



Three-layered absorptive glass mat separator with membrane for application in valve-regulated lead-acid batteries

V. Naidenov, D. Pavlov*, M. Cherneva

Institute of Electrochemistry and Energy Systems, Bulgarian Academy of Sciences, Acad. G. Bonchev Street, bl. 10, Sofia 1113, Bulgaria

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ABSTRACT

During charge and discharge of the lead-acid cell equal amounts of H_2SO_4 participate in the reactions at the two types of plates (electrodes). However, the charge and discharge reactions at the positive plates involve also 2 mol of water per every mole of reacted PbO_2 . Consequently, a concentration difference appears in the electrolyte between the two electrodes (horizontal stratification), which affects the reversibility of the processes at the two electrodes and thus the cycle life of the battery. The present paper proposes the use of a three-layered absorptive glass mat (AGM) separator, the middle layer playing the role of a membrane that divides (separates) the anodic and cathodic electrolyte spaces, and controls the exchange rates of H_2SO_4 , H^+ ions, O_2 and H_2O flows between the two electrode spaces. To be able to perform this membrane function, the thinner middle AGM layer (0.2 mm) is processed with an appropriate polymeric emulsion to acquire balanced hydrophobic/hydrophilic properties, which sustain constant H_2SO_4 concentration in the two electrode spaces during cycling. Three types of polymeric emulsions have been used for treatment of the membrane: (a) polyvinylpyrrolidonestyrene (MPVS), (b) polyvinylpyrrolidone "Luviskol" (MPVP), or (c) polytetrafluoroethylene modified with Luviskol (MMAGM). It is established experimentally that the MMAGM membrane maintains equal acid concentration in the anodic and cathodic spaces (no horizontal stratification) during battery cycling and hence ensures longer cycle life performance.

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1. Introduction

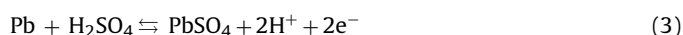
The following reaction proceeds at the positive plates of lead-acid batteries during charge and discharge:



In valve-regulated lead-acid batteries (VRLAB) and during battery overcharge, besides the above reaction a reaction of water decomposition with evolution of oxygen proceeds as well.



The reaction at the negative plates during charge and discharge of lead-acid batteries is:



In VRLA batteries, additional reactions of oxygen reduction and water decomposition with evolution of hydrogen proceed during battery overcharge.



During charge and discharge, a flow of H^+ ions moves between the positive and the negative plates, and electrons flow through the outer circuit. The H_2SO_4 concentration in the electrolyte filling the pores of the negative active mass and in the electrolyte layer near the negative plate decreases during discharge and increases during re-charge. Similar changes in H_2SO_4 concentration occur at the positive plates, too, but in this case, according to reaction (1), two moles of water are also involved per each mole of reacting PbO_2 . Hence, the changes in acid concentration in the electrolyte layers near the two types of plates are different. We have investigated these reactions earlier [1]. The electrolyte near the positive plates dilutes more notably than at the negative plates. The thus formed H_2SO_4 concentration gradient between the two electrolyte spaces triggers a concentration polarization, which reduces the capacity of the battery. Moreover, this concentration difference affects the dissolution of the PbSO_4 crystals, as the latter process is a function of H_2SO_4 concentration [2]. This may result in a disbalance between the amounts of PbSO_4 at the two electrodes on battery cycling and one of the plates may get partially sulfated.

When absorptive glass mat (AGM) separator is used, the diffusion of sulfuric acid between the two plates is impeded and, depending on the charge and discharge regime and on the depth of discharge, the different H_2SO_4 concentrations at the two types of plates are sustained for longer periods of time, which impedes

* Corresponding author. Tel.: +359 29710083; fax: +359 28731552.
E-mail address: dpavlov@labatscience.com (D. Pavlov).

the reactions of charge and discharge, and eventually reduces the capacity of the battery.

In an attempt to avoid this, Ferreira [3,4] has proposed a double-layer AGM separator with a denser layer of finer glass fibers forming smaller pores and a coarse fiber layer serving as acid (electrolyte) reservoir. The latter faces the positive plate.

