Optimization of the cycle life performance of VRLA batteries, working under high rate, partial state of charge (HRPSOC) conditions

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Abstract

On hybrid vehicle applications, batteries must work in a rather low state of charge (SOC), in order to be able to recover as much of the regenerative braking energy as possible. Usually SOC values around 60% are used, which promotes the development of new unexpected failure modes not previously found, mainly associated with heavy sulphation of the negative plates.

In order to try to optimise the cycle life performance to the point of making these batteries a real alternative for the application of hybrid vehicles, a series of tests have been undertaken, aimed to optimise the key parameters that from previous experience are known to determine life duration in high rate low state of charge (HRPSOC) conditions. Previous works have been focused on trying to determine the optimum composition of positive and negative active material, concerning paste density in the positive, and additives in negative. In order to overcome the deleterious effect of heavy sulphation in negative plates on cycle life, the use of conductivity enhancers additives such as graphite has been proposed.

The objective of this project is to optimize the performance of the glass microfiber separators, in order to maintain a high degree of compression in the group, as well as to avoid acid stratification and development of short circuits along the battery life. To do this, different glass microfiber separators with inert additives, as well as different fiber composition have been tested.

Results obtained up to now, indicate a remarkable good performance of the VRLA batteries with the new separators containing very fine fiberglass and silica fillers as an additive.

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1. Introduction

Batteries working under High rate partial state of charge conditions are exposed to quite unusual conditions that also promote the development of unusual failure modes. Such special conditions, include working under rather low state of charge, around 60%, to be able to recover as much of the regenerative braking energy, and discharges at high rate that promote battery heating.

Working under low state of charge conditions, promote new failure modes [1] associated with the following problems:

- Development along the life, of a high sulphate layer in the negative plate that provokes a heavy plate polarisation on charge and discharge.
- Also these high levels of sulphate create the adequate conditions for the development of short circuits across the separator (low acid density, and high concentration of sulphate ions).
- An increase of the internal resistance of the battery, that in combination with the high charge and discharge currents, tends to increase the battery temperature.
- Low utilisation of the negative active material, due to acid diffusion hindrance by the thick sulphate layer that develops mainly in the surface of the plate.

Results of the previous cycling tests performed in 6 V/20 Ah valve-regulated lead-acid (VRLA) modules, of SPIRAL technology, shows the high power capability of this technology in

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HRPSOC conditions [2]. Furthermore, the addition of expanded graphite, improves the charge acceptance, and cycle life with respect to other formulations (20–25% compared to standard formulation with carbon black). On the other hand flake graphite, due to its low specific surface area (SSA), does not increase cycle life. With respect to the use of micro glass fibers, the effect is unclear with respect to cycle life. Finally, increasing expander concentration from 0.2 to 0.3% does not influence cycle life. The best combination between initial performance and cycle life, is obtained with lower positive active material (AM) density, and addition of expanded graphite to the negative AM.

Failure mode under HRPSOC duty has been identified as heavy sulphation of negative AM. This sulphation increases electrical resistance of the cell, that limit the cell voltage on discharge, and provokes a marked polarisation on charge that promotes the evolution of hydrogen and cell drying out.

A new pattern of lead sulphate distribution has been observed in the SPIRAL design of the modules tested. Apart from the already known variations from the outside to the interior of the plate, as well as from top to bottom, a marked variation from the inner part to the outer part of the cylinder was observed, with higher concentrations on the inner part. This fact, seems to be determined mainly by the temperature distribution in the cylinder, with higher values in the inner part. This temperature increase, provokes a progressive drying out of the separator in this part, which in turn increases oxygen recombination efficiency markedly, and consequently higher concentration of lead sulphate. Also inner part, participates in more extent in charge/discharge duty, which also, tends to increase lead sulphate level.

2. Experimental

To try to counteract these deleterious effects, and optimise the performance of the battery especially in terms of cycle life, a series of tests, have been performed in prototypes in which different separators have been introduced.

The project objective is to optimise the glass microfiber separator to be used in VRLA batteries for the application of partial state of charge operation typically found in hybrid vehicle use. This is expected to be accomplished through the modification of the separator internal structure either by changing the characteristics of the base microfiber, modifying the ratio between coarse/fine fibers, or by the addition of inert fillers that strongly modify the internal structure of the material (pore size distribution and specific surface area). With the same purpose, membranes with very low pore size that is expected to create an effective barrier to avoid the development of short circuits will also be tested.

All are either commercially available materials or materials already developed and hence susceptible of being manufactured. This is so because the intention is to perform a practical test program in the sense of being able to use the resulting optimised material in VRLA manufacturing.

In the previous work [2] it is clear that passivating lead sulphate films are formed when the battery works continuously under HRPSOC conditions. This sulphate film becomes pro-

Table 1
Paste characteristics and formulation

	Positive	Negative
Lead oxide (kg)	100	100
Water (%)	15.2	14.1
Acid (1.4 g cc^{-1}) (%)	3.1	4.9
BaSO$_4$ (%)	–	1
Vanisperse (%)	–	0.2
Graphite (%)	–	1.5
Paste density (g cm^{-3})	4.3	4.2
Paste penetration	400	460

gressively irreversible, because a dense and thick layer develops as the time under low state of charge conditions increases. The way of dealing with this is to perform in real use systematic complete recharges to periodically eliminate all plate sulphation. In practice, this solution is quite difficult to be applied due to logistic reasons (availability of charging equipment on parking areas), being necessary to try to counteract the deleterious effects derived from hard sulphation.

Resilience characteristics of these materials have a direct relation with the pore size distribution. In fact the lower the size of the microfiber the more densely packed it is, and hence the lowest the loss of structure upon assembly and especially on the acid filling operation. This effect is especially true for the new materials charged with silica in which fiber accommodation is highly hindered because silica due to its extremely low particle size, fill the open space between microfibers and hence is more difficult for them to accommodate. Four materials with 2, 6% and two different materials with 10% silica are tested within the project. These dosages cover the practical values of silica content taking into account that silica addition has also some collateral adverse effects (mechanical strength decrease).

Concerning silica addition, it is quite important to have a good distribution all over the internal structure of the separator. On the other hand, from the point of view of manufacturing, it is not easy to make a completely uniform distribution of the silica and hence in order to try to decrease the cost of these materials as much as possible, two separators with different silica addition methods, one by spraying and the other by silica addition in the microfiber dispersion tank will be tested.

A common battery size to test the materials has been defined, that is a 15 Ah battery, being the assemblies as single cells. The main design details are the following:

- Grid alloy: binary lead tin.
- Active material: formulation for cycling application in Tables 1 and 2.
- Plate thickness: 1.0 mm positive and negative.
- Group design: seven positives/seven negatives.
- Separator compression: around 30% measured as the ratio between the final thickness of the separator once assembled, and the reference thickness at 10 kPa. Prior to the insertion in the container, all the groups were pre-compressed on a manual pneumatic press. In this way the group insertion in the container is facilitated as well as the groups receives a common treatment prior to assembly.

Table 2
Analysis of unformed plates

	Positive	Negative
Residual lead (%)	1.9	2.0
$PbSO_4$ (%)	N.A.	7.2
Porosity (%)	34.25	37.00
Apparent density (g cc^{-1})	4.99	4.51
Mean pore diameter (μm)	0.23	0.16
Surface area (m^2 g^{-1})	0.97	1.42

- Intercell connections: cast on strap welded using a binary lead tin alloy.
- Lid welding: ultrasonic welding.
- Electrochemical formation: the batteries were vacuum filled with an exact quantity of acid in each element, and afterwards submitted to the electrochemical formation process, consisting in three constant current steps at high, medium and low current rates with a total Ah input amounting to 6.5–7 times the battery capacity.

A total of 11 different materials have been collected from different manufacturers, including as already mentioned four main groups:

- Materials with silica addition in concentrations of 2, 6 and 10%.
- Materials with different coarse/fine fiber ratio.
- Double layer structure materials.
- Membranes.

The materials were provided by the most important manufacturers of this kind of products. Eleven materials have been analysed, including as already mentioned a first group of materials charged with inner filler (silica), a second group with different

fine/coarse fiber ratio, a material with a double layer structure, PVC and PE membranes.

Also, in the group of separators charged with silica, two materials with 10% silica, referenced as 10% Si-1 and 10% Si-2 are included. These two materials have completely different properties, apparently used due to the different way of dispersing the silica or to the different characteristics of the silica.

3. Result and discussion

3.1. Separator analysis

A complete analysis of the separator has been made. In the case of the PE membrane, due to its special nature, it is not possible to measure all the characteristics. Properties like compression loss, capillary rise or elasticity cannot be determined. In any case, the purpose of this membrane is to serve as a barrier to avoid the development of short circuits, not as an acid reservoir.

Separator density, mainly reflect the fiber composition as can be seen in Fig. 1. The higher the proportion of fine fibers, the higher the density will be. Density values have a direct influence on the properties of these materials especially with the ones related with pressure loss, elasticity, and in general with the characteristics that are determined by internal fiber accommodation.

