

Evaluation of separator influence on charge acceptance of negative plates of lead-acid batteries

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Separators play a key role in all batteries. Battery separators are complex multi-component membranes with high porosity (55-95%). In the current state-of-art of lead-acid battery manufacture two different types of separators are used made of absorbent glass mat (AGM) and polyethylene (PE) materials. The present study compares the influence of commercially available PE and AGM separators on the charge/discharge performance of the negative plates in a lead acid battery. Methods employed for this study include: linear sweep voltammetry, pulse potentiostatic method and open circuit test, as well as X-ray diffraction analysis and scanning electron microscopy to characterize the lead reactivity and identify the phases formed on the lead surface. It was established that over the time unknown organic substances used in the production of the PE separator are released in the electrolyte. These substances, most probably, adsorb onto the surface of the Pb and PbSO₄ crystals and alter their morphology. As a result the electrochemical processes of the negative electrode in the PE cells are negatively affected in comparison to AGM cells.

Keywords: lead-acid battery, separators, flat pure lead working electrode, linear sweep voltammetry, open circuit

INTRODUCTION

Separators play a key role in all batteries. A separator is a porous membrane placed between electrodes of opposite polarity, permeable to ionic flow but preventing electric contact between the electrodes. A variety of separators has been used in batteries over the years. They have been manufactured from cellulosic papers and cellophane to nonwoven fabrics, foams, ion exchange membranes, and microporous flat sheet membranes made of polymeric materials. The main function of separators is to keep the positive and negative electrodes apart to prevent electrical short circuits and at the same time allow rapid transport of ionic charge carriers that are needed to complete the circuit during the passage of current in an electrochemical cell [1,2].

A number of factors must be considered in selecting the best separator for a particular battery type and application. Separators for use in batteries should meet a number of various requirements regarding their physical, chemical and electric properties, e.g. be electronic insulators; have minimal electrolyte (ionic) resistance but maximum mechanical and dimensional stability; sufficient physical strength to allow easy handling;

chemical resistance to degradation under the action of electrolyte, impurities, and electrode reactants and products; be effective in preventing migration of particles or colloidal or soluble species between the two electrodes; readily wettable by electrolyte; uniform in thickness and others [3]. There are two general classes of lead-acid batteries: valve-regulated lead-acid batteries (VRLAB) and flooded cell batteries. The separator material used in VRLA batteries is absorbed glass mat (AGM). AGM separator is a non-woven fabric made of glass microfibers. The AGM separator has high porosity in the 90-95% range. Other characteristic properties of AGM separators are uniformity, fiber directionality, adaptability to imperfections in the plate surface, high-temperature stability, high liquid absorption, low electric resistance, high chemical purity. The main advantages of AGM VRLA batteries are that they are fully maintenance-free, the electrolyte is immobilized, practically no stratification occurs, and minimum terminal corrosion is observed. These batteries operate on the principle of oxygen recombination, using an immobilized electrolyte. Recent studies have demonstrated that higher levels of fine fiber and higher separator compression provide improved cycle life performance in VRLA batteries [4-8].

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Other studies have shown that modification of AGM separators with polymer composite or emulsion leads to (higher) tensile strength, reduced H_2SO_4 absorption and wicking rate, and increased chemical and thermal stability [9]. This eventually leads to less heat generation or prevents lead-acid batteries from thermal runaway [10].

Separator materials for flooded lead-acid battery applications are porous derivatives of cellulose, polyvinyl chloride (PVC), organic rubber and polyolefins. The materials consist of polyolefin separators that are either polypropylene (PP) or PE based. PE is a semi-crystalline material with excellent chemical resistance, good fatigue and a wide range of physical properties related to differences in the density values of the polymer [11]. Microporous PE separators currently represent about 90% of the lead-acid battery separator market. PE lead-acid battery separators are widely used because of their ultrafine pore size, which inhibits “dendritic” growth of metallic deposits (a short circuit risk), while providing low electrical resistance. Besides, PE separator material is characterized by high puncture strength, good oxidation resistance, and excellent flexibility. They have traditionally been produced by extrusion and subsequent extraction of a calendered sheet from a multi-component mixture of ultrahigh molecular weight PE (UHMWPE), precipitated silica, process oil, pore formers, surfactants, and antioxidant. A typical PE separator formulation comprises precipitated silica (~ 60 wt %), UHMW PE (~ 20 wt %) and mineral process oil (~ 15 wt %), as well as some processing aids like antioxidants and/or proprietary surface tension modifiers. PE separators can be produced in sheet or pocket size and applied in starter, deep-cycle, industrial and maintenance-free batteries [12-14]. The specific properties of the PE separator are low electric resistance, higher porosity and smaller pore size, adequate acid resistance, easy enveloping process. The chemical composition and the amount of above listed substances can all exert an effect on the electrical, mechanical and oxidation resistance of the separator. During operation and throughout the service life of a lead-acid battery, the microporous PE separator is exposed to a strong oxidizing environment of concentrated sulfuric acid, oxygen and hydrogen gases, and high temperatures [15,16]. Under such harsh environment conditions, some of the substances used in the production of the separator may possibly leach to the electrolyte. These substances may negatively affect the lead-acid battery performance by influencing the