The aim of the present paper is to show how the adverse effect of the introduction of AGM separators in VRLA batteries can be avoided by the use of a separator comprising two electrolyte spaces between the positive and negative plates, divided by a membrane which controls the exchange of ions between these two spaces. A three-layered AGM separator has been developed comprising: one thin layer of AGM, facing the negative plate, which forms the *cathodic space* in the cell containing a small volume of H_2SO_4 electrolyte; a second thicker AGM layer, facing the positive plate, which forms the *anodic space* containing a larger amount of electrolyte; and a third very thin layer (0.2 mm) of modified AGM separator with membrane properties inserted between the above two AGM layers thus separating the anodic and cathodic spaces. This membrane layer controls the transfer of H_2SO_4 , H^+ , O_2 and H_2O flows between the anodic and cathodic spaces in the cell. The membrane AGM layer is processed with an appropriate polymeric emulsion to acquire balanced hydrophobic/hydrophilic properties.

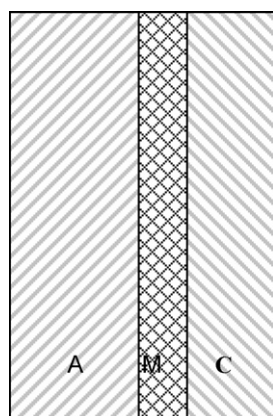
Through the use of such a three-layered separator, adequate amounts of electrolyte will be supplied to the cathodic and anodic electrolyte spaces as necessary for the respective reactions to proceed. This will guarantee the reversibility of the processes at the two electrodes and thus keep the battery capacity constant on cycling. The capacity of the battery will not decline with cycling, as is the case with existing valve-regulated lead-acid batteries. The battery will become a stable source of power and energy until some irreversible process, such as grid corrosion, passivation of the lead dioxide active mass, disintegration of the expander in the negative plates, etc., leads to its failure.

2. Experimental

2.1. Preparation of the three-layered AGM membrane separator

Fig. 1 shows a schematic representation of the three-layered separator.

Since the flow of oxygen should also pass through the membrane layer, the latter should have hydrophobic channels, too. This



A – Anodic space
C – Cathodic space
M – Membrane

Fig. 1. Schematic representation of the three-layered AGM separator.

is achieved by treating the membrane separator layer with polymeric emulsion comprising both hydrophilic polymers with proton conductivity (e.g. polyvinylpyrrolidone) and hydrophobic polymers (polytetrafluorethylene emulsion) in an appropriate proportion.

AGM separators of three different thicknesses: 2.4 mm (360 g m^{-2}), 1.8 mm (280 g m^{-2}) and 0.2 mm (30 g m^{-2}) were supplied by Hollingsworth & Vose (USA) and used for the manufacture of the three-layered separators. The thin separator sheet was modified with three different polymeric emulsions (polytetrafluorethylene, polyvinylpyrrolidone or polyvinylpyrrolidone) employing a technology developed in this laboratory [5,6]. The thin sheet of modified AGM separator was inserted between the 2.4 mm thick separator facing the positive plate and the 1.8 mm one facing the negative plate.

2.2. Cells and batteries used to study the influence of the three-layered AGM separator on cell (battery) performance

Three-layered separators sized $140 \text{ mm} \times 153 \text{ mm}$ were incorporated in cells comprising one positive and two negative plates. Commercial plates with lead–calcium grids and 10 Ah capacity were used. H_2SO_4 solution of 1.28 g cm^{-3} density was used as electrolyte at 96% saturation and 20% compression of the active block. A total of six test cells were assembled as follows:

- one reference cell with a three-layered separator comprising one 2.4 mm AGM separator sheet, one 1.8 mm AGM separator sheet and a 0.2 mm AGM (untreated) separator in between; this is actually a classical AGM separator of a 4.4 mm overall thickness (we will denote it as AGM);
- one cell with a 2.4 mm AGM sheet facing the positive plate, a 1.8 mm AGM sheet facing the negative plate and a 0.2 mm membrane AGM separator modified with polyvinylpyrrolidone-estylene emulsion Aldrich no. 43,445-0 (denoted as MPVS), 10 ml l^{-1} ;
- one cell with a 2.4 mm AGM separator, a 1.8 mm AGM separator and a 0.2 mm membrane AGM separator modified with Luviskol polyvinylpyrrolidone emulsion (denoted as MPVP), 3 g l^{-1} ;
- cells with the same outer separator sheets as above, but the middle membrane AGM separator treated with polytetrafluorethylene emulsion (Du Pont Teflon 30N) modified with Luviskol polyvinylpyrrolidone (denoted as MMAGM); the MMAGM membrane separator was produced employing the MAGM technology developed in this laboratory [5,6]; three types of MMAGM membranes were manufactured varying the emulsion concentration as follows: 1.25 ml or 10 ml or 30 ml per 1 l of H_2O .

