure of the separator material and the electrode is important. Having excellent gas transfer properties is part of the issue but also delivering the oxygen in a manor that can be utilised by the negative plate is another issue. The combination of a large pore separator with an electrode with fine pores leads to excessive gas filling of the separator, a low pressure and poor oxygen take up at the separator plate interface. In the case of a fine pore separator the separator has the same gas space but creates a higher pressure in the space between the electrodes as the pores introduce a barrier, which enhances the penetration of the gas into the pores of the negative plates [14].

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