

The key to success: Gelled-electrolyte and optimized separators for stationary lead-acid batteries

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Abstract

The lead acid technology is nowadays considered one of the best suited for stationary applications. Both gel and AGM batteries are complementary technologies and can provide reliability and efficiency due to the constant optimization of the battery design and components. However, gelled-electrolyte batteries remain the preferred technology due to a better manufacturing background and show better performance mainly at low and moderate discharge rates. Especially, using the gel technology allows to get rid of the numerous problems encountered in most AGM batteries: drainage, stratification, short circuits due to dendrites, and mostly premature capacity loss due to the release of internal cell compression. These limitations are the result of the evident lack of an optimal separation system. In gel batteries, on the contrary, highly efficient polymeric separators are nowadays available. Especially, microporous separators based on PVC and silica have shown the best efficiency for nearly 30 years all over the world, and especially in Europe, where the gel technology was born. The improved performance of these separators is explained by the unique extrusion process, which leads to excellent wettability, and optimized physical properties. Because they are the key for the battery success, continuous research and development on separators have led to improved properties, which render the separator even better adapted to the more recent gel technology: the pore size distribution has been optimized to allow good oxygen transfer while avoiding dendrite growth, the pore volume has been increased, the electrical resistance and acid displacement reduced to such an extent that the electrical output of batteries has been raised both in terms of higher capacity and longer cycle life.

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1. Introduction

Since their introduction into the market in the 1970s, maintenance-free batteries have been extensively improved [1,2] and are nowadays considered the best suited for standby end-uses, over other chemistries, especially for cost reasons. While AGM batteries are still preferred for very high rate discharge applications, gel batteries can better fit the requirements of most of stationary batteries. Especially the cranking power of gel batteries may be further improved by assembling a higher number of thinner plates with high porosity active masses. Additionally, it seems that stationary batteries are more and more submitted to cycling, as the power shortages can be frequent (once per day

in some countries). Gel batteries can better fit the dual function of floating and cycling than their AGM counterpart, as they are less prone to stratification and premature capacity decay related to compression loss.

The main progress achieved in gel technology over the past 5 years is due to the ongoing optimization of both the “gel process” (plates formation and gel filling) and the battery components [3]. Separator especially has become an important issue, as its function in this type of recombinant battery is not only to electrically insulate the opposite electrodes, but also to promote as far as possible the ion migration and allow a controlled oxygen recombination. Ideally it should be “transparent” (like non-existing) concerning ionic transfer, while being a regulator for gas transfer. For future developments and in order to achieve better performance at high currents, the inter-plate spacing may need to be further reduced. In that case, it will be crucial that the separator has the higher possible pore volume and the lower possible acid displacement in order to maximize the volume available for the

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gel, so that the cells are not electrolyte limited. As a result, the impact of separator physical properties on battery efficiency is much more pronounced in gel batteries than in flooded lead-acid systems [4,5] and has already been pointed out in many studies concerning both gelled-electrolyte and AGM power systems [6–10].

The recent boom of Asian economies gave rise to an increased need for powerful and reliable power supplies, not only for starting vehicles, but also for stationary applications. The fast growing local battery manufacturers can currently be divided into two main categories: some of them manufacture sealed batteries under western licences with high quality components (mainly for export markets), while some others try to decrease the total battery cost in order to be also locally competitive. The later started to manufacture mainly AGM batteries, but the quality problems encountered (especially thermal issues due to extensive stratification and compression loss) forced them to come back to gel batteries. While some manufacturers stick to the original European standards, most of them start to mix AGM separators with gelled electrolyte, which may lead to poor battery quality. This paper focuses on gel technology and aims to demonstrate why polymeric separators based on the extrusion of PVC and silica have shown the best efficiency for nearly 30 years all over the world and are still the preferred separators for gelled-electrolyte batteries.

2. The gel technology

2.1. Valve regulated lead acid batteries

The basics of the functioning of valve regulated lead acid batteries can be summarized as follows: contrary to flooded systems, where oxygen and hydrogen evolved from positive and negative plates during overcharge are vented off, leading to important water loss, in VRLA, a one way gas valve forces the gas to be maintained inside the container. Because the system is closed, the oxygen generated at the positive plate during charging does not escape, but can transfer to the negative plate, where it is reduced to molecular oxygen ions. These ions react at the negative plate surface, with the protons diffusing through the electrolyte from the positive plate to form water again, thus limiting water loss and maintenance needs.

Additionally to the required partial pressure of gas built inside the cell thanks to the valve, another requirement is that oxygen gas find passages through which it can travel in a controlled way between the two electrodes. It is also desirable that these paths are uniformly distributed across the surface of the plates, so that the reactions can take place as uniformly as possible.

As the kinetics of oxygen transfer through liquid electrolyte is far too low, the sulphuric acid has to be immobilized in structures having a certain percent free volume for gas paths.

The two techniques available for electrolyte immobilization are the absorption of liquid sulphuric acid into a glass micro-fibres felt (absorptive glass material or AGM) at saturation degree below 100%, or the formation of a gel by dispersing silica into sulphuric acid.

If AGM batteries are performing well in very high rate discharge applications due to their lower internal resistance, gel batteries remain the preferred technology for a majority of stationary applications, especially when discharge times are higher than a few minutes and when plates taller than 30 cm are needed. The reason is that AGM batteries undergo earlier capacity loss, mainly due to drainage and stratification of acid inside the separator, as well as loss of contact between the plates and the acid reservoir, due to the poor springiness of most conventional AGM separators.

2.2. Gelled electrolyte in VRLA batteries

The manufacture of any gelled VRLA cell has to follow specific conditions [14]. More than for flooded batteries, care must be taken at each manufacturing step to assure the highest possible degree of compliance to highly demanding specifications and extended periods of guarantee. One very important step that sets gelled VRLA apart from other lead acid battery technologies, is the gelled electrolyte and plates' formation process.