Glass microfiber separator materials when submitted to pressure, experiment a permanent loss of structure, due to an internal accommodation of the microfibers. This loss of structure implies a decrease of the pressure that the separator exerts on the adjacent plates, which in turn affect to the plate-separator contact. Intimate contact, between plates and separators, is essential because in VRLA batteries are equivalent to acid and plate contact. Low contact pressure can result in low utilisation of the active material by lack of acid, and an increase of the electrical resistance of the battery.
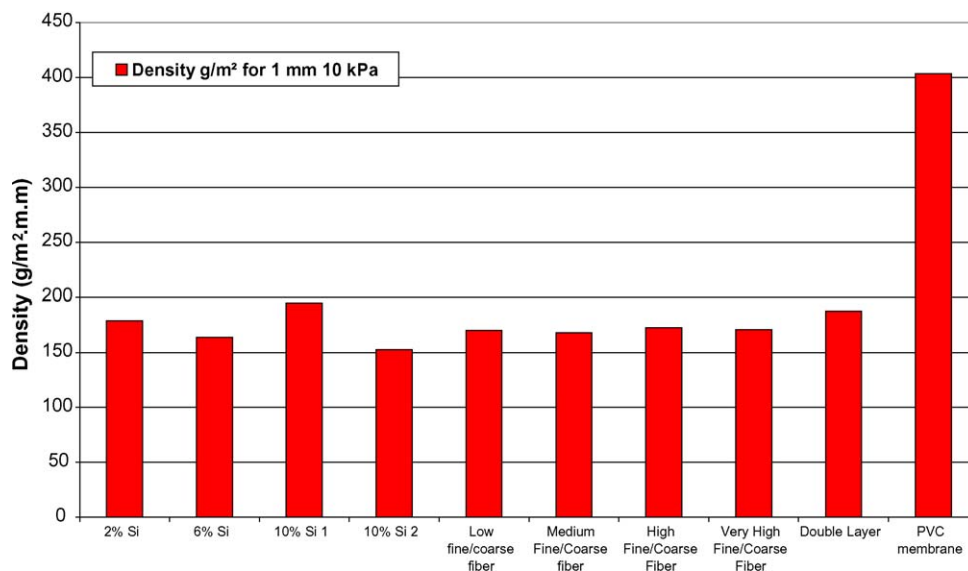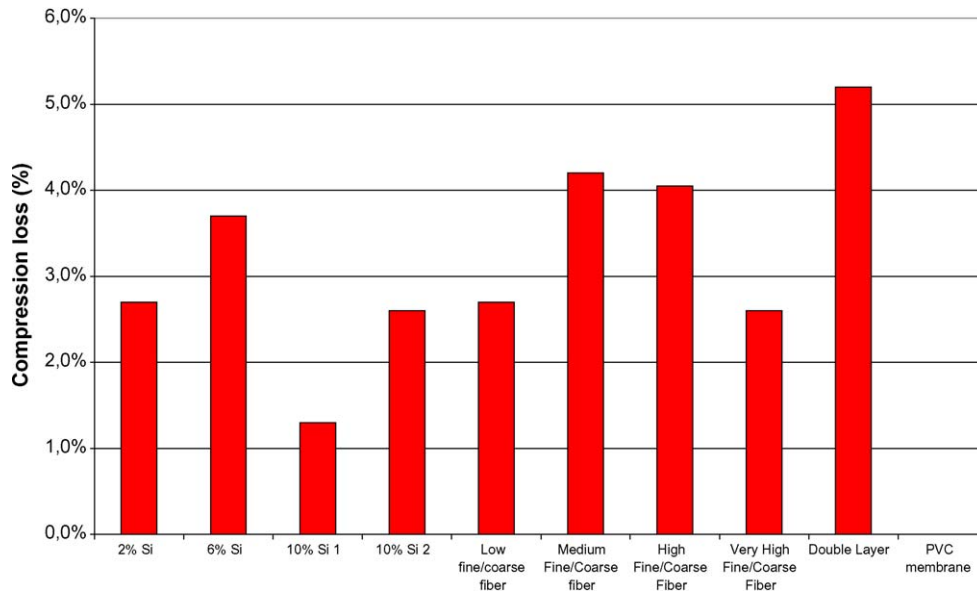

Fig. 1. Separator density at 10 Kpa.

Fig. 2. Compression loss of different separators.

Compression loss for the different materials is reported in Fig. 2. The values have a close dependence on the composition of the materials. Separators with inorganic fillers or with a high ratio of fine/coarse fiber, show a better performance exhibiting low values of compression loss, and the contrary. This is because internal fiber accommodation is more difficult in this case. Especially good result is the one of 10% Si-1 sample with only around 1% loss. Also the material with very high fine/coarse fiber shows a very good value.

Porosity values does not vary too much for the different materials, except for membranes, and are between 92 and 94%, being the most part of them around 93%. Porosity is inversely related with the separator density. The separator 10% Si-2 that has the lower density, shows the maximum value of porosity 94%, while on the other hand separator 10% Si-1 with the highest density, has the lowest porosity value 92.5% (Fig. 3).

Pore size distribution, has been measured by mean of a Coulter Porometer, and the values for maximum, minimum, and mean pore size, are represented in the attached Fig. 4.

The influence is clear. All pore sizes decreases as silica content increases. Decrease is more pronounced when going from 2 to 6%, especially in maximum pore size. Not only silica is important to modify pore size, but also fiber composition. This can be seen comparing the values of 10% Si-1 sample, with the ones of very high fine/coarse fiber ratio. Similar values for both samples are obtained.
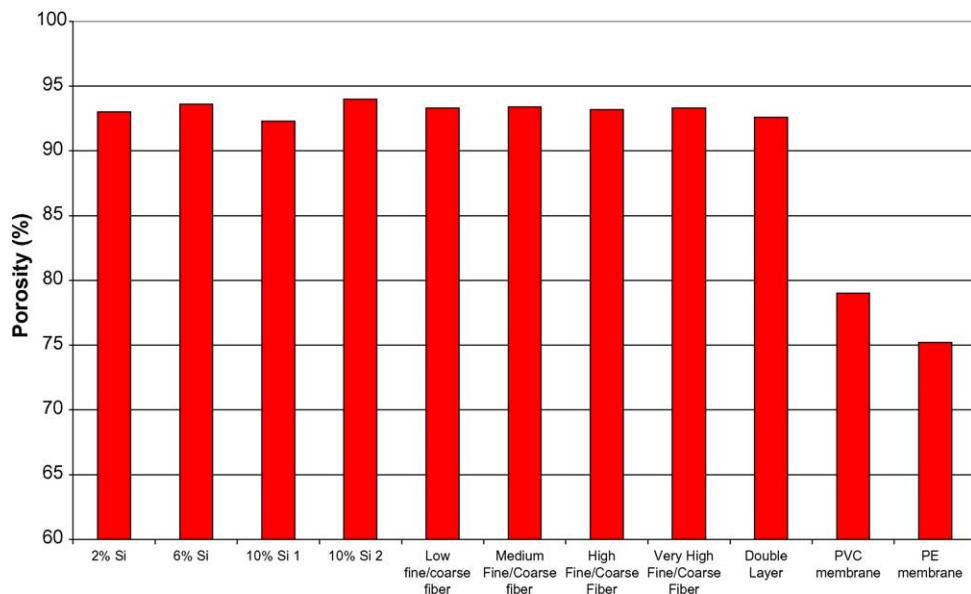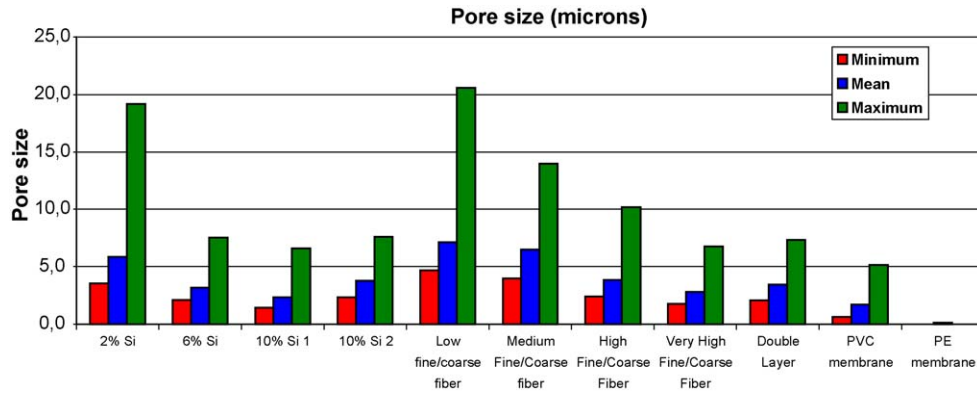

Fig. 3. Porosity of separators at 10 Kpa.

Fig. 4. Pore size distribution of separators.

The influence of fine/coarse fiber ratio is also quite clear. As the fine fiber content increases, pore size decreases. The values are especially interesting for very high ratio. Also important is the fact that for this material, maximum pore size is below 7 μm which is quite important for HRPSOC use in which, the high sulphate content caused by the low state of charge, promote the conditions for the development of short circuits by lead dendrites, and the only way to avoid them is to decrease as much as possible the pore size distribution of the separator.

Double layer structured materials, are equivalent to high fiber ratio and 6% silica content. Pore size for both PVC and PE membranes is quite low, especially for the later with a mean pore size of only 0.13 μm.

The specific surface area (SSA) values are included in Fig. 5. As it is clearly shown, silica has a dramatic influence. SSA values indicate, that is not only important the silica content, but also the characteristics of the silica added, and silica distribution. In fact samples 10% Si-1, and 10% Si-2, have quite different SSA values no matter the fact that they are supposed to have the same silica content. A possible explanation of the different SSA value could be that the silica used has different particle size and then different surface area.

Specific surface area, is a good measure of the silica content of the separator, assuming that the silica added has the same SSA. From previous tests with silica loaded materials in which different contents of silica with a specific surface area of $200 \, \text{m}^2 \, \text{g}^{-1}$ were added, the specific surface area, is the addition of silica contribution (silica SSA × silica content) + SSA of the base microfiber. From this relation silica content can be obtained.

Tensile strength of separators is quite important in manufacturing. Plate groups are assembled in automatic stacking machines that make the enveloping of the plates either by the bottom or laterally. In both cases it is necessary for the separator, to have the necessary strength to avoid the breaking of the material that would result on immediate battery failure due to short circuits.

