

Extending cycle life of lead-acid batteries: a new separation system allows the application of pressure on the plate group

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Abstract

Since 1983, it has been claimed that pressure applied on a lead-acid battery increases its cycle life. But until now, the use of pressure in production batteries was limited by the mechanical properties of the conventional separation systems (absorptive glass mat (AGM), and gel) which cannot withstand mechanical pressure. In 1997, Daramic developed the new acid jellying separator (AJS) with the aim of combining the advantages of both conventional separation systems and to allow the application of lasting plate group pressure. The new separation system was evaluated and much information was gained on the effect of pressure in a lead-acid battery, e.g. on the evolution of the mechanical pressure during one cycle and during cycle life. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Capacity loss by reduced conductivity is observed during cycling of lead-acid batteries [1]. It is related to the physical changes in the positive active material i.e. its expansion with increasing cycle number, causing the rupture of the conducting bridges between the lead dioxide particles. The application of an external mechanical pressure on the plate group proved to be a tool for overcoming the expansion and shedding of active material [2]. However, the practical application of a durable mechanical pressure in production valve-regulated lead-acid (VRLA) batteries was not possible until now due to the mechanical properties of the conventional separation systems, i.e. gel and AGM, the latter being mostly composed of glass and/or some synthetic fibres.

A new separator has been developed by Daramic [3] that is able to withstand high pressure [4]. Within the framework of a project (BE97-4085) financed by Advanced Lead-Acid Battery Consortium and the European Community, the new separator was evaluated and tested in real

valve-regulated lead-acid cells as well as outside the lead-acid system.

2. Experimental

2.1. Oxygen diffusion coefficient measurement

In order to quantify the oxygen transfer through the separator, a test design has been constructed that is based on the method shown in Fig. 1.

The oxygen and nitrogen flows are set constant and the oxygen partial pressure is recorded. The saturation of the separator progressively decreases while the gas flows dry it out. For different saturation levels, the separator is removed from the system, the part where the oxygen flow took place is cut out and the saturation is calculated from its weight. From the value of the oxygen partial pressure in the nitrogen flow before measurement interruption, the oxygen diffusion coefficient through the separator is deduced.

2.2. Recording of the mechanical pressure on the walls of VRLA cells

In order to get a value of the mechanical pressure on the plate group during cycling, whole cells are inserted into a pressure recording device as shown in Figs. 2 and 3.

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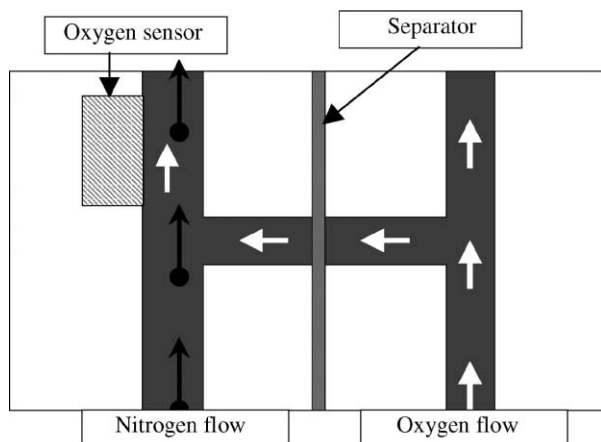


Fig. 1. Method for the measurement of oxygen diffusion coefficients as a function of the saturation rate of the separator.

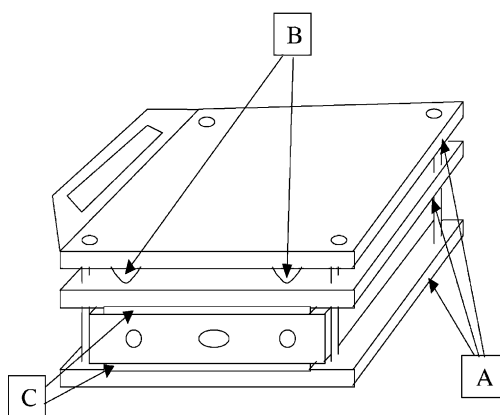


Fig. 2. Schematic pressure recording device. (A) aluminium plates; (B) feet of the balance connected to deformation sensors; (C) plastic spacers that transfer the compressive force on the electrode surfaces only.