The gel formation consists on creating a three-dimensional silica gel structure in which the electrolyte is immobilized. Traditionally, the gel has been obtained by introducing fine particles of silica into the liquid sulphuric acid electrolyte. The preferred type of silica used to be fumed silica with an average aggregate size of only a few nanometers in diameter. These particles have the ability to react with the sulphate ions of the electrolyte and solidify in the desired three-dimensional gel matrix [15], the hardness of gel depending on the fumed silica content. Recently however, the use of concentrated aqueous solutions of colloidal silica tended to replace fumed silica gels and to generalize. There is no argument more in favour of the former or the later silica, as long as the main requirement for the particles (or aggregates) size is fulfilled: it has to be big enough to avoid entering the pores of the active mass, which should act as a filter. As a result, not only the pore volume is not decreased, but the electrolyte remains liquid inside the plate, thus maintaining an optimal ionic transfer.

The plate formation process consists on electrochemically transforming the active material of the cured plates (basically a mixture of tribasic and tetrabasic lead sulphate) into the final stage, namely lead dioxide (PbO_2) in the positive electrode and spongy metallic lead (Pb) in the negative electrode.

The plate formation and gel filling step can be completely independent processes, like in tank formation, or part of a unique process like in "direct formation" or "gel formation":

- In tank formation, the green plates are formed inside large tanks in fairly diluted sulphuric acid bath. The positive and negative plates are connected in parallel with a rectifier, and the active material of the cured plates is transformed into its final stage (PbO_2 in the positive plate and Pb in the negative plate). When the formation process is finished, the plates have to be washed and dried, with special care to the negative plate, which has to be protected from oxygen to avoid oxidation (silicon oil impregnation).

The gel filling is performed after the formed plates have been assembled and inserted into the container.

There are still three main methods used to fill cells with fumed silica gel. The first two techniques are very similar and imply fully charged plates and the previous formation of the tixotropic gel and its subsequent introduction to the cell under vacuum. The third one is based on formed but fully discharged plates filled with a mixture of fumed silica and water:

- First patented method: The formed charged plates are assembled inside the container and a mixture of sulphuric acid and fumed silica is prepared separately as a batch process. The tixotropic gel, still having low viscosity because under stirring, is then pumped in order to fill under pressure the container in less than 60 s. During filling, vacuum is applied for better penetration of the gel inside all parts of the cells, including the separators pores. The advantage of this technology is that the gel is very homogeneous, because the mixture of acid and silica is made in a separate step under stirring. Also the batch process to mix silica and acid allows a very precise control of the temperature, silica content and concentration of sulphuric acid.
- Second method (Fig. 1b): The formed charged plates are assembled inside the container and fumed silica mixed with water is pumped separately from sulphuric acid. Both components are mixed just before being inserted in the cell, by turbulences occurring inside the head of the filling device. Vacuum is also applied to enable the freshly formed gel to fill properly the inter-plate spacing.
- Third method: Fully discharged plates are assembled in the container. Water instead of acid is mixed with fumed silica, in order to keep the mixture liquid. Then this liquid is added very easily inside the discharged cells. The gel solidifies during the charging step, when sulphuric acid is released from the plates due to PbSO_4 oxidation into PbO_2 at the positive plate and PbSO_4 reduction into Pb at the negative plate.
- In direct or gel formation, the battery is assembled first with green (or unformed) plates, then filled with electrolyte and finally the formation process is carried out within the com-

plete battery. This method is equivalent to the so-called “jar formation” for flooded batteries. During the formation process, the battery is highly overcharged and generates both hydrogen and oxygen with resulting bubbles, heat and water loss. Two methods are used, either direct formation occurring in two steps, or gel formation (this process is quite new, as it was not known until quite recently that plate formation directly with gel was possible):

- Direct formation: The first step is comparable to jar formation, where unformed (green) plates are assembled and filled with liquid sulphuric acid. The formation is done inside the container with controlled current and temperature. The second step is jellifying of the electrolyte by addition of a solution of water and concentrated colloidal silica (40% silica and 60% water). The batteries have to be put upside down and free volume has to remain in order to mix the colloidal solution with the sulphuric acid and have a homogeneous gel.

The advantage of this method is that it does not need any plates drying and washing of the plates, nor a second charging step. The limiting factor is the battery height due to the mixing and increase of temperature during formation.

- Gel formation: For big batteries, direct formation is difficult because of temperature increase, therefore gel formation is applied, where green unformed plates are inserted in the container, filled with a very liquid gel (mixture of water, sulphuric acid and concentrated aqueous solution of colloidal silica). The formation occurs at a controlled temperature by applying a certain current. The excess water is lost during the formation step, leading to a harder gel. This is a single step, several days process comparable to jar formation but in gel. The batteries have to be charged after the formation.

The advantages of direct formation are mainly due to the absence of the “washing, drying, and impregnation” production steps, leading to reduced production cost (especially no concern about effluents on account of the acid and lead traces in the washing water). On the other hand, tank formation has the following advantages: (i) the formation conditions like acid concentration and temperature can be optimized and (ii) dry charged plates can be produced and these plates, as well as batteries assembled with these plates, can be stored for practically unlimited time, the service life of the battery starting with electrolyte filling.

As a result, which of the two methods is to be preferred depends not only on the manufactured battery type, but also on the particular situation of the battery manufacturer. However, whatever the method used to form and fill the cell, one key aspect for a good functioning of the cell is to reach a minimal internal cell resistance for a given design. One condition is that the gelled electrolyte must be able to perfectly fill any volume available in between the opposite plates, in order to allow an optimal ionic transfer between them.

Additionally, gas paths have to take place to allow controlled oxygen recombination.