Two 12 V test batteries were also assembled with 4 negative and 3 positive plates per cell and a capacity of 34 Ah. Three-layered AGM separators were used as described in (d) above in concentration 10 ml l^{-1} H_2O . The electrolyte saturation of the cells was again 96% (H_2SO_4 of 1.28 g cm^{-3}) and the compression of the active block was 20%.

2.3. Charge–discharge algorithm used for the tests

The cycling tests of the cells and batteries were conducted using Bitrode (USA) testing equipment. The following charge–discharge algorithm was employed:

- for the 10 Ah test cells: charge with $I_1 = 5 \text{ A}$ to $U = 2.50 \text{ V}$; further charging at $U = 2.50 \text{ V}$ to 115% overcharge; discharge with $I = 2 \text{ A}$ (corresponding to 5 h discharge rate) to an end-of-discharge voltage $U = 1.70 \text{ V}$.

- for the 34 Ah test batteries: charge with $I = 12$ A to $U = 15$ V, followed by charge at 15 V to 115% overcharge; discharge with $I = 6.8$ A (corresponding to 5 h discharge rate) until an end-of-discharge voltage $U = 10.2$ V.

Water (25 cm^3) was added to the cells and batteries periodically to avoid limiting of their life by the amount of electrolyte.

2.4. H_2SO_4 concentration measurements in the anodic and cathodic electrolyte spaces of the three-layered separator

The changes in H_2SO_4 concentration in the anodic and cathodic spaces were measured with the help of a refractometer after the end of charge and discharge of the cells with three-layered separators employing a method developed earlier [1]. Samples of the electrolyte were taken from nine different positions of the 2.4 mm AGM separator forming the anodic space and of the 1.8 mm separator forming the cathodic space, namely: from three horizontal and three vertical zones along the height of the plates. The obtained results were averaged to three H_2SO_4 concentration values corresponding to the three horizontal zones along the cell height.

3. Results and discussion

3.1. H_2SO_4 concentration in the anodic and cathodic electrolyte spaces after the end of charge and discharge

The acid concentration on both sides of the membrane was measured immediately after end of charge and after discharge of cells with three-layered separators comprising 0.2 mm AGM membranes unmodified or modified with emulsion. The cells were set to 10 preparatory cycles before the acid s.g. measurements.

Fig. 2 shows the H_2SO_4 concentration distribution in a cell with three-layered AGM separator with untreated membrane, when fully charged (Fig. 2a) and after discharge (Fig. 2b). This separator is essentially an equivalent of a standard single-layer AGM separator (4.4 mm thick). The acid concentration in the anodic space of the fully charged cell is higher by 0.03 g cm^{-3} than in the cathodic space (Fig. 2a). The reverse situation is observed in the discharged cell (Fig. 2b). The water produced during the discharge has further diluted the electrolyte in the anodic space to a concentration lower (by 0.02 g cm^{-3}) than that in the cathodic space.

The data in Fig. 2b indicate also that the discharge reactions proceed mostly in the middle horizontal zone of the cell. The substantial difference in the H_2SO_4 concentration between the anodic and cathodic spaces suggests that the exchange of H_2SO_4 flows between them is strongly impeded. This results in non-homogeneity of the H_2SO_4 concentration and of the processes that proceed at the two electrodes in the active block, which eventually leads to decline in cell capacity. Hence, cells with the above AGM separator will be subject to considerable concentration polar-

ization. This is actually the case with VRLA batteries with AGM separators.

Fig. 3 presents the H_2SO_4 concentrations measured in the anodic and cathodic spaces of a cell with three-layered MMAGM separator in charged (Fig. 3a) and discharged (Fig. 3b) state. In this cell, the acid concentration in the anodic and cathodic spaces is controlled by the MMAGM membrane.

No acid concentration difference between the two electrolyte spaces is observed. This means that the MMAGM membrane facilitates substantially the transfer of H_2SO_4 and H_2O flows through the three-layered separator and sustains equal H_2SO_4 concentration in the two electrolyte spaces, thus preventing formation of concentration difference between the anodic and cathodic spaces. The acid stratification is insignificant both horizontally and vertically. The sustained equal acid concentration in the two spaces will contribute to higher reversibility and homogeneity of the processes at the two electrodes and will thus maintain constant capacity of the cell on cycling.