positive and/or negative electrodes charge/discharge processes.

The aim of the present investigation is to evaluate the influence of one kind of commercial PE separator on the charge/discharge performance of the negative plates in a lead-acid battery. The performance of the studied PE separator material is compared to the effect of a commercial AGM separator.

EXPERIMENTAL

Two types of separators were investigated, denoted as AGM and PE separator, respectively. The Glass Mat Separator used was with a thickness of 0.2 mm (30 g/m^2), produced by Hollingsworth & Vose (USA). The PE separator had a vertical rib profile with a backweb thickness of 0.175 mm and a rib thickness of 0.900 mm, manufactured by Microporous (USA).

Because of the different nature and characteristics of the two types of separators basic electrochemical and structural studies were needed to evaluate the processes which lead to different behavior of lead electrodes with separators of the two types immersed in sulfuric acid solutions. Various methods were employed for these studies, including: linear sweep voltammetry, pulse potentiostatic method and open circuit test, as well as X-ray diffraction analysis and scanning electron microscopy to characterize the lead reactivity and identify the phases formed on the lead surface.

A small Pb (99.99 % purity) sheet embedded in epoxy resin was used as working electrode. The electrode geometrical area exposed to the electrolyte was 0.5 cm^2 . A bit bigger Pb sheet with 2.5 cm^2 area exposed to the electrolyte was used as counter electrode. All electrodes were enveloped in separators of the respective type, AGM or PE. These electrodes were assembled in a small cell and 5 ml of 1.28 g cm^{-3} sulfuric acid solution was added. The reference electrode was $Ag/Ag_2SO_4/H_2SO_4$ (1.28 g cm^{-3}). The two types of cells with studied separators are denoted as AGM cell and PE cell, respectively. All experiments were carried out at a temperature of 25°C . The electrochemical tests were performed using Arbin BT2043 potentiostat/galvanostat. The crystal structure of the modified negative plate was examined by X-ray diffraction using ARD-15 PHILIPS diffractometer with $Cu \text{ K}\alpha$ radiation. Scanning electron microscopy (SEM) images were obtained on a JEOL 200 CX microscope. As a first step of the electrochemical tests, the electrodes were chemically cleaned with ammonium acetate solution, then they were subjected to cathodic

electropolishing for 1 hour at a potential of -1.20 V (vs. $\text{Ag}/\text{Ag}_2\text{SO}_4$).

RESULTS AND DISCUSSION

Linear sweep voltammetry within the potential region from -1.2 V to 1.6 V

The potential of the working electrode was linearly swept at a scan rate of 1 mVs^{-1} to 1.60 V and then back to -1.20 V. The obtained potential-current curves for the AGM and PE cells are presented in Fig. 1.

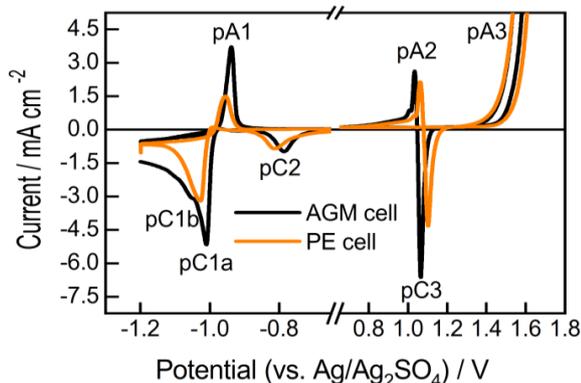


Figure 1. Linear sweep voltammetry curves for AGM and PE cells with 1.28 g cm^{-3} H_2SO_4 solution over the whole potential region from -1.20 V to 1.60 V.