The following sections will point out the essential role of the separators properties to achieve optimal ionic and oxygen trans-

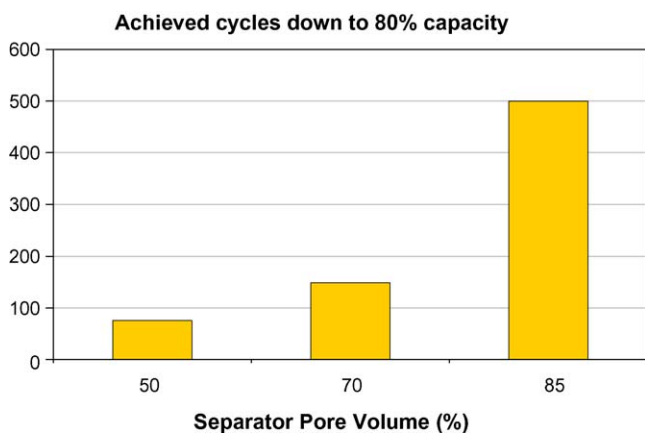


Fig. 1. Impact of the separators' pore volume on the electrical performance of 130 Ah gel cells. The accelerated life cycle test has been performed at C_5 , 47 °C and 80% DoD.

fer and reach improved electrochemical performance in gelled VRLA cells.

3. The separator as a key component for gel cells

3.1. Wettability, pore volume and ionic transfer

The internal resistance of gel batteries is naturally increased compared to flooded systems because the kinetics of ion diffusion through the viscous gelled electrolyte is generally one-third of their kinetics of diffusion in liquid electrolyte. Therefore, it is very important that the separator does not participate to further increase too much the internal resistance of the system.

Various properties have to be optimized in order to reach the best performance.

Especially, the pore volume has to be maximized in order to insert the less amount of insulating material as possible in between the plates. The results of a previous study performed on 130 Ah gel cells insulated with different types of separators with various pore volumes, have confirmed that high pore volume material can increase the performance of the battery [6–13]. The results are summarized in Fig. 1: cells assembled with 50% pore volume separators reached only 75 cycles, while cells assembled with 70% and 80% pore volume separators achieved 150 and 500 cycles, respectively.

However, if this pore volume is not properly filled by electrolyte, i.e. if air bubbles remain trapped inside the pores of the separator, the ionic exchanges will be reduced because ions are not able to travel through gas phases, but only via more or less viscous ionic media (liquid or gelled sulphuric acid). Therefore, another key property for the separator, additionally to a high pore volume, is to have a good wettability to enable the electrolyte to perfectly fill the whole pore volume.

In case both wettability and high pore volume are fulfilled, then the direct consequences would be a minimized electrical resistance and acid displacement of the separator.

Table 1 illustrates the above mentioned properties (pore volume and wettability) for a series of polymeric separators widely spread in the lead acid market: Amer-Sil (ribbed or corrugated patterns), as well as Amersorb (ribbed or corrugated patterns) are

microporous PVC/silica separators, obtained by a unique extrusion process; polyethylene (respectively polyethylene/rubber) separators result from the hot extrusion of ultra high molecular weight polyethylene powder with silica and mineral oil (respectively rubber); the separators made of rubber have been added to the table for comparison, even if they are generally not used for gelled-electrolyte batteries. Another separator used in gel batteries is made of a polyester mat impregnated with a cured phenolic resin.

The last row of Table 1 shows that only the PVC based materials have the best wettability. The values indicate that a drop of acid needs less than 2 s to be completely absorbed by the Amer-Sil and Amersorb separators. On the contrary, all the other materials are much more hydrophobic: 200 s are necessary for a drop of acid to be absorbed by the phenolic resin/polyester separator, while polyethylene/rubber and polyethylene separators have so hydrophobic surfaces, that more than 1200 and 5000 s are respectively needed.

This is illustrated by the scanning electron microscopic view of the different separators surfaces in Fig. 2, and can be easily explained by the different manufacturing processes.

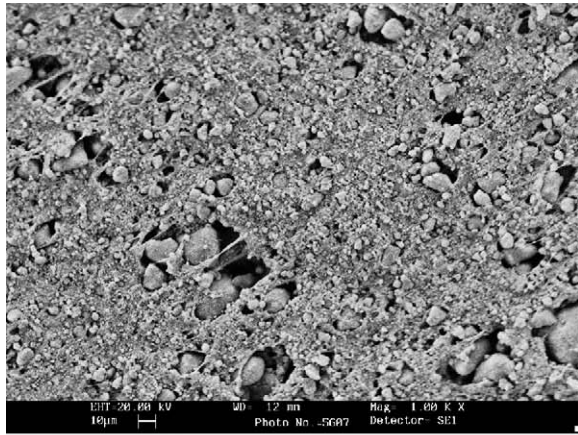
The reason why the Amer-Sil and Amersorb separators are so hydrophilic, is that the extrusion of the PVC and silica mixture is made at room temperature with an appropriate solvent. As elevated temperature is not required, the PVC grains are not melted, but simply glued together with the silica aggregates by a solvent. Consequently, the electrolyte has free access to the highly absorbing filler not only at the surface of the separator, as shown in Fig. 2a and b, but also all through the total volume of the separator and inside the more tortuous pores.

On the contrary, polyethylene separators are processed by melting the polymer at high temperature, leading to the complete embedding of the filler in the polymer matrix. As a consequence, the surface is very smooth and “closed” (Fig. 2c and e): sulphuric acid can only have a very restricted access to the hydrophilic compound (silica), and is mainly in contact with the hydrophobic polymers.