The results of the H_2SO_4 concentration measurements presented in Fig. 4 refer to cells with three-layered separator with AGM membrane treated with emulsions of polyvinylpyrrolidone-styrene (MPVS) (Fig. 4a and b) or Luviskol polyvinylpyrrolidone (MPVP) (Fig. 4c and d), in fully charged and discharged states. A H_2SO_4 concentration difference between the anodic and cathodic spaces is observed in both types of cells. This difference is of the order of 0.01 g cm^{-3} . If we compare this difference with the one measured for the cell with untreated AGM membrane (Fig. 2), we will see that both the MPVS and MPVP modified AGM membranes accelerate considerably the exchange of H_2SO_4 and H_2O between the two electrolyte spaces, but still less so than does the MMAGM membrane.

It can be generally concluded that the three-layered separator with AGM membrane modified with polymeric emulsion creates conditions facilitating more uniform progress of the discharge and re-charge processes throughout the cell volume, thus reducing the stratification of electrolyte both horizontally and vertically.

The data in Figs. 2–4 evidence that the cells with three-layered membrane separators have lower acid concentration after the end of discharge as compared to the cell with untreated AGM separator, i.e. the discharge process is more efficient in these cells and hence they have higher capacity than the cells with untreated AGM middle layer.

3.2. Effect of the three-layered membrane separator on the capacity of lead-acid cells and batteries on cycling

Lead-acid cells (10 Ah) were assembled with three-layered separators comprising untreated AGM, MMAGM, MPVP or MPVS membranes and set to cycling tests at 5 h discharge rate ($I = 2$ A) until an end-of-discharge voltage $U = 1.70$ V and charge as per the regime described in Section 2.3 above. The end-of-life criterion was when

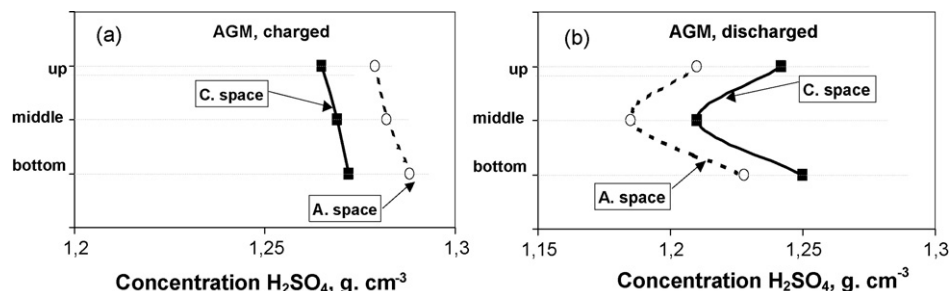


Fig. 2. H_2SO_4 concentration in the positive plate anodic (A) and negative plate cathodic (C) spaces of a cell with three-layered AGM separator with untreated membrane: (a) fully charged cell, (b) discharged cell.

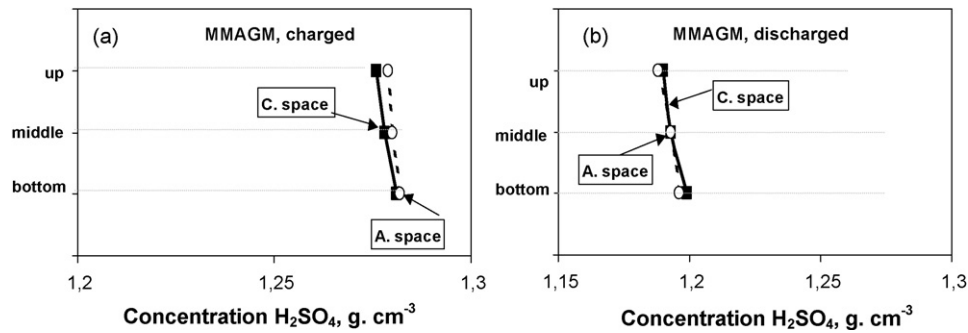


Fig. 3. H_2SO_4 concentration in the positive plate anodic (A) and negative plate cathodic (C) spaces of a cell with three-layered separator with AGM membrane modified with polytetrafluoroethylene emulsion with addition of “Luviskol” polyvinylpyrrolidone (MMAGM): (a) fully charged cell, (b) discharged cell.

the cell capacity decreased below 7 Ah. Fig. 5 presents the capacity versus cycle number dependences for the four types of cells with different membranes.