Results are presented in Fig. 6, and from them it is quite clear the importance of the fine fiber content. Tensile strength increases steadily as fine fiber content increases, overpassing the values of all the rest of materials. Mechanical strength in glass microfiber materials is directly related to the degree of interlocking of the fibers within the structure. The lower the length of the microfiber, the higher the degree of interlocking, and consequently the higher the mechanical strength.
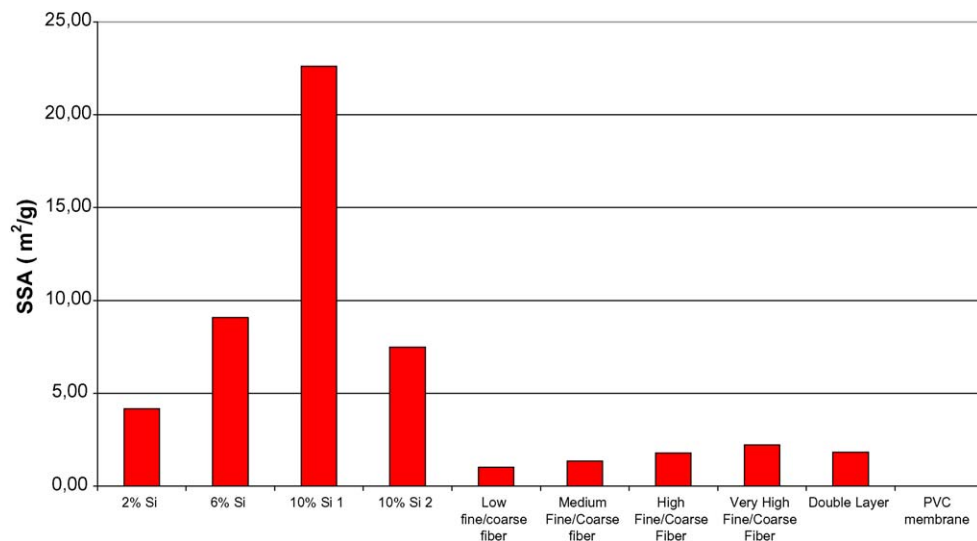

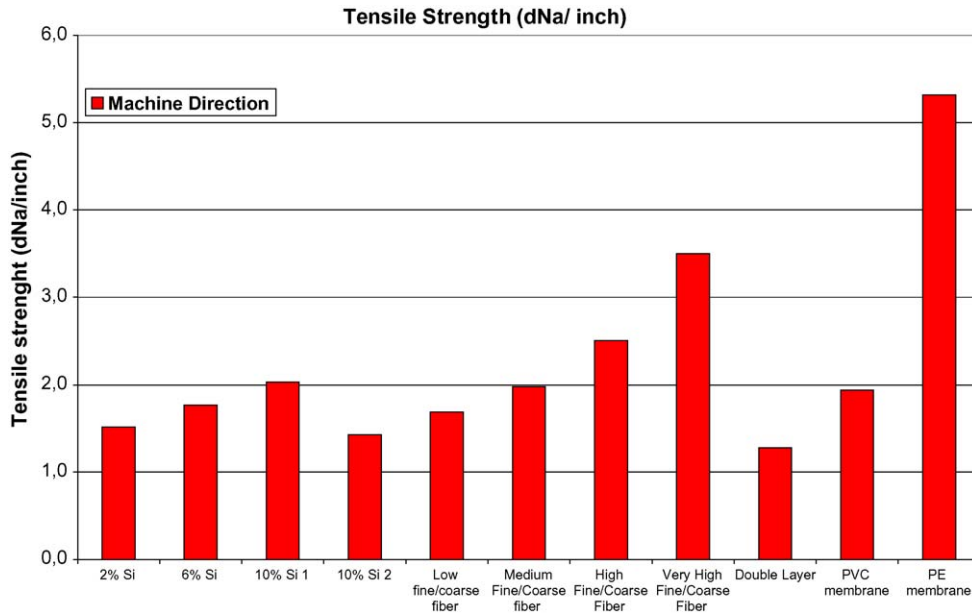Fig. 5. Specific surface area of separators.

Fig. 6. Tensile strength of separators in the machine direction.

Concerning the effect of silica, no clear conclusions can be drawn because no mater the fact that a small increase is observed, this increase seems to be due to the different reinforcing plastic fiber content. The value of the 10% Si-2, is quite strange because the very low value observed does not correspond with the higher content of reinforcing plastic fiber (16% with respect to 8% for the rest of materials).

Capillary rise at short times (1 min) is a property directly related with the pore size distribution. Acid climbing through a porous media is in equilibrium between capillary forces that makes the electrolyte to climb, and viscosity forces that tend to decrease the climbing rate [3,4]. Viscosity forces are more important as pore size decreases and climbing rate is then related

to the pore size in the sense that the lower the pore size, the lower the wicking rate. This can be seen comparing the values of Fig. 7 of capillary rise at 1 min, with the graph of pore size distribution. The highest wicking rate is obtained for the separator with low fine/coarse fiber ratio, and the lower for the material 10% Si-1.

The practical importance of this parameter is related with the filling operation. During filling it is important that the acid access all the areas of the plate and separator in the lowest possible time, otherwise if the wicking rate is low, and few acid quantity access some areas of the plate group, alkaline conditions can develop in these areas promoting the conditions for the development of short circuits between adjacent plates by lead dendrites. This kind of situations can happen when using separators with very
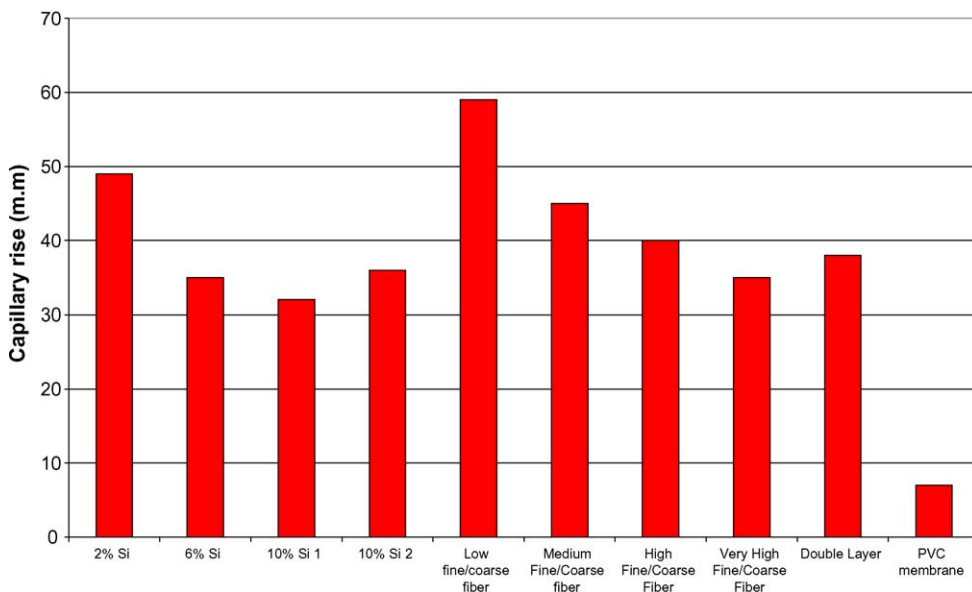

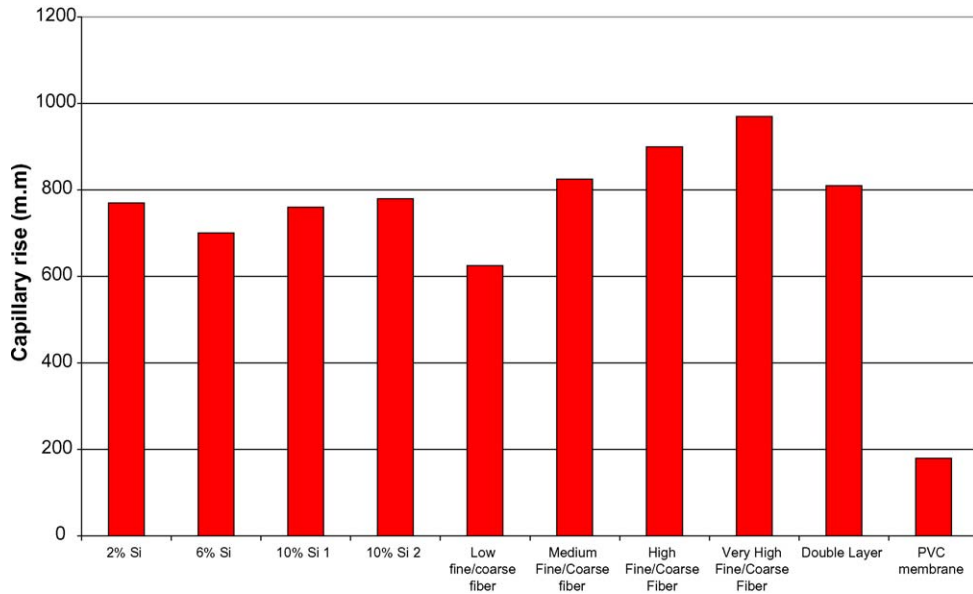Fig. 7. Capillary size of separators at short time (1 min).

Fig. 8. Capillary size of separators at long time (24 h).

low pore size, especially if the assembly is made under high compression. An equilibrium must be reached concerning pore size between beneficial and detrimental effects in terms of the development of short circuits, and in case of using low pore size materials or high compression assemblies, the filling operation should be made under high vacuum to force the acid to enter into the plate group structure as fast as possible.

Results of capillary rise at longer times (24 h), are included in Fig. 8. The situation is just the inverse to the one at short times. The lower the pore size, the higher the wicking height. This is because the capillary forces that oppose the gravitational ones, become more and more important, as pore size decreases, and

this is reflected in the total wicking height reached at long times [5,6].

The highest value is obtained for the material with very high fine/coarse fiber ratio, whereas material 10% Si-1 with the same pore size distribution, achieves lower wicking height. Probably silica interferes in the wicking creating some gelling action within the material increasing in this way the viscosity of the climbing acid, which slow the process.