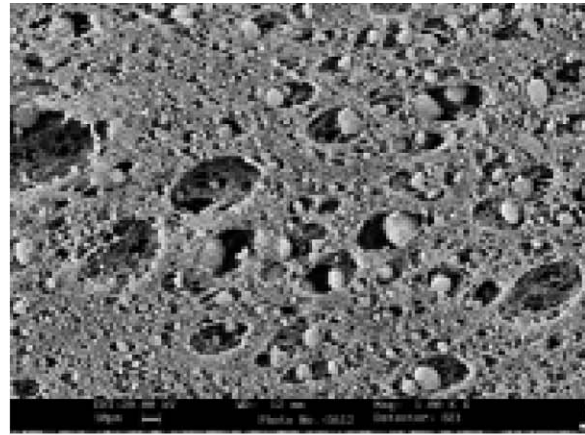
The phenolic resin/polyester separator (Fig. 2d) exhibits large openings, but its surface even inside these openings is dominated by the sub-micron pores of the cured resin grains. Even if some

Table 1
Physical properties of main separators available on the market (typical values)

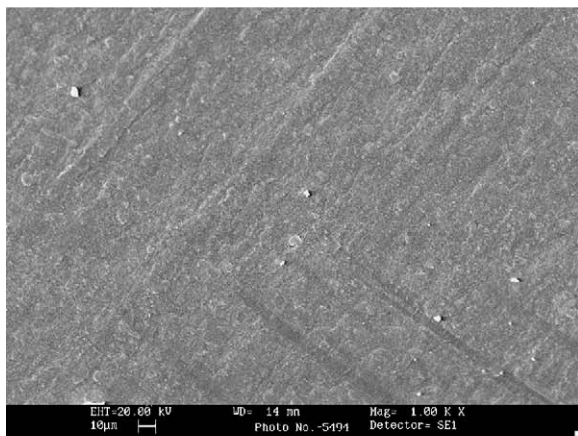
Typical values	Amer-Sil ribbed	Amersorb ribbed	Amer-Sil corrugated	Amersorb corrugated	PE	Rubber	Phenolic resin	PE/rubber	AGM
Thickness (mm)	2.0	2.0	2.0	2.10	2.0	2.0	2.0	1.85	2.0 @ 20 kPa
Backweb (mm)	0.50	0.57	0.57	0.42	0.50	0.57	0.55	0.50	2.0
Total porosity (cm ³ g ⁻¹)	1.20	–	1.58	–	0.90	0.85	1.20	0.73	–
Pore volume (%)	68	76.9	73.9	82.4	55	53	70	45	92–95
Pore size (μm)									
Minimum	0.05	0.05	0.05	0.05					3.0
Mean					0.10	0.17	0.50	0.09	10.0
Maximum	1	1–5	1–3	1–7					30.0
Electrical resistance (mΩ cm ²)	130	89	80	35	200	300	110	400	80
Displacement of acid (ml m ⁻²)	300	207	180	140	300	450	220	>400	–
Oxidation weight loss (%)	3	3	3	3	5–20	15–30	29	23	3
Wettability (s)	2	1	2	1	5000	15	200	>1200	1



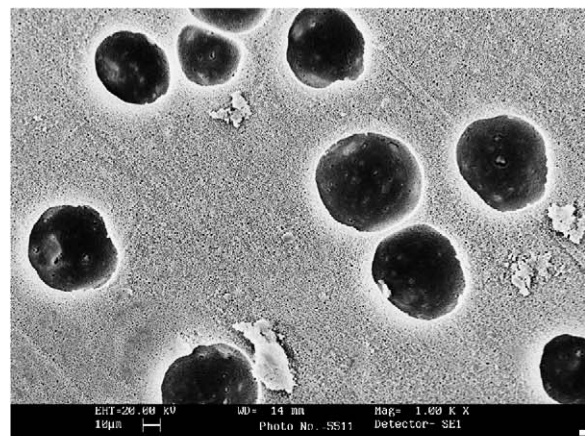
(a) PVC/silica ribbed separator



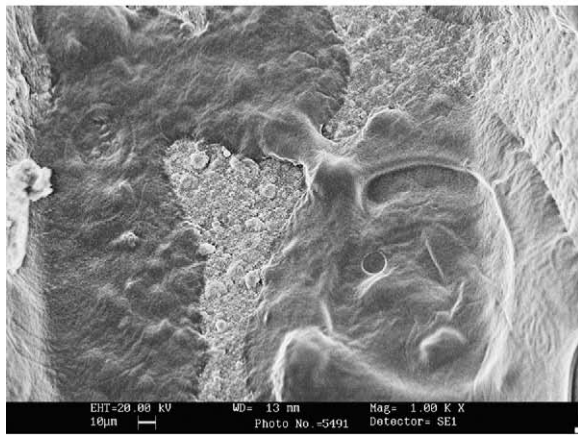
(b) PVC/silica corrugated separator



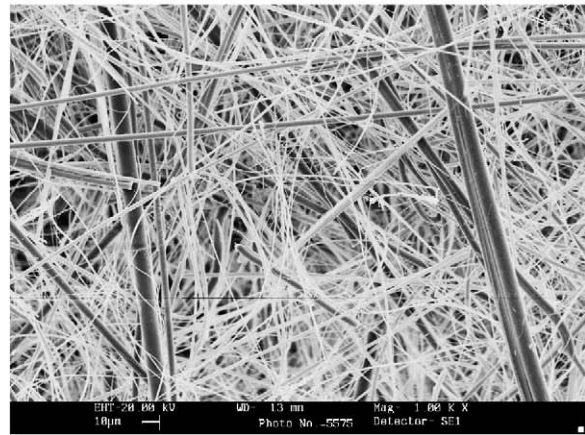
(c) Polyethylene separator



(d) Polyester mat + phenolic resin



(e) Polyethylene/Rubber separator



(f) AGM separator

Fig. 2. Surface of different types of separators by scanning electron microscopy (SEM) with a magnitude of 1000 \times . (a) PVC/silica ribbed separator; (b) PVC/silica corrugated separator; (c) polyethylene separator; (d) polyester mat + phenolic resin; (e) polyethylene/rubber separator; (f) AGM separator.

silica has been mixed with the phenolic resin, the wettability measurement shows that the hydrophilicity of the separator is far from optimal.