The cell with untreated AGM separator exhibits continuous slow capacity decline with cycling and its capacity decreases to 70% of the rated value after 23 cycles. The AGM separator slowly increases the heterogeneity of the electrolyte solution in the cell and thus reduces its capacity and cycle life. The capacity of the cells with AGM membranes modified with any of the three types of polymeric emulsions decreases to 7.5–8.5 Ah within the first 20–30 cycles, but then this value is sustained for hundreds more cycles until some irreversible process(es) occur, which reduce the cell capacity. These results indicate that there is a fundamental difference between the processes that take place in the cells with AGM separators processed with polymeric emulsion as compared to their untreated counterparts.

The initial capacity decline registered with the cells with polymer-treated membranes is, most probably, due to adjustment of the acid concentrations in the two electrolyte spaces to the cycling mode, i.e. to changes in the separator, including formation of gas transfer channels in the separator for the transfer of oxygen from the anodic to the cathodic electrolyte spaces, as well as forma-

tion of the transport paths for the movement of H_2O and H^+ flows between the two spaces during charge and discharge.

After this initial adjustment of the system to the cycling mode, a period of reversible charge–discharge processes starts which sustain relatively constant cell capacity on further cycling. The cell reacts to any temperature or current changes by changes in capacity. That is the reason for the fluctuations in the capacity/cycles curves. Some irreversible processes take place in the cells on cycling (such as grid corrosion, expander oxidation, etc.), which also cause the capacity to decline below 70% of the rated value and thus limit battery cycle life. Fig. 5 shows that the cycle life of the cell with MMAGM membrane is 400 cycles, against 300 cycles for the MPVP and 330 cycles for the MPVS cells, respectively. These results illustrate the important role of the membrane layer on the cycle life performance of batteries (cells) with three-layered AGM separators. The composition of the polymeric emulsion used to process the AGM membrane needs to be optimized so as to keep up high cell/battery capacity on cycling. A juxtaposition of the data in Fig. 5 with those in Figs. 2–4 shows that the cells with small H_2SO_4 concentration difference between the two electrolyte spaces of the plates have longer cycle life than the cells with greater concentration difference. Hence, the difference between the H_2SO_4 concentrations in