Loss on ignition is a measure of the organic material content of the separator (Fig. 9). This organic material is in the form of reinforcing plastic fibers to impart mechanical strength to the separator. Taking apart membranes that are polymeric, all the
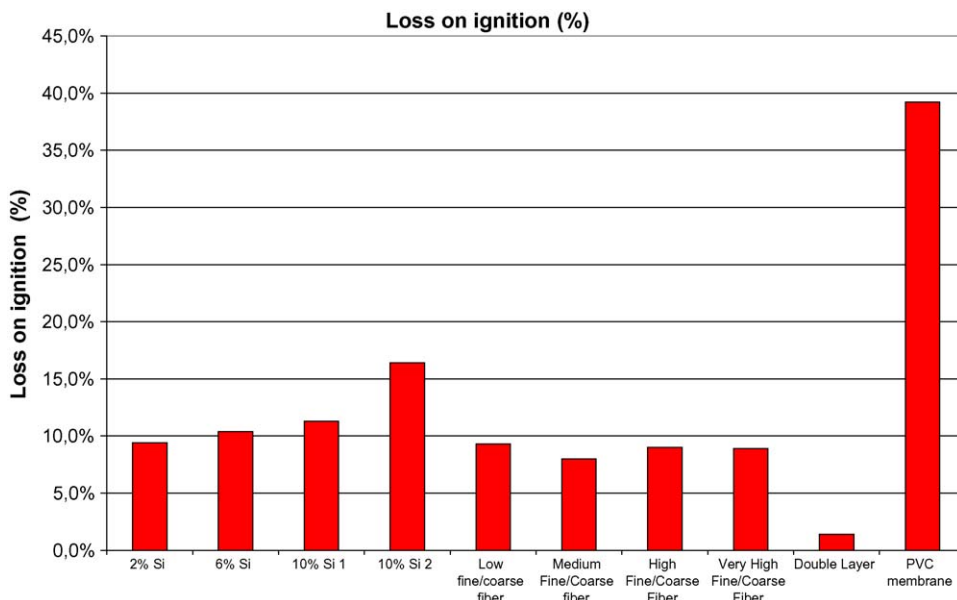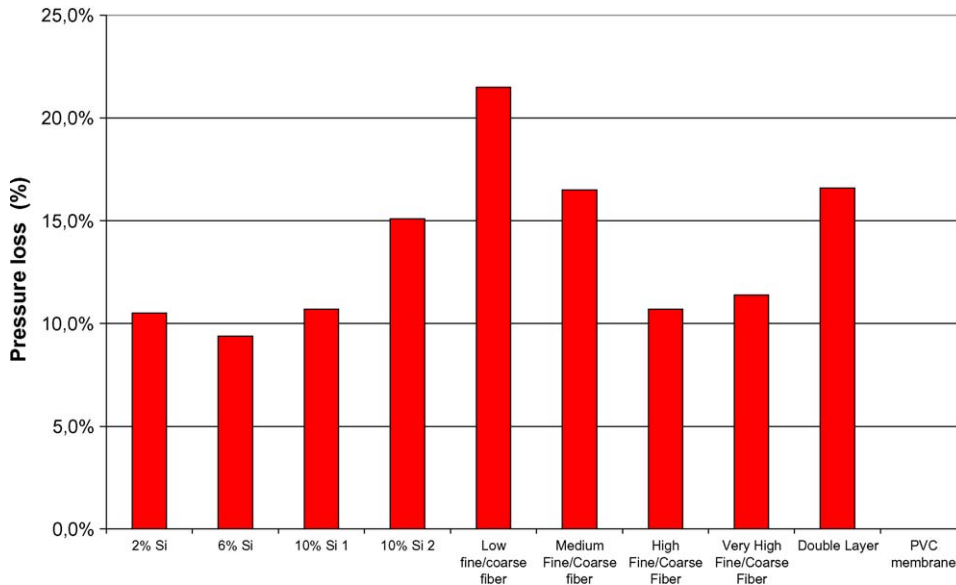

Fig. 9. Loss on ignition of separators.

Fig. 10. Separator pressure loss in acid (%).

glass microfiber materials incorporate around 8% plastic fiber. Only 10% Si-2 material has a greater content around 16% and double layer has very low content (mainly fiber glass).

Glass microfiber separators experience structural internal changes when submitted to pressure, due to internal accommodation of the microfibers, that results in a loss of structure, and as a consequence in a decrease of the pressure that the separator exert on the plates. The same process occurs even enhanced, when acid is poured in the battery during the filling operation. In this case, accommodation of the fibers is more important and is the process in which pressure loss is more pronounced. It is quite important to have the lower possible pressure loss both on assembling and especially on filling operation in order to preserve enough pressure in the battery to achieve high cycle life.

Fig. 10 shows the pressure loss in acid of different separator samples under a pressure of 50 kPa for 4 min. At the end of this period acid is poured into the separator measuring the pressure that the separator exert until stabilisation, and calculating the pressure loss with respect to the initial 50 kPa. The test is repeated with the same procedure for an initial pressure of 30 kPa. The values of pressure loss found for the two initial pressures are the same. Only when initial pressure is too high around 80 kPa, pressure loss increases, but these high initial pressure values have not practical relevance.
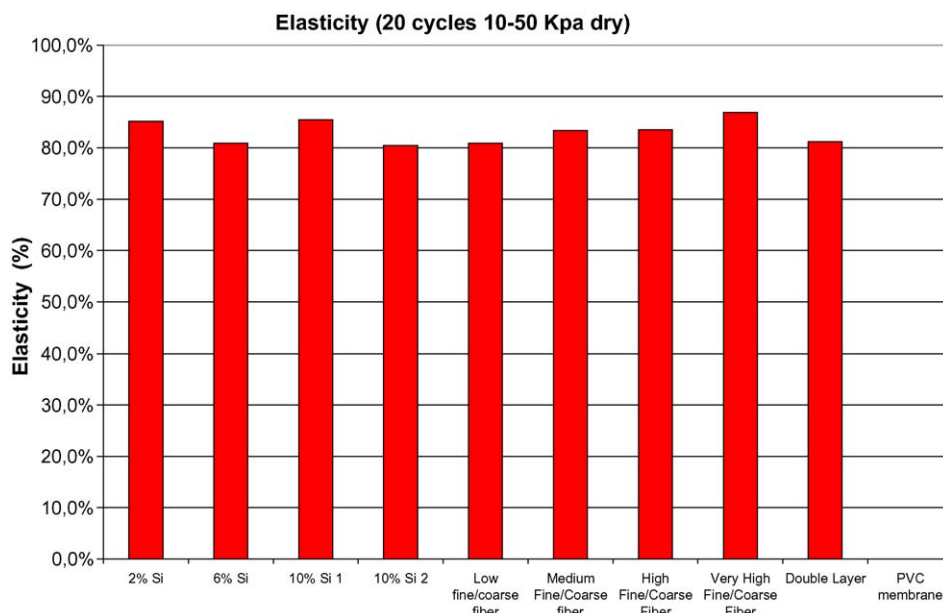

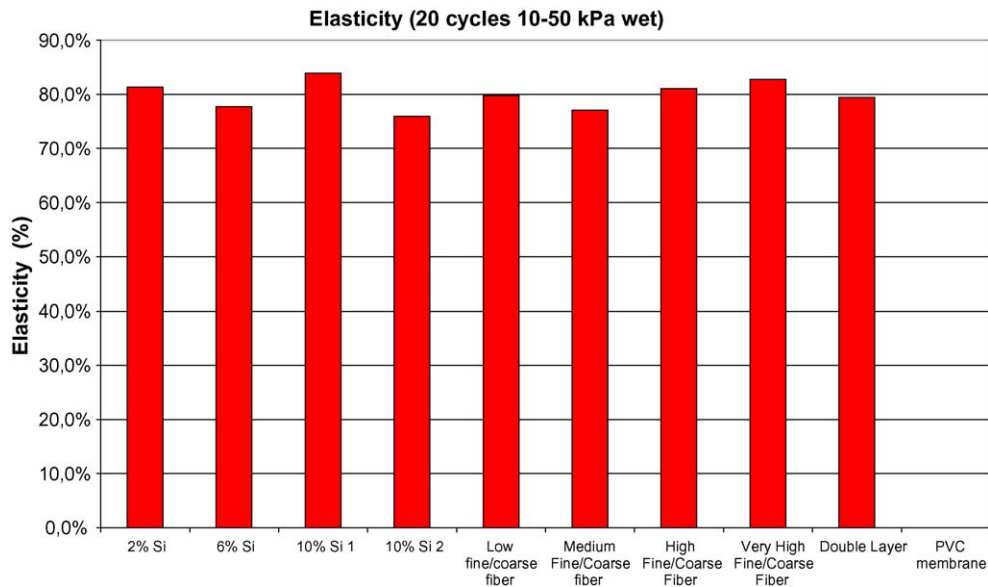Fig. 11. Elasticity of separators in dry conditions.

Fig. 12. Elasticity of separators in wet conditions.

Results are included in the attached figure in which a direct relation between pressure loss and the content of fine fibers or inorganic additives like silica, can be seen. In fact, the materials that exhibit lower pressure loss, are the ones charged with silica, except the one referenced as 10% Si-2, that again shows an anomalous result. Especially good are the results of both the high and very high fine fiber content, with values similar to the materials with silica. On the other hand the separator with low fine fiber content, shows a very high-pressure loss higher than 20%.

Elasticity on dry conditions, also called resilience test, measures the recovering ability of these materials when submitted to repetitive compression cycles. The sample under test is submitted to 20 sinusoidal cycles of compression, decompression from 10 to 50 kPa. Elasticity is calculated as the ratio between the final thickness of the separator at the end of the test, and the initial one.

Results are included in Fig. 11. The best results are again obtained for materials charged with silica, and materials with high content of fine fiber. The evolution is quite clear with respect to the fine fiber content, increasing elasticity as fine fiber content increases. Materials with (6 and 10% Si-2) silica shows some apparently anomalous results, being their values lower than the ones of 2% silica.

Elasticity in wet conditions is determined by the same test procedure as before, being the only change that the separator is wetted with acid. Results are shown in the attached figure in which it is observed that the differences are more important than when the separator is dry, being the reason that in wet state, both dry and wet fiber accommodation process take place. Again the best results are obtained for materials charged with silica, and materials with fine fiber content, being in this case the 10% Si-1 silica loaded material slightly superior. Results from these two tests show that in order to preserve enough compression inside the battery it is important to use separators whose internal structure has been modified by the addition of inorganic fillers

like silica, or materials whose degree of fiber accommodation is lower due to the use of large proportion of fine fibers. This is especially true for applications like the one in hybrid vehicles in which the battery is submitted to repetitive cycling (Fig. 12.).