Concerning pore volume, the target is to increase the pore volume to a maximum value in order to reach the ideal “transparency” to ionic transfer. Table 1 shows that the PVC/silica

separators have pore volume from 68% to 82.4% for the same 2.0 mm thickness, depending on the type and pattern: the standard Amer-Sil ribbed separator has 68% pore volume, while the Amersorb ribbed reaches 76.9%. The corrugated patterns, obtained by deforming a flat sheet under hot calendar rolls, can reach 73.9% pore volume for the Amer-Sil (compared to

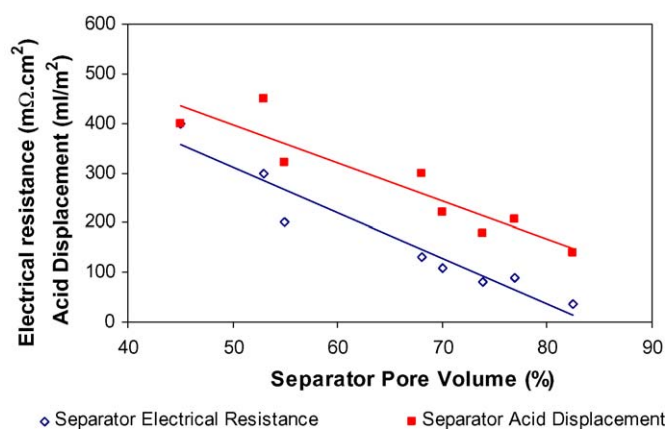


Fig. 3. Polymeric separators' electrical resistance and acid displacement as a function of the separators' pore volume (for comparable backweb and overall thickness).

68% for the ribbed pattern), and be as high as 82.4% for the Amersorb (compared to 73.9% for the ribbed pattern). These PVC/silica separators are the most porous separators nowadays available. For comparison, only the phenolic resin separator can compete with the former materials with 70% pore volume. All the other types have a much lower pore volume: only 45%, 53% and 55% for polyethylene/rubber, rubber and polyethylene, respectively.

The impact of the pore volume on the other physical properties is illustrated in Fig. 3. The direct correlation indicates that the higher pore volume leads to the lower electrical resistance and lower acid displacement. Both properties are of first importance for reaching good performance in gelled-electrolyte lead-acid batteries. It can therefore be anticipated that the battery assembled with the corrugated patterns of the PVC/silica separators will have an optimal electrical output, as schematically represented in Fig. 4, and confirmed by the battery test results detailed in Section 3.3.

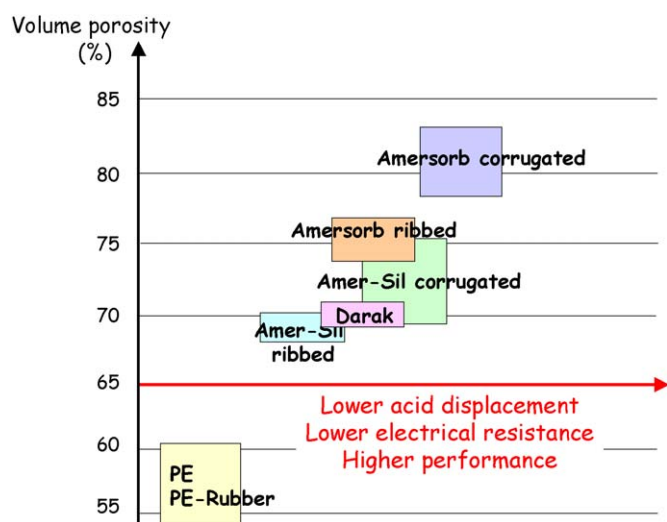


Fig. 4. Performance of polymeric separators in gel batteries as a function of their volume porosity.

3.2. Pore size distribution for optimized oxygen transfer

Still today, the prevailing theory for oxygen transfer from the positive to the negative plate in gel batteries is the model of gel micro-channels structure [6].

Initially, when the gel is formed by mixing silica and sulphuric acid, there is total liquid saturation. The electrolyte is supposed to perfectly fill the separator (in case the wettability is good enough, as mentioned in the previous paragraph), the active material, as well as the gel/electrode interface. Due to the presence of sub-micron pore size, the separators and active material act as filters, which have the ability to absorb only the liquid sulphuric acid by capillary effect, while leaving the silica particles outside their porous structure.

Therefore, in the early stages of operation, the gel cell functions more like a flooded cell, as no path is initially available for gas transfer. Then, the gas evolved at the end of the charging period are forced to escape through the valve and some water is lost.

Depending on the gel consistency, leading to a weaker or a stiffer three-dimensional structure, the amount of cycles and water loss necessary to break it can vary. Anyway, as soon as enough dry out has occurred, micro-channels have a chance to built up randomly through the gel. Since oxygen is liberated at the positive plate as a gas, it has a natural tendency to follow the paths of least resistance and to travel preferentially upwards due to gravity. However, the active material/gel interface is closed by the presence of an electrolyte film, as explained earlier. Therefore, as soon as enough pressure is built up, oxygen gas has to make its way through the gel itself, via the micro-cracks resulting from early dry out.

At the early stages of operation, when the cell is closed to full saturation, it is reasonable to assume that the separator is also fully saturated and will not allow any passage of gas. However, as more water will be lost from the cell, some pores of the separator will also become free of electrolyte and ready for oxygen transfer across the tortuous polymeric structure.

Based on this model, it is obvious that the internal structure of the separator, especially its pore size distribution will be of first importance to optimize the oxygen transfer from the positive plate to the negative plate. The pore size, the pores' tortuosity, and the distribution of the pores at the separator surface have to match as well as possible the gel micro-channels, to allow oxygen gas to continue its route from the gel micro-cracks on the positive side, to the gel micro-cracks on the negative side, via the separators interconnected pores.