Fig. 3. Pressure recording device.

Table 1
Drawbacks of the conventional separation systems in VRLA batteries

| Drawbacks of most traditional AGM | Drawbacks of the traditional gel system |
|-----------------------------------|---|
| Crushes when compressed | No compression possible |
| Shrinks when wetted | Difficult filling process |
| Acid stratification | Low initial oxygen recombination |
| Liquid drainage | |
| Risk of thermal runaway | |
| Risk of short circuits | |

3. Results and discussion

3.1. Properties of the separator

3.1.1. Mechanical properties of AJS

The separation systems used in valve regulated lead-acid batteries are mostly AGM or gel. The drawbacks of these systems are summarized in Table 1.

The new AJS promises to solve most of these problems. Measurements have been undertaken that prove it hinders liquid drainage and acid stratification [4]. In the same way, the separator is easy to handle and its low pore size limits the risk of short circuits.

Initially, the mechanical properties of the new AJS separator were evaluated outside the lead-acid battery. Fig. 4 represents the evolution of the thickness versus applied pressure for two separators: an acid jelling separator and an absorptive glass mat [4].

The new AJS is clearly less compressible in comparison with conventional AGM. Additionally, the new separator is stable with time. The compressibility of a sample that was inserted in a cell for 467 full cycles is comparable with that of a new separator. After this many cycles, the separator is still able to withstand high pressure.

3.1.2. Oxygen transfer properties of AJS

The principle of the VRLA battery is based on the oxygen cycle in the battery. The rate of the oxygen transfer from the positive to the negative electrode is a critical question. The appropriate recombination rate is not clearly defined yet as too high an oxygen recombination rate results in undercharging of the negative electrode. Fig. 5 shows the dependence of the oxygen diffusion coefficient on the separator saturation for the new AJS and an absorptive glass mat.

Just as expected for a separator of lower porosity and smaller pore size, the diffusion coefficient of oxygen is lower for AJS than for AGM at the same saturation level. However, overcharge measurements at 2.4 V/cell show that a recombination current of 1 A is possible for a 48 Ah AJS cell with a saturation degree of about 84%. This recombination current would correspond to a diffusion coefficient of $3.57 \times 10^{-4} \text{ cm}^2/\text{s}$ and saturation below 75%. The effective saturation of the cell being much higher, either

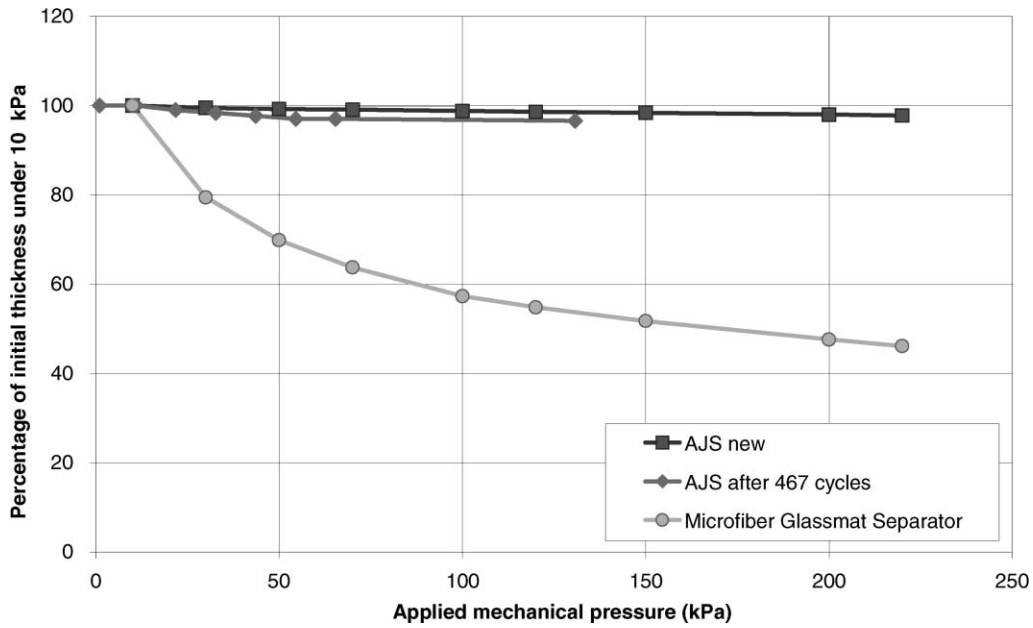


Fig. 4. Thickness variation versus applied pressure.