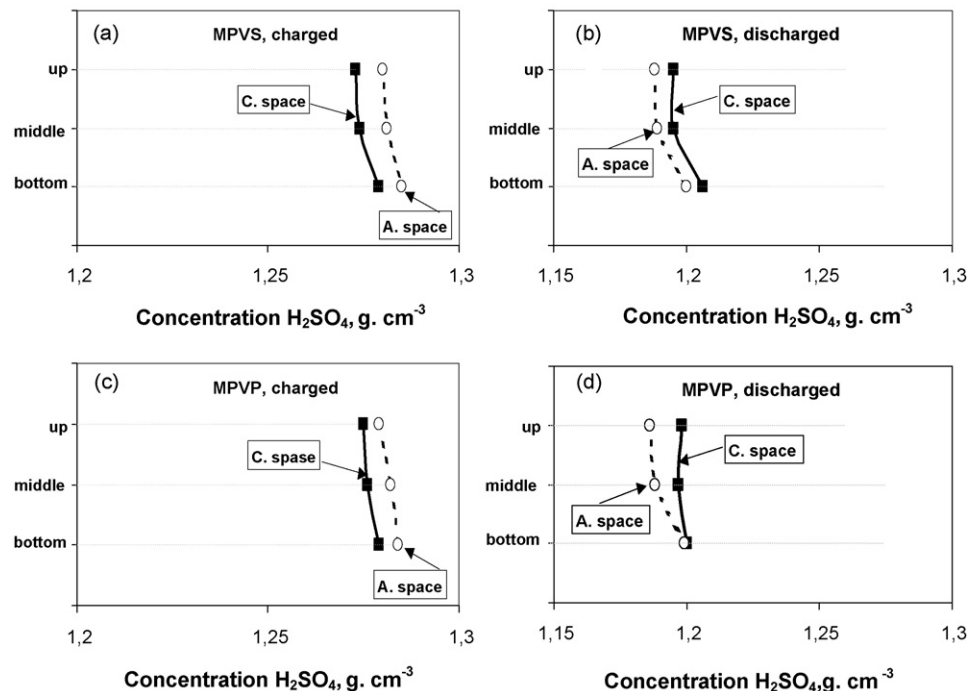


Fig. 4. H_2SO_4 concentration in the positive plate anodic (A) and negative plate cathodic (C) spaces of fully charged (a and c) and fully discharged (b and d) cells with three-layered separator with AGM membrane modified with polyvinylpyrrolidonestyrene (MPVS) (a and b) or “Luviskol” polyvinylpyrrolidone (MPVP) (c and d).

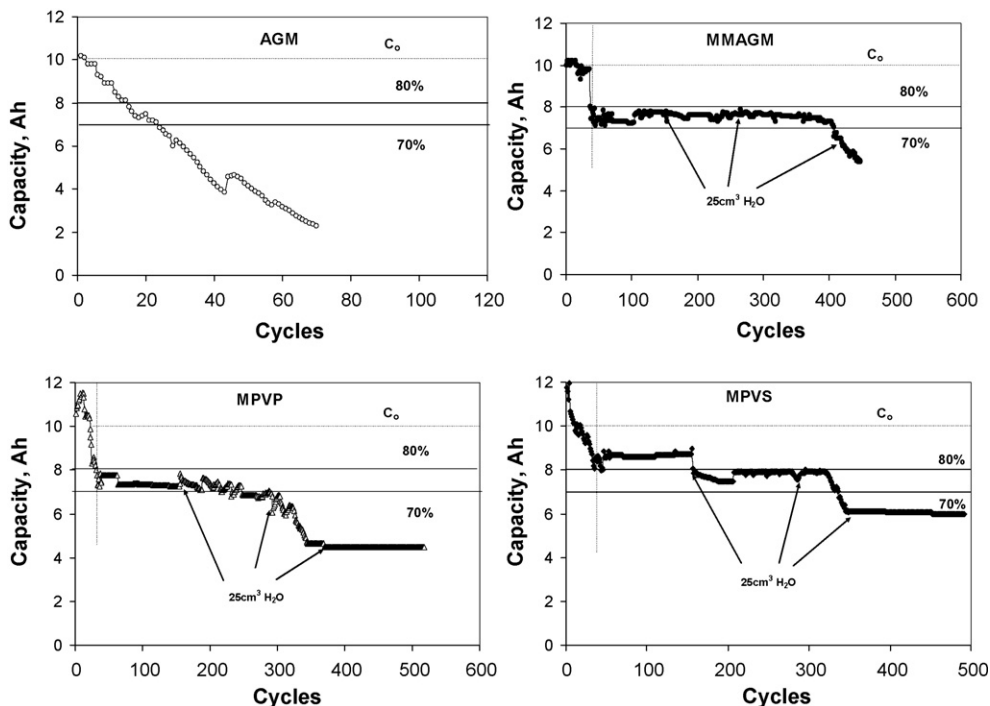


Fig. 5. Capacity versus cycle number dependences for the four types of cells with different AGM membrane separators.

the two electrode spaces is an important parameter limiting the cycle life of the cells.

On comparing the capacity curves for the cells with the three types of polymer-modified membranes it can be seen that the cell with MMAGM membrane has the longest cycle life of all cells under test, but the cell with MPVS membrane sustains the highest capacity on cycling. The properties of the polymer-treated separator membranes affect both the cycle life and the capacity performance of the cells.

In an attempt to verify the reproducibility of the influence of the three-layered membrane separator on the capacity of lead-acid batteries on cycling we set two identical 34 Ah batteries with three-layered MMAGM membrane separators to cycling tests. The obtained results are presented in Fig. 6.

The data in the figure evidence almost equal changes in capacity with cycling for the two batteries. To follow the effect of temperature on battery capacity the batteries were heated to 50 °C for 5 cycles (between cycles 35 and 40), but no changes in capacity were observed on further cycling at room temperature. It can be concluded that both batteries have undergone identical structural changes since the beginning of the cycling test and the changed separator structure is sustained on further cycling. Hence, the changes in capacity of batteries assembled with the same membrane separator follow the same profile. These results prove experimentally that three-layered AGM separators with identical membranes exert the same influence on the energetic and cycle life performance of the batteries.