3.2. Testing of VRLA single cells

Ten different groups of VRLA cells corresponding to 10 different separator materials have been assembled in the conditions indicated before. They have been assembled as 2 V/15 Ah cells that can be externally connected to form 6 V batteries. They have been assembled in three cells of a 12 V container, leaving between each of them a void cell. The batteries include the following separators:

- Silica loaded materials: 2, 6, 10% Si-1 and 10% Si-2 separators.
- Fine/coarse fiber ratio: separators with medium, high and very high ratio.
- Membranes: PE and PVC membranes.
- Double layer separators.

Electrochemical formation has been made with a three-step constant current formation process, at high, medium and low rate, charging a total of 7.8 times the rated capacity (15 Ah), or 6.5 times the real capacity (18 Ah).

Cells were submitted to the power assist cycle life test. The aim of this test is to try to determine the possible influence of the glass microfiber separator and membranes in the life duration of the cell. To know this both cell capacity, voltage, and internal resistance, were followed on partial state of charge cycling at 2.5% DOD. The profile includes an initial discharge step at 5 C rate that simulates the electrical boosting during the acceleration stage. Next steps simulate regenerative braking and include three steps at 4.5, 2.5 and 1 C rates. This profile called "microcycle", is repeated 10,000 times (one unit), with the battery at 60% SOC,

2V/15Ah CELLS. POWER ASSIST CYCLING.
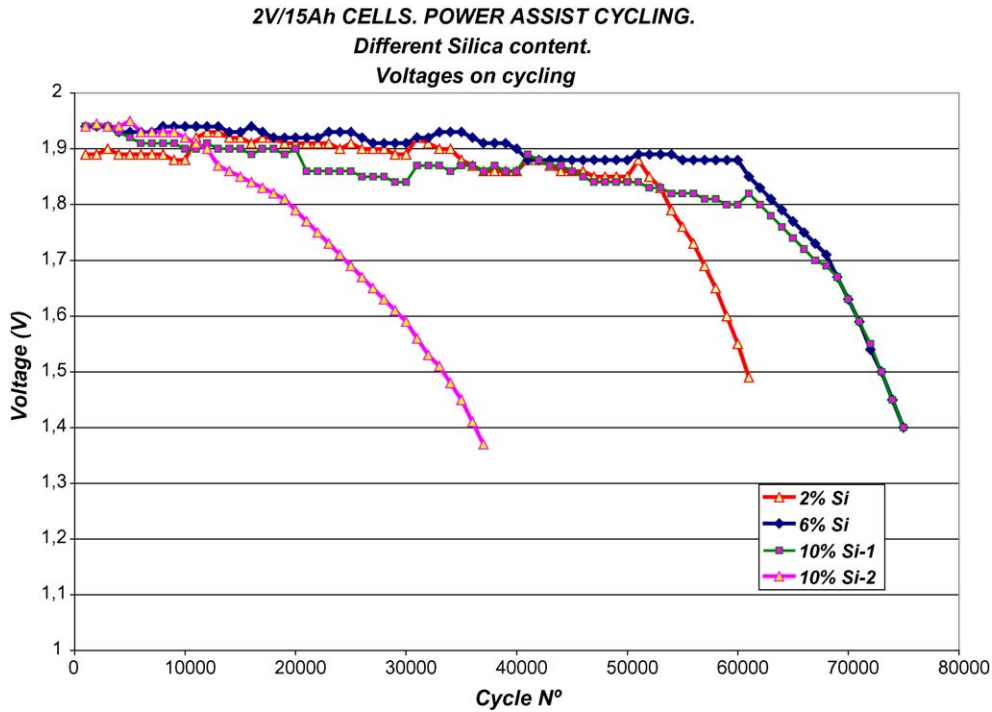**Different Silica content.**
Voltages on cycling

Fig. 13. Cell voltage on cycling for separators with silica additive.

after which, a capacity, weight, and internal resistance checking is performed. The cell is considered to fail, when an end of discharge voltage during cycling of 1.66 V, corresponding to 10 V per 12 V module is reached, or the battery capacity decreases to 50% of the initial value.

Because the assembly of the single cells was made in a standard 12 V container not in consecutive cells, that is allowing a free cell between two consecutive assemblies, is was considered not necessary to provide refrigeration through the cycling test, due to the higher heat dissipation surface allowed. The test was made at an ambient temperature of 25 °C.

Final results of this test, are included in Figs. 13–21, that show the evolution of cell voltage, cell capacity, internal resistance and weight loss, during cycling.

2V/15Ah CELLS. POWER ASSIST CYCLING.
Different silica content.
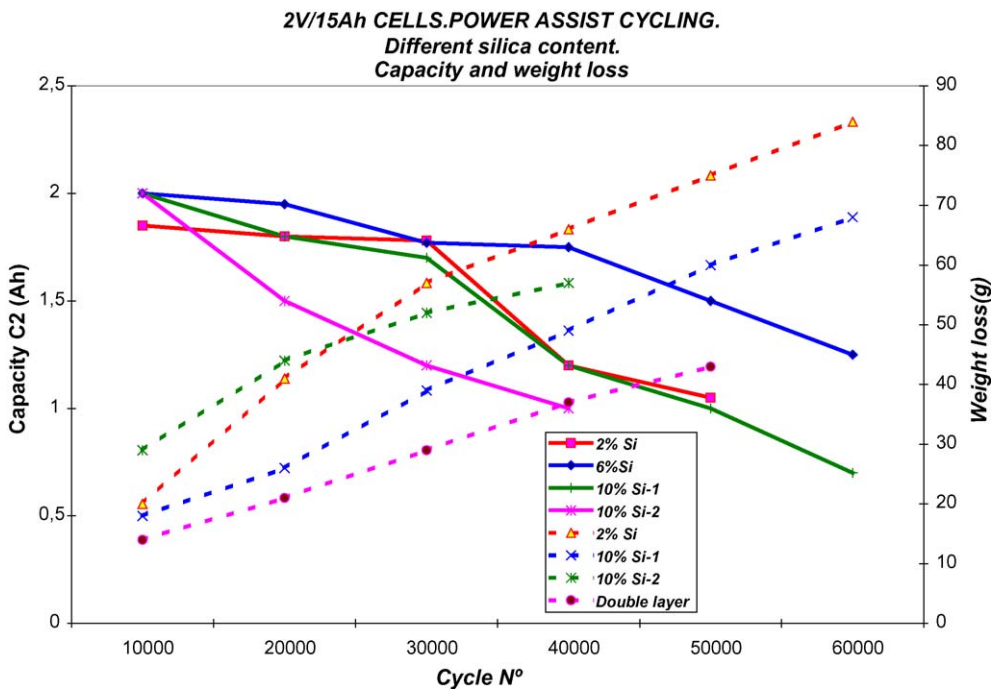**Capacity and weight loss**

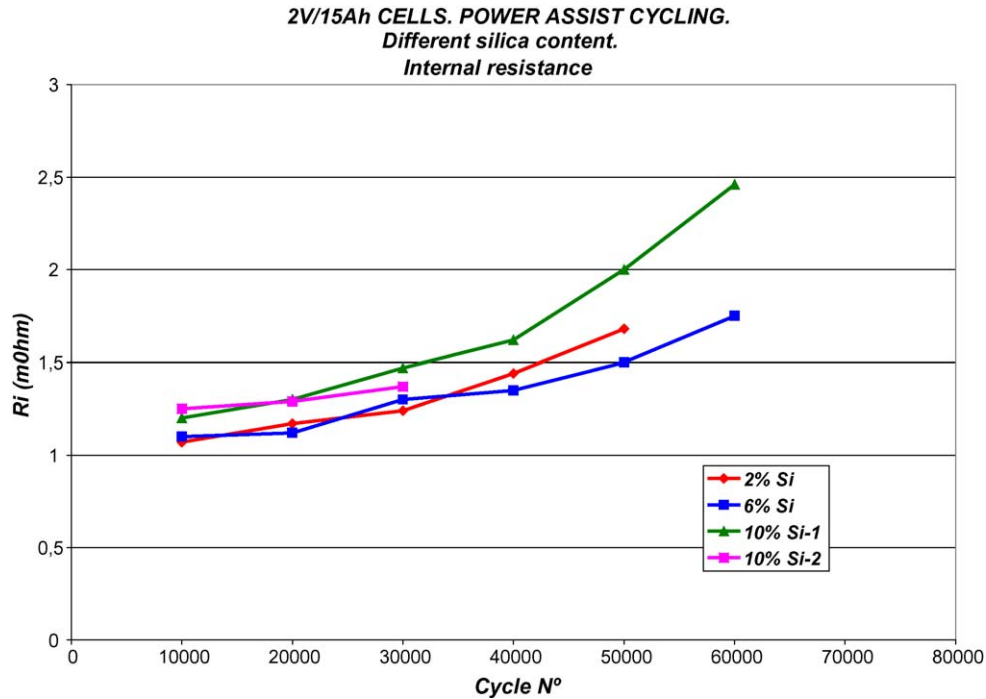Fig. 14. Cell capacity and weight loss for separators with silica additive.

Fig. 15. Cell internal resistance for separators with silica additive.

3.3. Analysis of the results

3.3.1. Silica loaded separators

Voltages on discharge along cycling can be seen in Fig. 13. Total duration for the groups of 2, 6, and 10%Si-1, is quite similar, reaching a total of 70,000 power assist cycles with a very uniform and steady decay of the voltages. The performance of these three groups is basically equivalent. Only the group with 2% silica shows a lower value, reaching a total of 60,000 cycles.