the oxygen transfer path is not only through the separator or the diffusion of oxygen through the separator is accelerated by a possible pneumatic effect. The way the oxygen transfer takes place in the cell is still not clear and will be part of our further work. It will help to find out if any gas goes from the positive plate to the negative one through the free room of the cell and if a sufficient pressure difference can appear between both sides of the separator to allow an enhanced gas transfer through it on the base of a pneumatic effect.

3.2. The positive effect of mechanical pressure

After the evaluation of the separator outside the lead-acid battery, the positive effect of mechanical pressure on the cycle life of a real VRLA cell has been demonstrated. Fig. 6 shows the evolution of the C/5 capacity of cells containing either the new incompressible AJS or an AGM separator. For the AJS system, two cells were cycled that were placed under two different initial mechanical pressures, namely 30 and 80 kPa. As for one of the AJS cells,

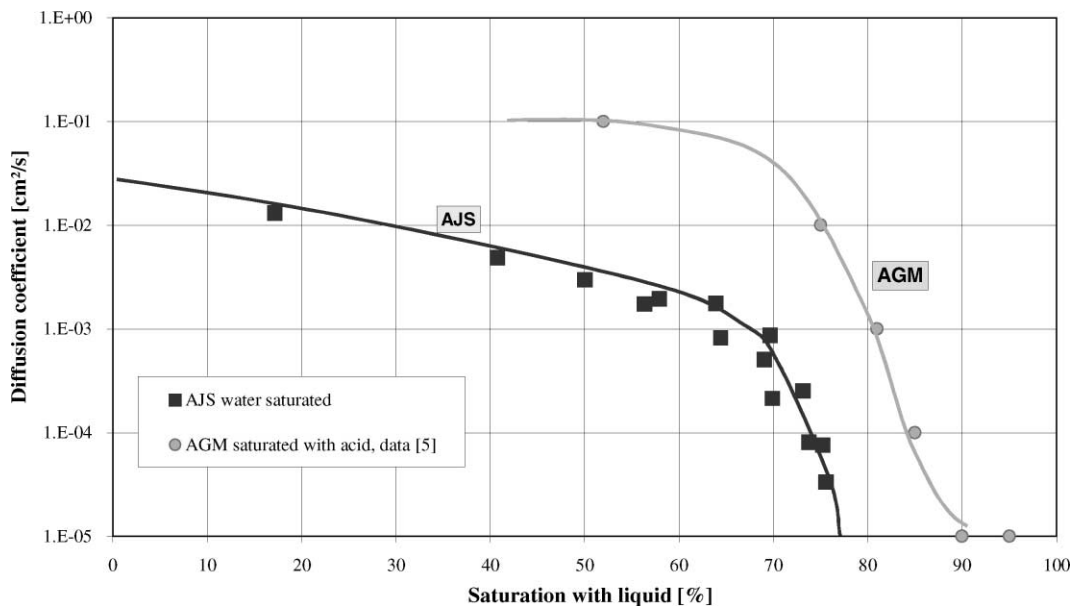


Fig. 5. Oxygen diffusion coefficient dependence on separator saturation [5].