At this stage of the study, a deeper look at the different separators pore size distribution is therefore necessary to better discriminate the suitability of each type of material for this highly demanding gel battery technology.

Generally speaking, separator porosity refers to all the voids spaces existing within the structure of the material. In the case of silica containing polymeric membranes, two sources of voids contribute to the overall pore volume: (i) the silica agglomerate void volume which is the empty space existing within each silica aggregate (intra-granular porosity) or between different aggregates (inter-granular porosity), and (ii) the extraction or curing

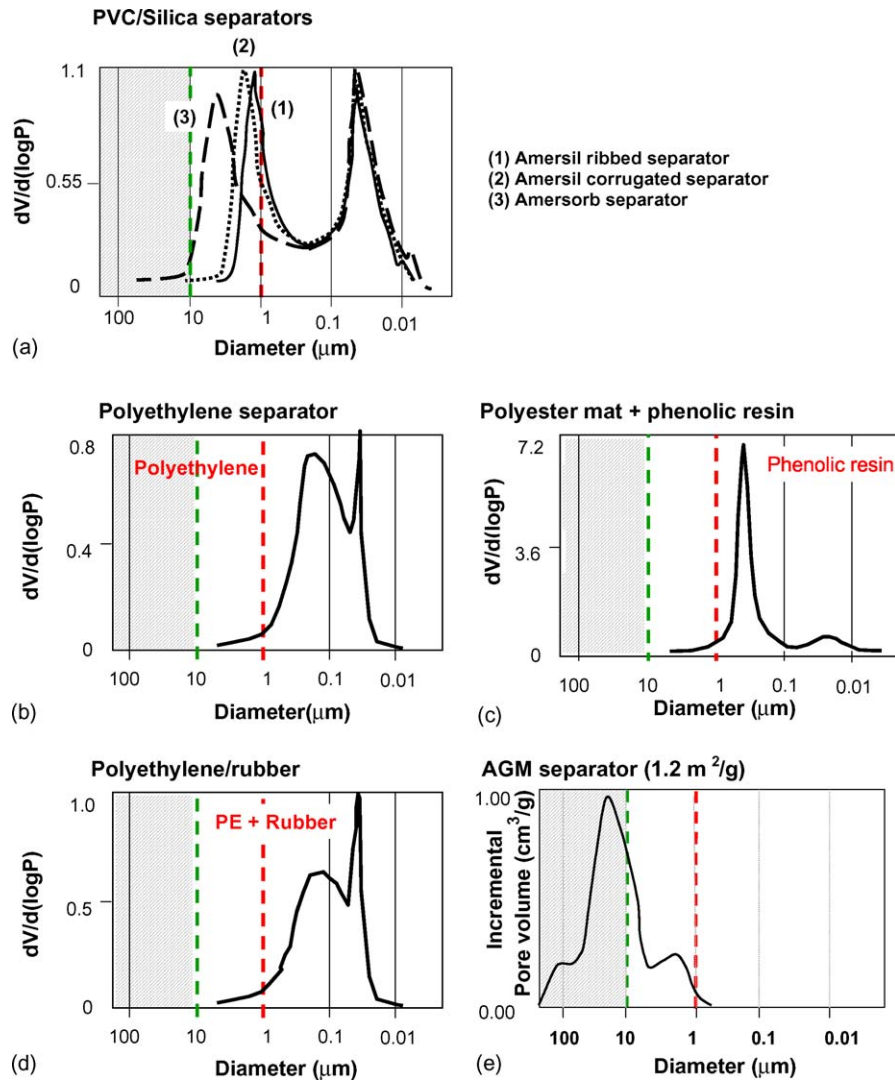


Fig. 5. Pore size distribution of the different polymeric and AGM separators available on the market. (a) PVC/silica separators: (1) Amer-Sil ribbed separator, (2) Amer-Sil corrugated separator and (3) Amersorb separator; (b) polyethylene separator; (c) polyester mat + phenolic resin; (d) polyethylene/rubber; (e) AGM separator ($1.2 \text{ m}^2 \text{ g}^{-1}$).

void volume. The latter result from the extraction of the solvent needed for the polymer extrusion in the case of Amer-Sil and Amersorb PVC/silica separators, from the partial extraction of the mineral oil introduced during the extrusion step in the case of polyethylene separators, or from the curing of the phenolic resin in the case of phenolic resin/polyester separators.

Fig. 5 shows the different ratios of these two types of void volumes for the different separators, measured by the mercury intrusion method. As AGM separators have been used quite recently in order to build gel cell, the pore size distribution of a standard AGM material of $1.2 \text{ m}^2 \text{ g}^{-1}$, measure by the Coulter porosimeter, has been added for comparison (Fig. 5e), even if the performance of these kinds of “Hybrid” batteries are poor. The main reason is that most of the batteries that could be analysed contained colloidal silica gel only above and around the plates stacks, while only electrolyte was found inside the separator. As a result, the main problems generally encountered with AGM batteries still remain, especially the thermal issues related to electrolyte stratification, drainage and compression loss.

Additionally, as illustrated in Fig. 5e, AGM materials have the majority of their pores above $10 \mu\text{m}$, even reaching $30\text{--}50 \mu\text{m}$ for the lower quality material made with a majority of coarser micro-glass fibres. It has been fully experienced that too many pores above $10\text{--}15 \mu\text{m}$ increase tremendously the risk of dendrite growth through the separator. Therefore, it is anticipated, and has already been well documented that AGM separators can lead to early failure due to dendrite growth across the separator openings. Again, these types of products have to be avoided as far as possible in gel stationary batteries, for which $15\text{--}20$ years guarantee are most of the time requested.