3.3. Effect of the three-layered membrane separator on battery charge voltage on cycling

Fig. 7 shows the changes in charge voltage during the first 100 min of charge with constant current $I = 1.5$ A to a cut-off voltage of 2.26 V for a cell with MMAGM membrane separator between cycles 157 and 245.

It is evident from the figure that with increase of the number of cycles the profile of the charge voltage/cycle number curve changes

after 220 cycles but only within the first 30 min of charge, featuring a decrease of the initial charge voltage at cycles 227 and 245, but further changes in the charge voltage curve do not depend on cycle number. These results indicate that no substantial changes occur in the three-layered MMAGM separator that would affect the exchange of H_2SO_4 electrolyte between the anodic and cathodic spaces of the separator.

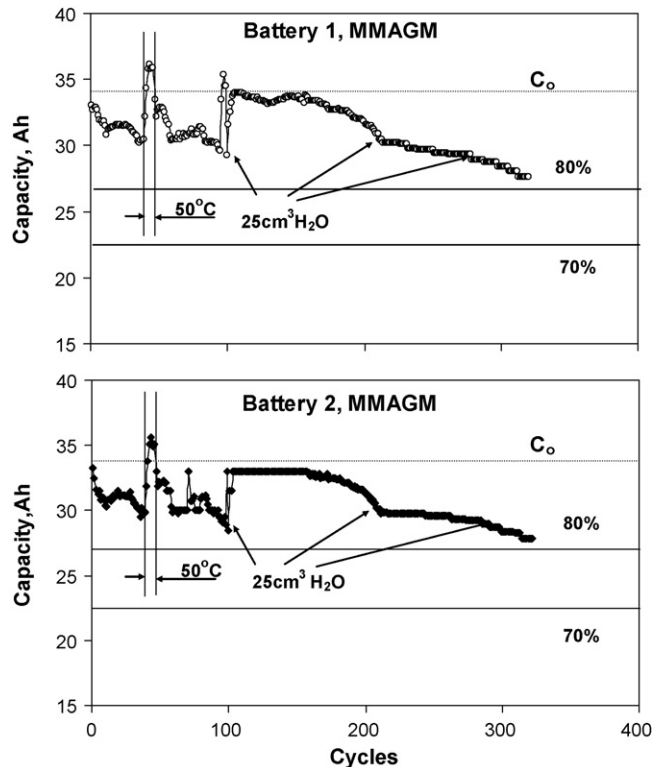


Fig. 6. Capacity versus cycle number dependences for two identical 34 Ah batteries with MMAGM membrane separators.

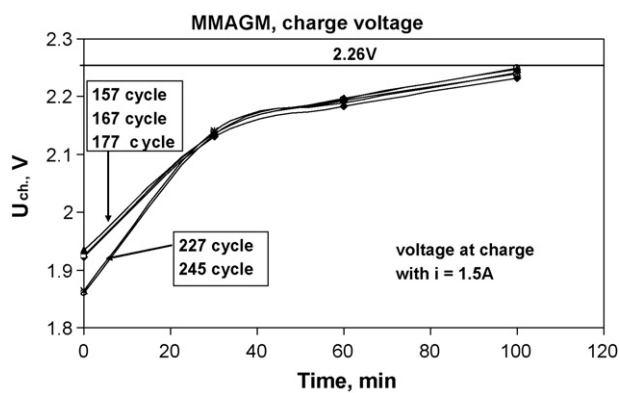


Fig. 7. Changes in charge voltage of a cell with MMAGM membrane separator during the first 100 min of constant current charge: $I = 1.5$ A to a cut-off voltage of 2.26 V.