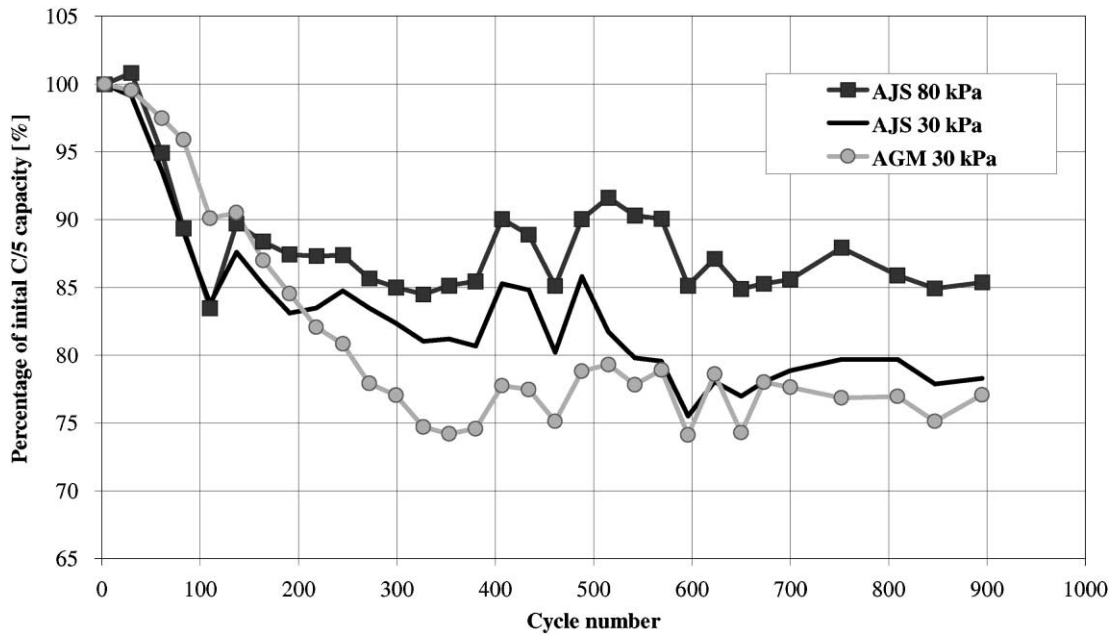


Fig. 6. Evolution of the relative C/5 capacity of cells with different separation systems or initial mechanical pressure.

the AGM cell was placed under 30 kPa initial mechanical pressure.

By definition, a cell has reached the end of its cycle life when its capacity falls below 80% of the initial value. With respect to that criterion, the cells have the following cycle lives:

- AJS 80 kPa: over 900 cycles (the cycle test is still running);
- AJS 30 kPa: around 530 cycles;
- AGM 30 kPa: around 250 cycles.

The advantage of using a separator that is able to withstand pressure is obvious. For the same initial pressure, the cell containing an incompressible separator has double the cycle life. Additionally, an increase in the initial pressure on the cell walls from 30 to 80 kPa leads to a dramatic increase in cycle life. It should be noted that the AGM separator used for this experiment was a standard product with approximately 25% fine fibres. Better cycle life might be achievable with a high content of fine fibres and higher external mechanical pressure. For example, some cells