Also, the impact of the optimal pore size distribution, and especially the beneficial effect on the electrical output of gel batteries of the pores between 1 and $10 \mu\text{m}$ has been investigated. Gel cells of 130 Ah have been assembled with separators having all less than $1 \mu\text{m}$ pore size, and separators with a big proportion of pores between 1 and $5 \mu\text{m}$ or between 5 and $10 \mu\text{m}$ [6]. The cells have been cycled with a C_5 current at 47°C with 80% depth of discharge. The results showed that cells assembled with

separators with pores below $1\ \mu\text{m}$ failed after 400 cycles, while cells assembled with separators having pores between 1 and 5 or 5 and $10\ \mu\text{m}$ reached 675 and 1000 cycles, respectively, before the capacity drops below 80% of its nominal value.

The characteristic of the PVC/silica microporous separators is that the pore size distribution is perfectly bimodal. Pore size analysis performed by the mercury intrusion porosimetry on Amer-Sil and Amersorb ribbed or corrugated separators shows that the pores coming from the silica aggregates are around $0.05\ \mu\text{m}$, whereas the extraction pores have an average diameter between 1 and $7\ \mu\text{m}$ depending on the type and pattern (Fig. 5a and Table 1).

The analysis of the other separators pore size distribution shows that PVC/silica microporous separators are the only one to have a big proportion of pores above $1\ \mu\text{m}$. On the contrary, all pore sizes recorded on phenolic resin, polyethylene and polyethylene/rubber separators are far below $1\ \mu\text{m}$ (Fig. 5b–d).

This category of larger pores above $1\ \mu\text{m}$ is homogeneously distributed in whole the PVC/silica separator, as illustrated by the SEM picture of the separator surface (Fig. 1a and b). This optimal repartition constitutes an advantage to assure a continuity in the gas paths between the gel micro-channels and the separator, therefore leading to an optimal oxygen transfer and recombination.

From Fig. 5, it is clear that only the PVC/silica microporous separators have the optimal pore size distribution. Moreover, their high volume porosity is a real advantage, as it allows the separators to keep enough volume saturated with electrolyte (and therefore available for ionic transfer and good electrical performance), even if part of the pores are free of electrolyte for gas transfer.

3.3. Battery test results

The corrugated PVC/silica separators have been tested in comparison with the phenolic resin separator. Two different battery types have been assembled:

- (i) Type I, which is a typical stationary battery with thick plates and thick separators ($3.2\ \text{mm}$ thickness including glass mat). Tank formation has been applied for the plates of this series.
- (ii) Type II, which is a battery dedicated to stand by applications but also needing a certain ability to be cycled ($2.7\ \text{mm}$ separator thickness including glass mat). Gel formation has been applied in this case.

For batteries of Type I, typical floating at $2.27\ \text{Vpc}$ have been performed during periods of 30 days at a temperature of $60\ ^\circ\text{C}$. After each period, the C_3 and $C_{0.16}$ capacities have been checked. In this particularly severe testing procedure, a cycle of 1 month represents 1 year of service life.

Fig. 6 shows that the three batteries assembled with the corrugated PVC/silica separators achieved 6 cycles, as well as two batteries assembled with the alternate separator, the remaining one being at 7 cycles. The C_3 capacity, however is between 10% and 15% higher for the three batteries insulated with the PVC/silica separators. This good result can be explained by the

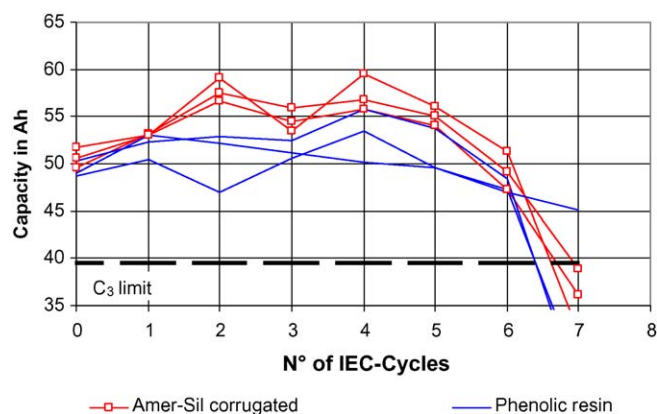


Fig. 6. C_3 capacity of 12 V batteries of Type I assembled with PVC/silica corrugated separators and phenolic resin separator after each IEC cycle (floating at $2.27\ \text{Vpc}$ at $60\ ^\circ\text{C}$).

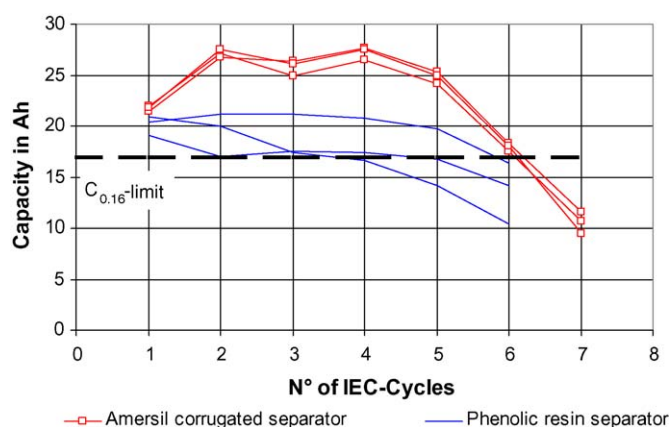


Fig. 7. $C_{0.16}$ capacity of 12 V batteries of Type I assembled with PVC/silica corrugated separators and phenolic resin separator after each IEC cycle (floating at $2.27\ \text{Vpc}$ at $60\ ^\circ\text{C}$).

lower electrical resistance and acid displacement of the material. The advantage is even more pronounced at higher discharge rates. As illustrated in Fig. 7, the batteries assembled with corrugated PVC/silica separators can reach up to 50% more capacity than their counterpart. In addition, all three batteries