The big difference is in the 10% Si-2 group, with a remarkable poorer performance. Steady and progressive voltage decay occurs, with a total duration of 35,000 cycles. This result is in agreement with the ones obtained during the characterisation of the separators. In fact this material is the one that shows in general the poorer results. Especially important in this sense, is the
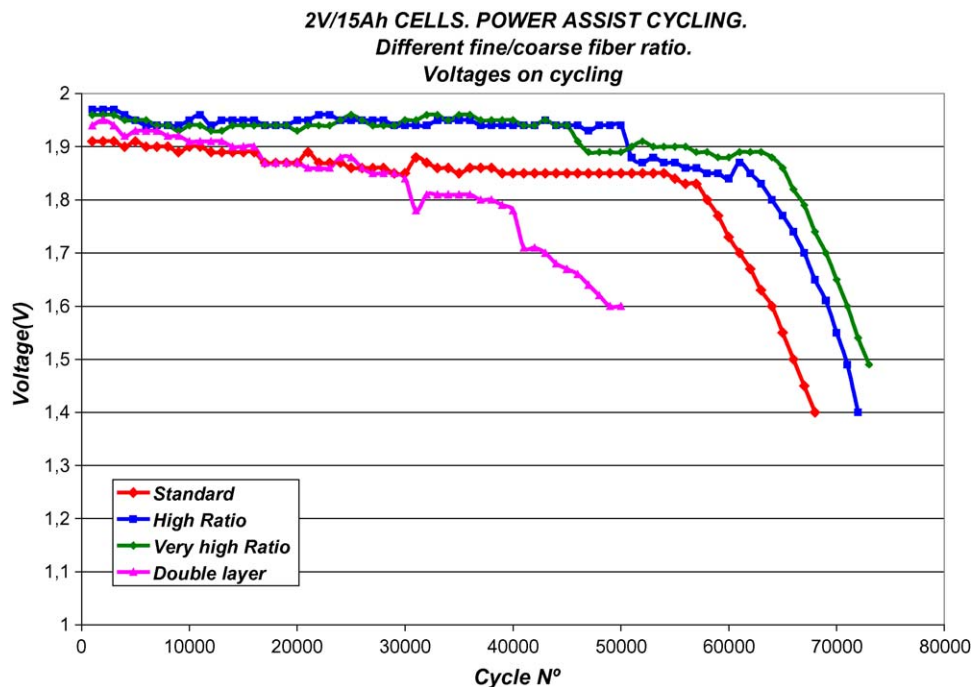

Fig. 16. Cell voltage on cycling for separators with different fiber/coarse fiber ratio.
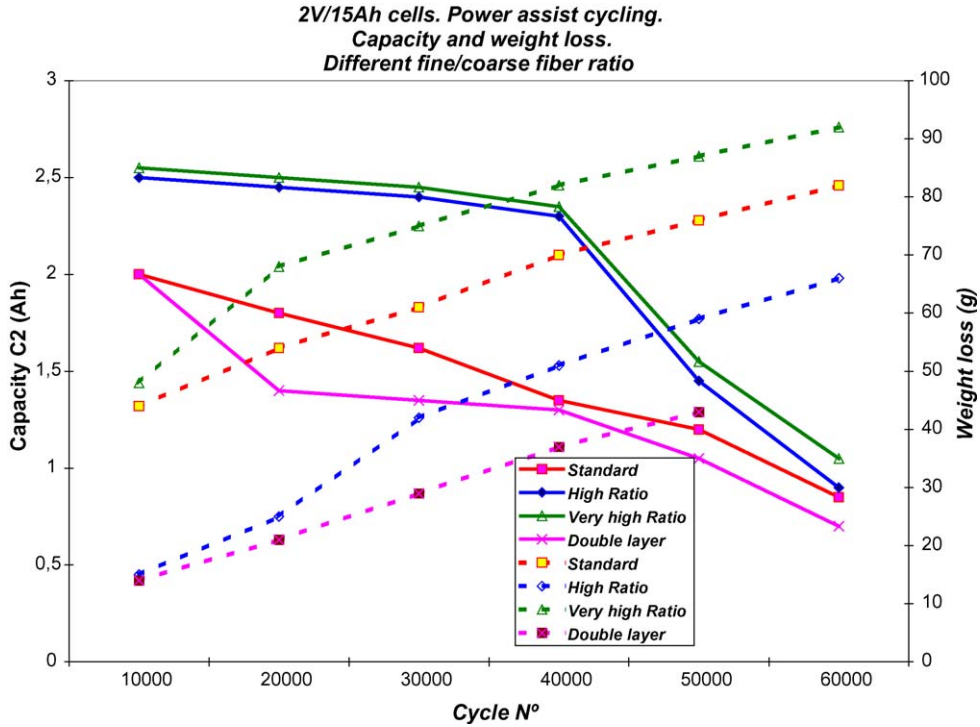
Fig. 17. Cell capacity and weight loss for separators with different fiber/coarse ratio.

elasticity characteristics in wet conditions. This material shows the highest loss of compression during this test. It is well known the capital importance that the degree of compression plays in the cycle life performance.

The main problem with this material seems to be related with the low density that it shows at all degrees of compression. When looking at the table showing the data of the different separators, it can be seen that this material has a density at 10 kPa of 153 g m^{-2} mm, in comparison with an average value of around 170 for the rest. The process of fiber accommodation is easier in this material and hence the loss of compression upon assembling and acid filling is higher.
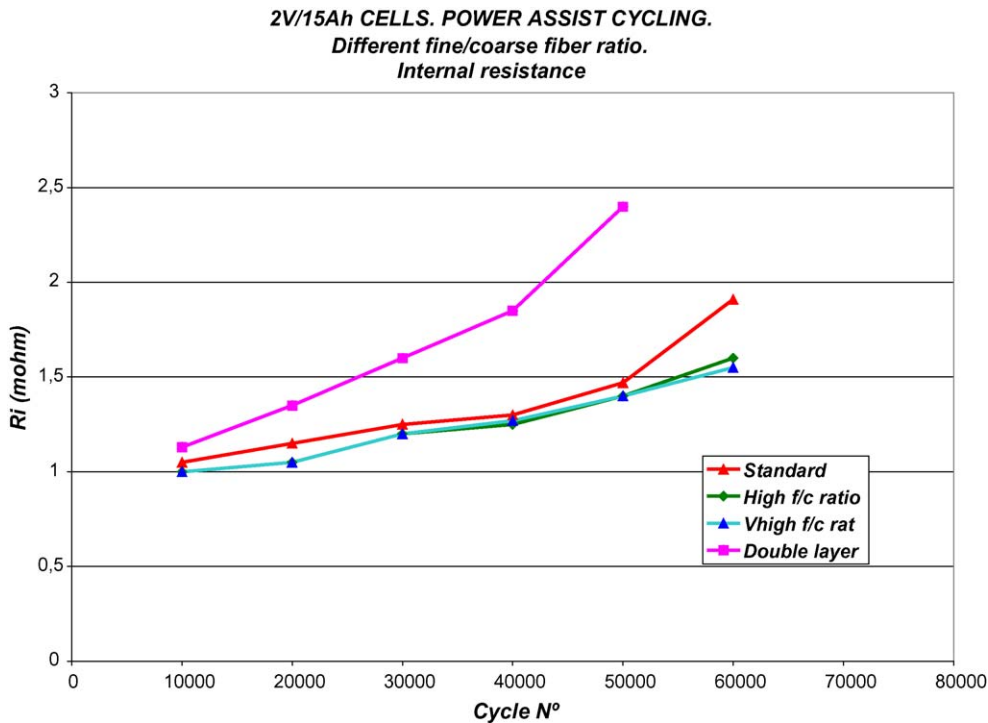

Fig. 18. Cell internal resistance for separators with different fiber/coarse ratio.
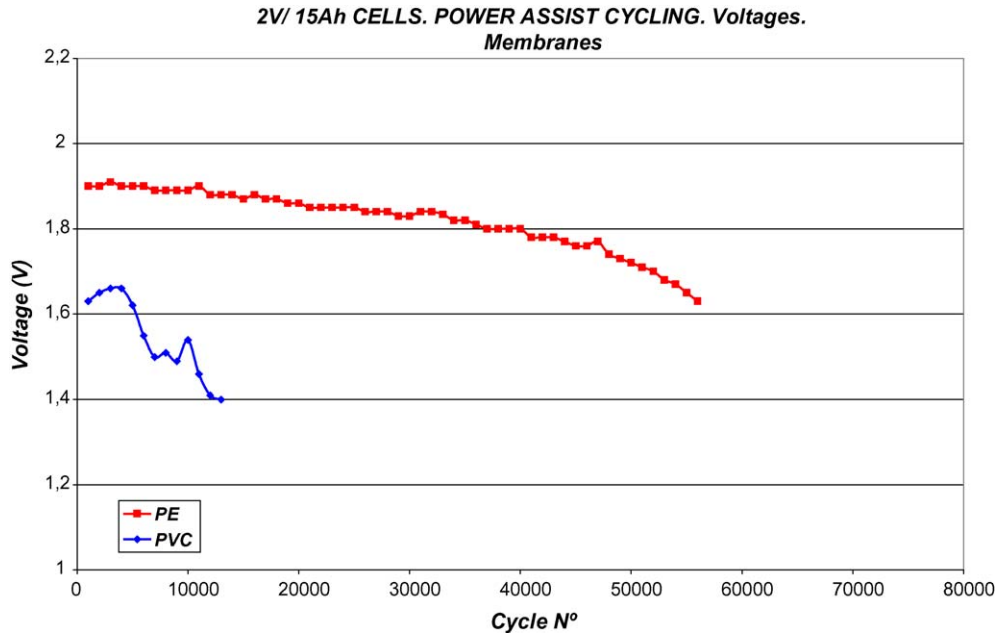
Fig. 19. Cell voltage on cycling for PVC and PE membranes.

The evolution of capacity on power assist cycling, is included in Fig. 14. Results shows a comparable performance for the groups of 2, 6, 10% Si-1, with the only exception that the group of 6%, shows the same tendency, but with higher values from 30,000 cycles.

Again the group of 10% Si-2, is the one that shows the poorer results, showing a marked decrease of capacity from the very beginning. Again the lower compression that this material keeps in the cell influences the obtainable capacity, in this case because low degrees of compression, tend to isolate the active material of the plate from the acid, and limit the available capacity due to the lack of acid in the plates.