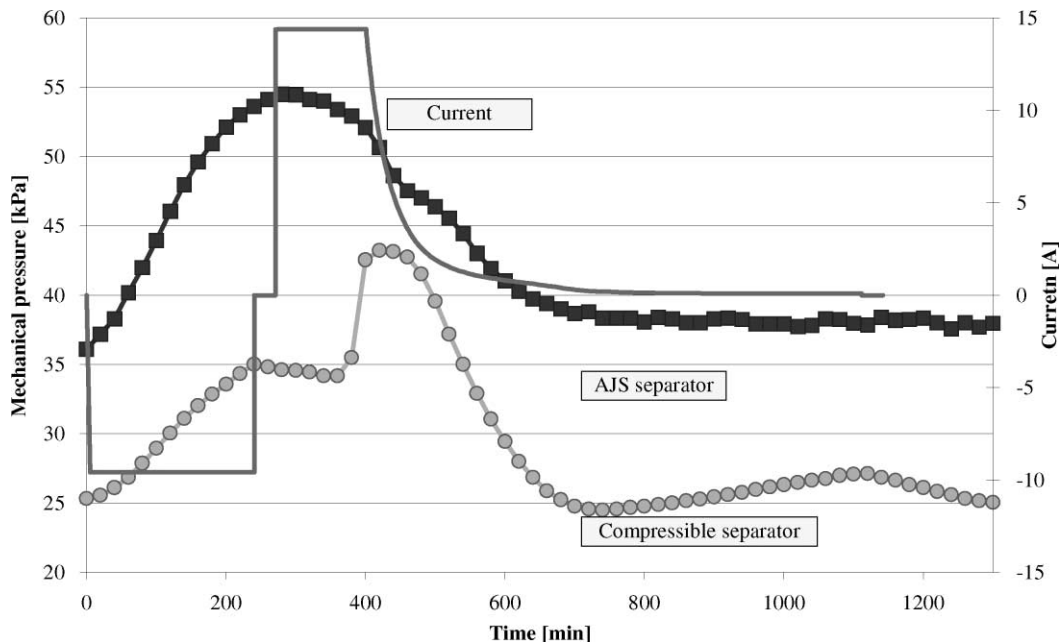


Fig. 7. Evolution of mechanical pressure during one cycle for an AJS and an AGM cell.

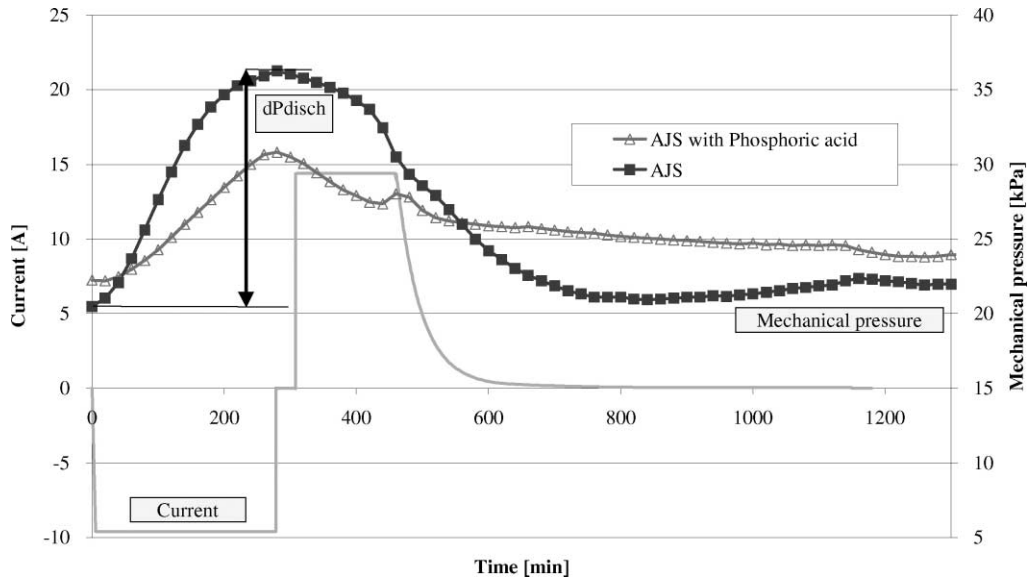


Fig. 8. Evolution of the mechanical pressure during one cycle for AJS cells with and without phosphoric acid.

containing a separator with 75% fine fibres and compressed at 25 to 30% lasted for over 900 $C_5/4$ cycles at 75% depth of discharge until they reached 75% of their initial capacity [6].

3.3. Evolution of mechanical pressure

Fig. 7 represents the evolution of the mechanical pressure during one cycle for two cells with different separation systems, i.e. the compressible AGM and the almost incompressible AJS as shown in the Figs. 7–9.