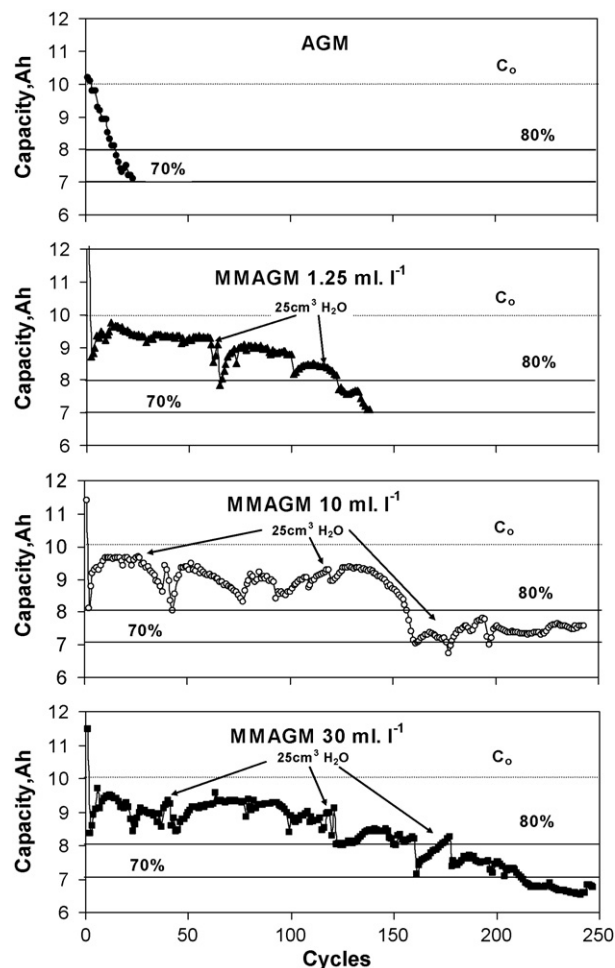


Fig. 8. Capacity versus cycle number dependences for cells with three-layered AGM separators with membranes treated with MMAGM emulsion of four different concentrations.

3.4. Three-layered separators with membranes modified with different amounts of MMAGM polymeric emulsion and their effect on the capacity and cycle life of lead-acid cells

As mentioned in Section 3.2. above, cells with three-layered separator with MMAGM membrane have the longest cycle life of

all investigated cells. It was interesting to determine the optimum concentration of the MMAGM polymeric emulsion used to modify the 0.2 mm membrane separator sheet. For the purpose we produced three types of three-layered MMAGM separators modified with a mixture of Luviskol polyvinylpyrrolidone and polytetrafluorethylene emulsion, varying the amount of the polymeric emulsion as follows: 1.25 ml, 10 ml or 30 ml per 1 l of H₂O. The thus prepared three-layered separators were used for the assembly of 10 Ah cells, which were set to cycling employing the cycling regime described in Section 2.3. Fig. 8 summarizes the obtained results.

The data in Fig. 8 evidence that the cell with the three-layered separator with MMAGM membrane treated with 10 ml emulsion per 1 l H₂O has the highest capacity and the longest cycle life. The figure shows also that all three cells with MMAGM membrane separators exhibit considerably better capacity and cycle life performance as compared to the reference cell with untreated AGM separator.

On grounds of the results of this study it can be generally concluded that the three-layered separator with MMAGM membrane has most balanced specific hydrophobic and hydrophilic properties that facilitate the charge and discharge reactions in lead-acid cells.

4. Conclusions

The present paper proposes a method to suppress the formation of H₂SO₄ concentration difference in the electrolyte spaces near the two electrodes during charge and discharge, leading eventually to disbalance of the processes at the two electrodes of VRLABs. This is achieved by the use of a three-layered absorptive glass mat (AGM) separator, comprising a thicker AGM separator sheet facing the positive plate, a thinner AGM sheet facing the negative plate and a very thin AGM membrane inbetween. The AGM membrane is processed with polymeric emulsion to acquire balanced hydrophobic/hydrophilic properties and thus controls the exchange rates of H₂SO₄, H⁺ ions, O₂ and H₂O flows between the anodic and cathodic electrolyte spaces. Three types of polymeric emulsions have been used for treatment of the membrane and the test results evidence that the MMAGM membrane (i.e. AGM modified with polytetrafluorethylene emulsion with addition of "Luviskol") sustains equal H₂SO₄ concentration in the two electrolyte spaces, thus ensuring reversibility of the processes at the two electrodes and hence longer battery cycle life. The other two types of polymeric emulsions under test (polyvinylpyrrolidone-styrene – MPVS and polyvinylpyrrolidone "Luviskol" – MPVP) also improve the reversibility of the charge and discharge processes at the two electrodes, but with less contribution to the cycle life performance of VRLA batteries. The results of this study prove that the proposed three-layered membrane AGM separator can be used as an efficient component in VRLA battery design improving the performance characteristics of valve-regulated lead-acid batteries.

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