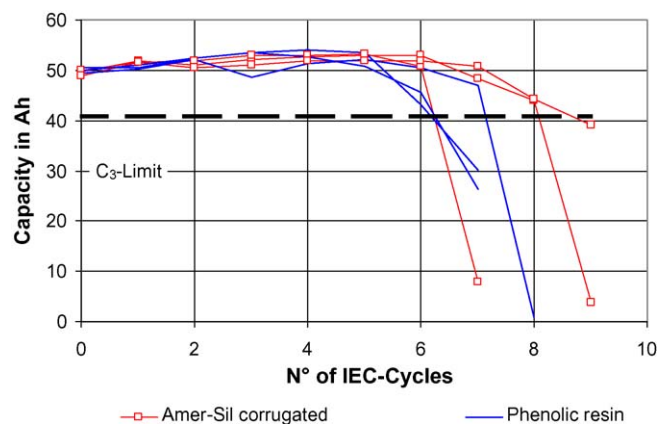


Fig. 8. C_3 capacity of 12 V batteries of Type II assembled with PVC/silica corrugated separators and phenolic resin separator after each IEC cycle (floating at $2.27\ \text{Vpc}$ at $60\ ^\circ\text{C}$).

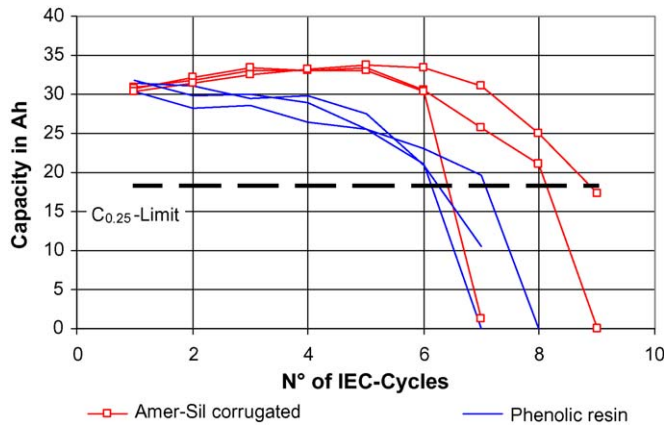


Fig. 9. $C_{0.25}$ capacity of 12 V batteries of Type II assembled with PVC/silica corrugated separators and phenolic resin separator after each IEC cycle (floating at 2.27 Vpc at 60 °C).

have achieved 6 cycles, while the batteries with phenolic resin separators failed after 2, 3 and 5 cycles.

The IEC testing performed at 60 °C on batteries of Type II confirmed the above results: the performance with corrugated PVC/silica separators is higher both in terms of number of achieved cycles (6, 8 and 8 compared to 6, 6 and 7 with the phenolic resin separators), and in terms of capacity (the C_3 capacity is similar, while $C_{0.25}$ is between 20% and 40% higher). These results are illustrated in Figs. 8 and 9.

The cycling ability of Type II batteries has also been checked, as these batteries are subjected to frequent discharges due to power shortage. Fig. 10 shows that the results are comparable for both types of insulating materials. The batteries assembled with the corrugated PVC/silica separators started with 52 Ah, then reaching 56–60 Ah after 50 cycles, with a stable capacity around 60 Ah until 200 cycles. The cells assembled with the phenolic resin separator started with the same initial capacity (around 52 Ah), increased to around 62 Ah after 50 cycles, and stabilized around 60 Ah until 200 cycles.

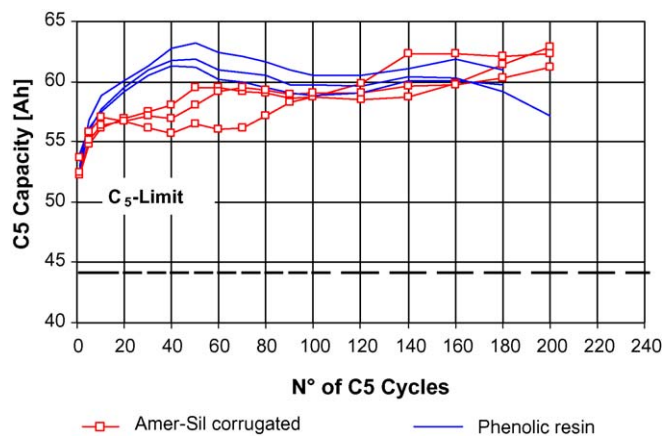


Fig. 10. C_5 capacity of 12 V batteries of Type II assembled with PVC/silica corrugated separators and phenolic resin separator during cycling (100% DoD). The test has been stopped after 200 cycles, as 100 cycles are requested.

4. Conclusion

The present study demonstrates that the separator plays an essential role in the performance of gelled-electrolyte valve regulated lead acid batteries. This component, nowadays considered as the third electrode, has to be much more than an obstacle to dendrite growth between the opposite plates. Besides the requirement of high porosity (at least 68–70%), and perfect wettability needed in order to minimize the cell internal resistance, the separator must have an optimal pore size distribution, in order to assure a perfect connection for oxygen transfer between both plates via (i) the micro-channels built up inside the gel during the very first step of dry out, and (ii) the separator, which should be partially permeable to gas, while keeping enough saturated pore volume in order to ensure good ionic exchanges and electrical performance.

Even if different plates formation and types of gel (mainly in terms of hardness and homogeneity) will be obtained with the different techniques available, it can be anticipated that, for a given type of gel, silica and formation process, the best performance will be obtained with highly hydrophilic separators having the higher possible pore volume, with a maximum of pores between 1 and 10 μm (not larger to avoid dendrite growth).

Up to date, the Amer-Sil and Amersorb separators based on the extrusion of PVC and silica are the only ones to combine all the requirements and that is the reason why they have shown excellent efficiency in any kind of gelled-electrolyte batteries.

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