The general trend is independent of the separation system. For each system, the pressure increases during discharge and decreases during charge. During discharge, the pressure increase can be related to the volume increase of both active materials:

On the negative electrode : Pb ($\approx 18 \text{ cm}^3/\text{mol}$ for pure lead)
 $\Rightarrow PbSO_4$ ($\approx 48 \text{ cm}^3/\text{mol}$)

On the positive electrode : PbO_2 ($\approx 25 \text{ cm}^3/\text{mol}$)
 $\Rightarrow PbSO_4$ ($\approx 48 \text{ cm}^3/\text{mol}$)

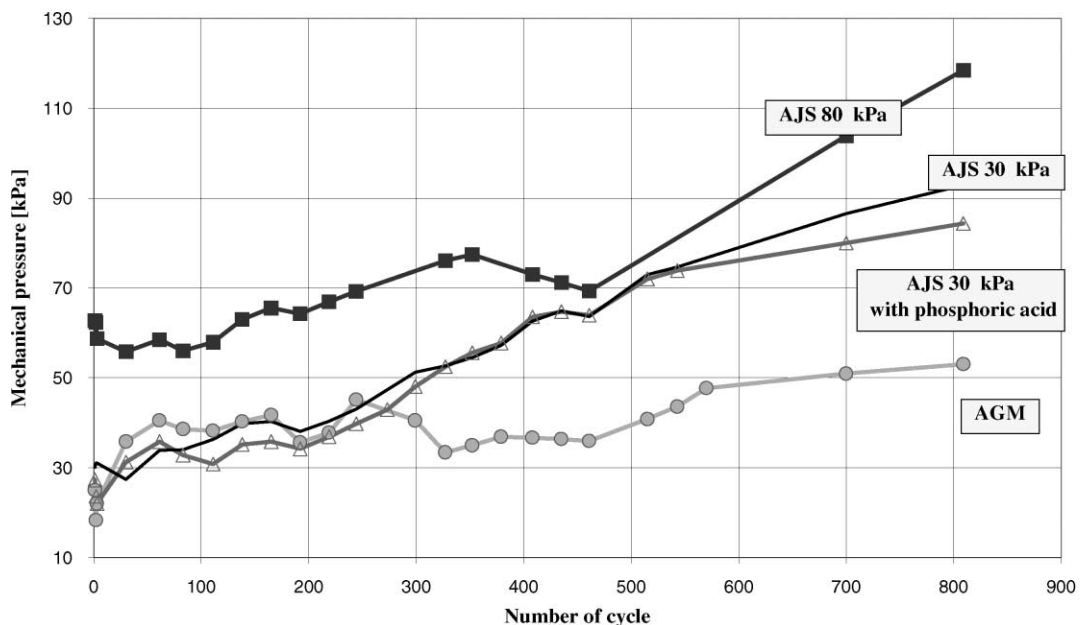


Fig. 9. Evolution with cycle number of the mechanical pressure on the cell walls at the end of discharge.

During charge, the pressure is the superimposition of two factors:

- the volume decrease of the active materials;
- the gas formation that is responsible for the peaks, for example at the end of the constant current period for both cells.

In this measurement, the pressure increase during discharge is much smaller for the AGM cell than for the AJS cell. The only difference between the two cells is the separation system. This behaviour is one further proof that the compressibility of the AGM does not allow a full transfer of the force produced by the active material expansion to the cell walls, which consequently does not prevent the expansion of the active material.

Fig. 8 shows the evolution of the mechanical pressure on the cell walls for two AJS cells, one with phosphoric acid, one without phosphoric acid.

The presence of phosphoric acid is responsible for the lower amplitude of the pressure variation. This means that the active material does not expand as much in presence of phosphoric acid. This is related to the effect of phosphoric acid on the crystallisation of the positive active material. In fact, the lead dioxide crystals formed in a lead-acid battery are smaller in presence of phosphoric acid. During discharge, the small lead dioxide crystals act as sites for the formation of lead sulphate, thus possibly leading to the formation of smaller sulphate crystals.

The pressure on the cells walls at a same stage of charge increases as shown in Fig. 9.

Obviously, for the cells with the AJS separator, the pressure increase with increasing cycle number is much higher than for an AGM cell. Also, when the cells are placed

under high initial pressure, the active material expands with increasing cycle number.

The presence of an incompressible separator leads to a high pressure on the plate stack after several cycles, even if the cell was not compressed to high levels at the beginning.

4. Conclusions

The new AJS has good mechanical properties and seems to be a promising separator for deep cycling VRLA batteries. It allows the exertion of pressure on the plate stacks of lead-acid batteries even if the battery is not placed under great compression from the beginning.

Acknowledgements

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