The weight loss values are included in the same graph and show a similar tendency for all the groups. In principle the performance should be similar for all the materials, because total porosity that determine the oxygen recombination efficiency is quite similar. Weight losses especially at the beginning, are more strongly affected by the internal conditions of the cells, concerning the degree of acid saturation of the separator. Only the slope of the graphs could show a different performance of the separator that is not appreciated in this case.
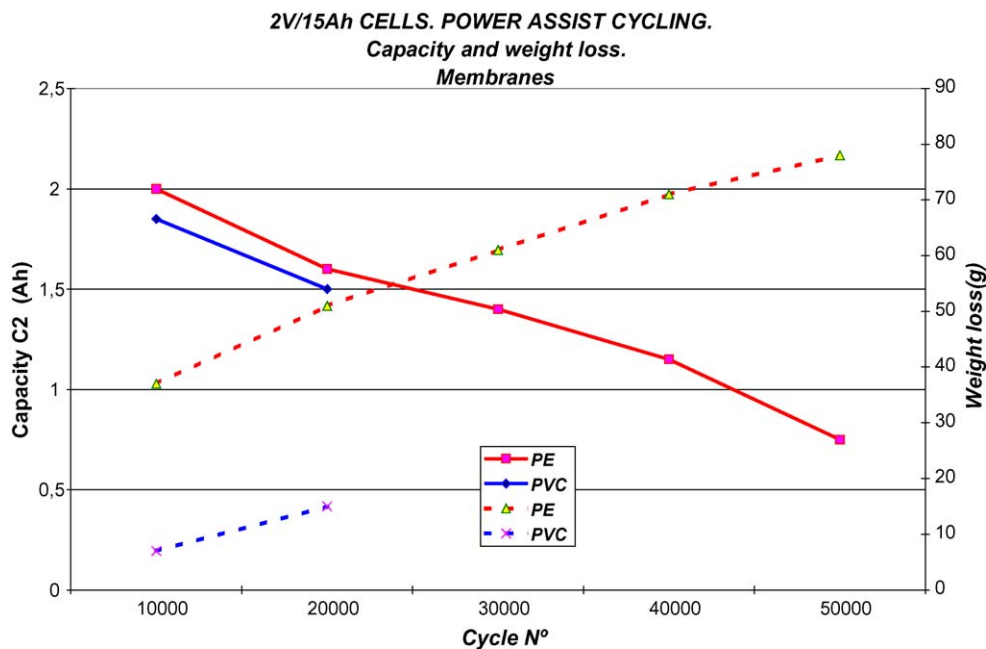

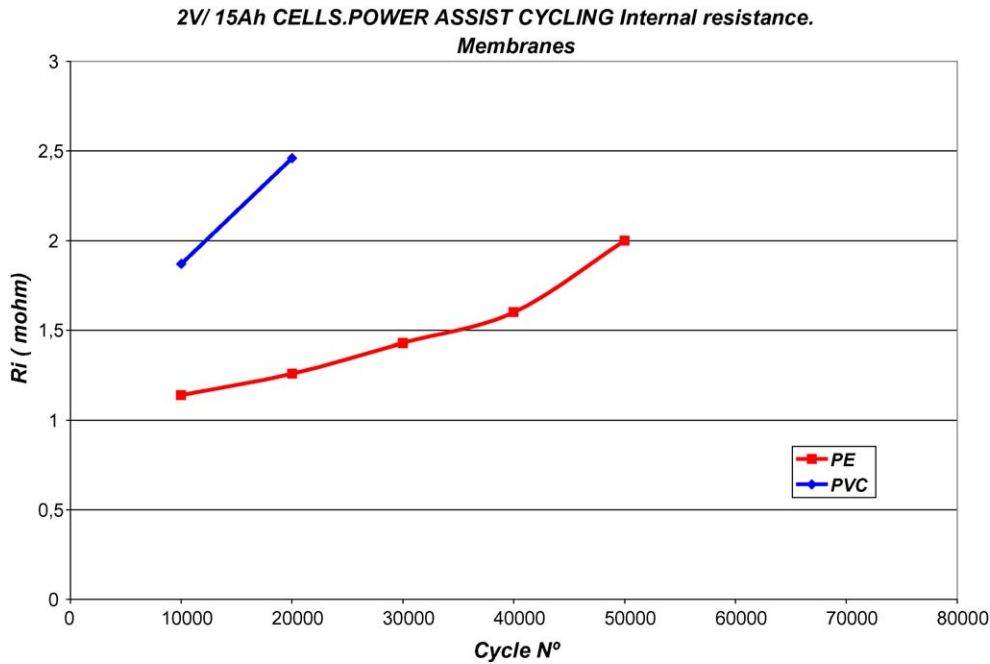Fig. 20. Cell capacity and weight loss for PVC and PE membranes.

Fig. 21. Cell internal resistance for PVC and PE membranes.

In Fig. 15 can be seen the evolution of the internal resistance with cycling. No noticeable differences can be appreciated, showing all the groups almost the same tendency. Differences are quite small.

3.3.2. Materials with different fine/coarse fiber ratio

The evolution voltages on discharge can be seen in Fig. 16. In this case, there are some differences between the different groups. The ones with high and very high ratio exhibit the best performance, reaching a final figure of 75,000 cycles. The group with very high ratio shows a slightly better performance concerning voltage evolution.

Separator with double layer structure shows a slightly lower performance than the rest. Evolution is similar until reaching 30,000 cycles. From this point to the end of the test cell voltages are inferior, but without showing any catastrophic or sudden decay.

Capacities evolution is in agreement with the performance outlined before (Fig. 17). The groups with high, and very high ratio, shows also the best performance in terms of capacity.

From the previous graph, it can be seen, that the slope of the curves showing the weight loss along cycling, is the same for all the groups. That means that recombination efficiency is also the same. The same considerations as in the case of the materials charged with silica, with respect to the porosity of the different separators, can be made. Total porosity is not affected by varying the proportion of fine and coarse fibers, only pore size distribution is affected but it does not produce any noticeable effect in the oxygen transport properties through the separator and as a consequence in the efficiency of the oxygen recombination within the battery. The initial differences in water consumption are due to the different internal conditions of the cells concerning saturation of the separator. These differences in water consumption

during the first 10,000 cycles, eliminates the excess of water in the cells, with the result that from this point onwards oxygen recombination is similar for all the groups.

The tendency and values of internal resistance are similar for the three groups with different ratio of fine and coarse fiber. On the other side, the material with double structure shows an increase with respect to the other groups. This fact explains the differences observed in the evolution of the voltages on discharge in which this material showed a voltage decrease with respect to the other groups.

3.3.3. Membranes

The cycling performance is quite different between PE and PVC membranes. While prototypes with PE achieve 55,000 cycles, the ones with PVC only reach 12,000. Voltage evolution is also different. Cells with PE membranes shows a smooth variation, while on PVC cells voltage variation shows more scattering and also the tendency to fall is more pronounced.

A general conclusion about membranes is that they are inferior in electrical performance with respect to the glass microfiber separators.

The capacity decline tendency is the same for both membranes, as can be seen in Fig. 20.

Weight loss comparison between PE and PVC is difficult due to the low duration of the prototypes with PVC membranes. Initial differences in water consumption does not reflect necessarily any difference in separator performance, but as explained before, mainly reflect the internal condition of the cells, with respect to acid content.

Comparison with glass microfiber separators, shows a similar performance. In fact, for both PE membrane and AGM separator the slope of the curve is around 10 g/10,000 cycles, no matter the fact that PE membrane has a lower pore size

Table 3
Positive plates analysis after power assist cycling

Separator type	PbO$_2$ (%)	PbSO$_4$ (%)	Porosity (%)	Mean pore size (μm)	Apparent density (g cm^{-3})	SSA (m^2 g^{-1})
Silica loaded separators						
2%	74.4	20.8	51.3	1.22	4.05	0.92
6%	95.6	<0.3	51.7	0.46	4.36	2.15
10% Si-1	88.1	8.1	49.9	0.46	4.49	1.89
10% Si-2	95.3	<0.3	50.4	0.34	4.35	2.92
Different fine/coarse fiber ratio						
Medium	95.7	<0.3	51.6	0.39	4.31	2.42
High	87.1	9.0	50.2	0.51	4.27	1.75
Very high	94	1.4	53.5	0.64	4.2	1.99
Double layer	95.7	<0.3	53.0	0.46	4.35	2.45
Membranes						
PE	95.7	<0.3	51.9	0.39	4.42	2.65
PVC	95.1	<0.3	51.9	0.43	4.32	2.74

(0.13 μm versus 4 μm for mean pore size) that clearly represents a higher barrier for oxygen diffusion. Nevertheless, this fact is compensated by the extremely low thickness of the PE membrane. No conclusions can be derived for the PVC due to its low duration.

The internal resistance evolution is quite different for both PE and PVC. While PE membranes shows values and tendency similar to AGM separators, PVC membranes have considerable higher values as well as a strong tendency to increase at least in the limited duration of the cycling. Higher absolute values for PVC membranes cells can be explained simply by the difference in electrical resistance between PE and PVC membranes (13 mΩ cm^2 versus 45 mΩ cm^2). Higher slope of increasing on the other hand could have relation with the fact, that being the PVC membrane relatively uncompressible, it is unable to adapt itself completely to the surface roughness of the plates and due to this, gas bubbles can develop between the membrane and the plates a process that increases with cycling.

3.3.4. Cells teardown and analysis

After completing cycle life tests, all cells were opened and analysed. Before teardown, all cells were submitted to a complete recharge. Once opened, all cells were inspected looking for any defect that can be the responsible for the cell failure. Samples of both positive and negative plates were taken and immediately washed with water until total acid elimination. Finally the plates were dried under vacuum and sent to physicochemical analysis.

After cells visual analysis, it becomes evident, that the main cause of battery failure, has been cell deformation and growth due to the heating that occurred during cycling. Almost all the cells experimented some degree of deformation being in most part of the cases quite important.

Results or the physicochemical analysis of plates are presented in the attached tables for positive and negative plates (Tables 3 and 4).

The most relevant fact is the high concentration of lead sulphate that develops in the negative plates upon cycling. Values as high as 70% can be found in some cases. Lead sulphate concentration, bears a direct relation with the number of cycles that the

cell has withstand. Not clear difference between top and bottom of the plate is found in this case.

3.3.5. Power assist tests with refrigeration

As indicated before, the cells suffered unexpected failure modes due to the excessive heating that occurred during cycling. It was then decided to repeat cycling providing external refrigeration. Only the groups that showed a better electrical performance in the previous tests were put on cycling. These were:

- Silica loaded separators: 2, 6 and 10% S-1
- Different fine/coarse fiber ratio. High and very high ratio, as well as double layer separator.

Voltage evolution during cycling is included in Fig. 22. As can be seen, a clear difference exists between the group of cells incorporating separators with silica, and the one with different proportion of fine/coarse fiber. The group of cells with silica separators achieve a duration between 110,000 and 130,000 cycles, whereas the other group achieves only 60,000–70,000 cycles.

Table 4
Negative plates analysis after power assist cycling

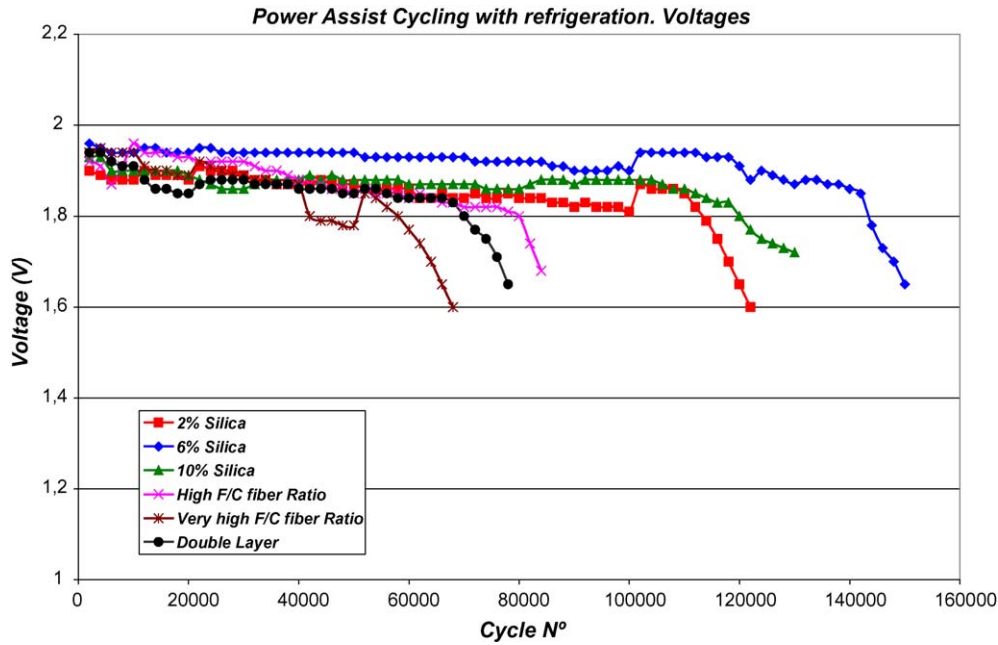| Separator type	Lead sulphate (%)		SSA (m^2 g^{-1})	
	Top	Bottom	Top	Bottom
Silica loaded separators				
2%	52.9	24.7	0.26	0.18
6%	35.9	33.6	0.52	0.55
10% Si-1	44.9	48.2	0.55	0.51
10% Si-2	60.3	41.4	0.50	0.57
Different fine/coarse fiber ratio				
Medium	36.1	41.2	0.50	0.45
High	77.6	73.0	0.34	0.43
Very high	75.9	56.3	0.38	0.47
Double layer	29.8	40.8	0.57	0.53
Membranes				
PE	30.3	41.0	0.51	0.54
PVC	18.5	30.1	0.61	0.64

Fig. 22. Cell voltages on power assist cycling with air refrigeration.

Silica content seems to be not so important, being the results for 6 and 10% similar. From the results, a silica concentration of 5–6% seems to be the optimum.

Capacity evolution along cycling is represented in Fig. 23. It follows the same path as the voltages. A sharper decline for the groups with different fine/coarse fiber content, and a smooth decline for the group of silica. Finally weight loss is included in Fig. 24.

After completing cycle life tests, the cells were opened and analysed. In this case, no excessive heating occurred during cycling, and hence no deformation of cells and group growth

was observed. The main facts observed upon visual analysis, were a moderate corrosion on positive grid that nevertheless conserved its structure, soft and muddy positive active mass in the cells with longer duration, and negative active mass with light grey colour, an indication of the existence of lead sulphate.

Plate analysis results are included in the two following tables. Results of the 6% silica are not included because have not yet completed cycling tests. As in the previous test, the most noticeable fact is the development of high concentration levels of lead sulphate with some tendency to increase in the upper part of the plate, confirming other tests (Tables 5 and 6).
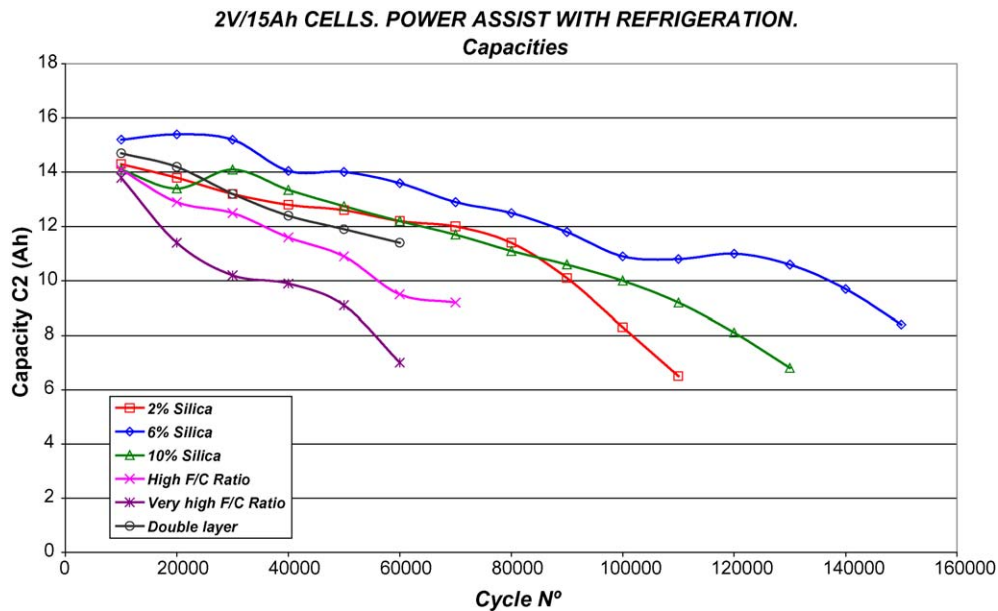

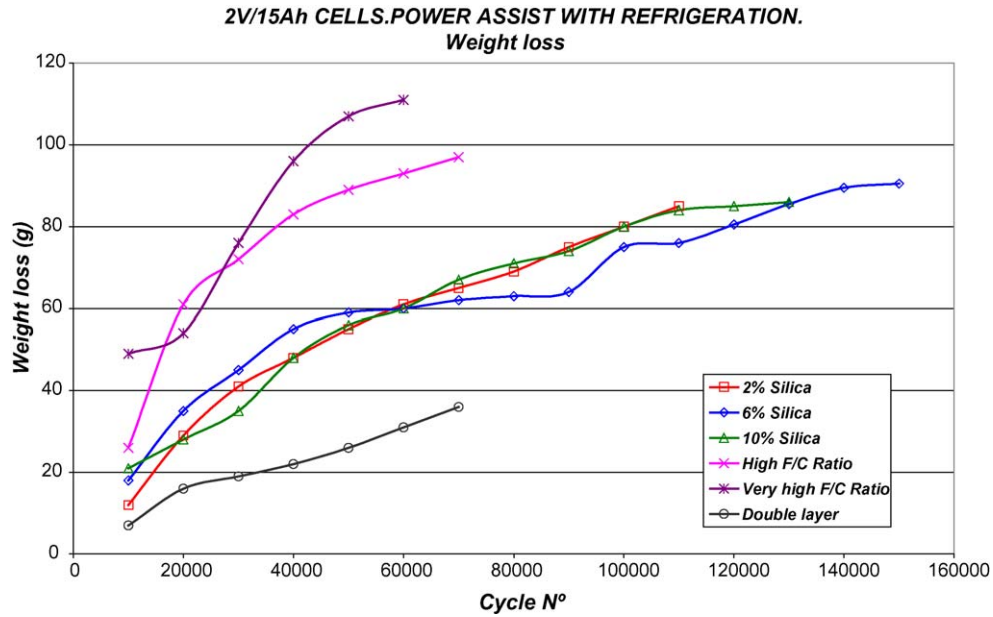Fig. 23. Cell capacity on power assist cycling with air refrigeration.

2V/15Ah CELLS.POWER ASSIST WITH REFRIGERATION.
Weight loss

Fig. 24. Weight loss on power assist cycling with air refrigeration.

Table 5
Positive plates analysis after power assist cycling

Separator type	PbO_2 (%)	$PbSO_4$ (%)	Porosity (%)	Mean pore size (μm)	Apparent density (g cm^{-3})	SSA (m^2 g^{-1})
Silica loaded separators						
2%	95	1.0	53	0.59	4.23	2.41
10%	95.5	0.9	53	0.9	4.25	1.82
Different fine/coarse fiber ratio						
High	93	2.0	55	0.31	4.05	3.4
Very high	94.6	0.3	53	0.21	4.3	4.28

Table 6
Negative plates analysis after power assist cycling

Separator Type	Lead sulphate (%)		SSA (m^2 g^{-1})	
	Top	Bottom	Top	Bottom
Silica loaded separators				
2%	48.9	50.7	0.45	0.85
10%	58	48	0.39	0.47
Different fine/coarse fiber ratio				
High	40	30	0.36	0.39
Very high	50.5	39.4	0.47	0.56

4. Conclusions

From the results of the tests performed with different glass microfiber separators, it is clear the positive influence that the addition of silica to the structure of the separator exerts in the electrical performance of the batteries. All the groups with silica have achieved cycle life durations in the range 110,000–130,000 cycles, a marked increase with respect to the other groups with durations in the range 60,000–70,000 cycles. A concentration of 5–6% silica seems to be the optimum.

From the cycling tests with and without refrigeration it becomes clear the importance of an adequate thermal management, providing some kind of refrigeration, to avoid the development of high temperatures in the batteries that provokes cell deformation, high corrosion and group growth that finally limit battery life and mask the possible influence of any other possible parameter.

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