The corresponding peaks in the voltammograms are denoted in Fig. 1 as follows: pA1, pA2 and pA3 reflecting anodic processes, and pC1a, pC1b, pC2 and pC3 reflecting cathodic processes, respectively. A comparison between the recorded voltammograms for the AGM and PE cell configurations shows that they feature common anodic and cathodic peaks of different current magnitude. For the PE cell, the current peaks that occur in the positive potential region are shifted to more anodic values (by 25-40 mV). In contrast, the peaks in the negative potential region are shifted to more cathodic values (by 10-25 mV). The AGM cell produces higher current peaks as compared to the PE cell. Furthermore, the most pronounced difference in current magnitude is observed for the peaks pA1, pC1a, and pC1b, reflecting the anodic oxidation of Pb to PbSO_4 and the subsequent cathodic reduction of PbSO_4 to Pb, respectively. It can be seen that the PE cell yields a single reduction peak pC1a, whereas the respective peak in the voltammogram for the AGM cell is split into pC1a and pC1b. The peak pC1a for the AGM cell has higher current magnitude compared to the

respective value for the PE cell. It could be concluded that the lead sulfate crystals formed in the AGM cell appear to be more easily reducible back to lead. Moreover, the experimental results indicate that maybe the PE separator material releases some substances in the electrolyte which could further adsorb onto the electrode surface and thus inhibit the electrochemical reactions. The reactions of Pb oxidation and PbSO_4 reduction are more sensitive to the presence of these substances in the electrolyte.

Pb/ PbSO_4 electrode system

Cyclic voltammetry at a scan rate of 5 mV/s was employed to study the reactions that proceed between -1.2 V and -0.8 V. The electrodes were subjected to 40 cycles. After the end of the voltammetry test, the surface of the electrode under the test (in the charged state) was analyzed by XRD. The recorded voltammograms at cycle 40 are presented in Fig. 2a for both AGM and PE cells. The anodic peak (discharge reaction; positive current values) increases with the number of scans reflecting the formation of a porous lead layer on the electrode surface with larger surface area. The oxidation peak for cell PE is 3.5 mA/cm^2 , whereas that for cell AGM is about 12 mA/cm^2 . Obviously, the PE separator has contaminated the acid with active organic substances that impede the dissolution/precipitation of lead sulfate. The reduction peak (charge reaction; negative current values) maximum is about 2 mA/cm^2 for both PE and AGM cells. It is interesting that after passing its peak maximum value, the reduction current of the PE cell steeply decreases to extremely low values; in contrast, the AGM cell exhibits a gradual decrease. These results indicate that the processes of charge/discharge in the PE cell are strongly hindered.

The X-ray diffraction patterns of the surfaces of the two types of electrodes, after the completion of the cathodic scan at cycle 40, are presented in Fig. 2b. The data in the XRD patterns indicate that the electrodes are covered by residual lead sulfate even in the “reduced” state and the PE electrode contains much more sulfate than the AGM electrode. The presence of much more residual lead sulfate on the surface of the PE cell working electrode indicates that the charge reaction (conversion of PbSO_4 to Pb) is strongly retarded.

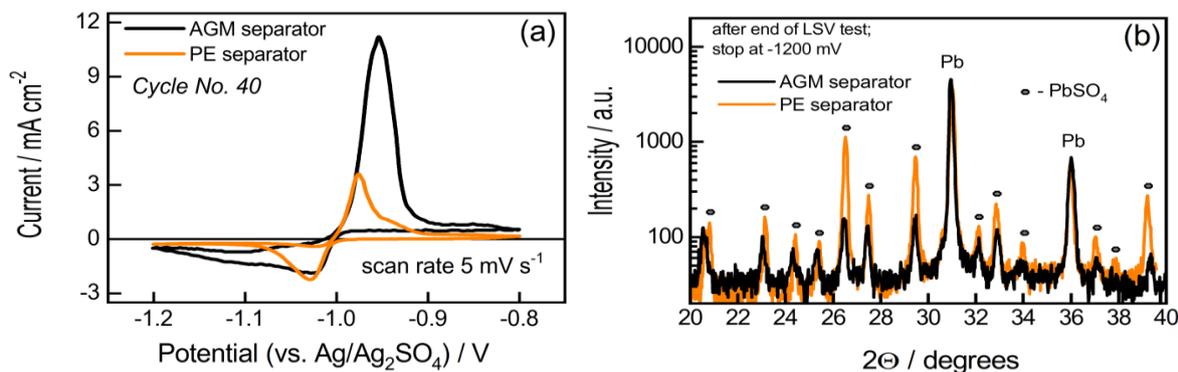


Figure 2. (a) Current-voltage curves in the region from -1.20 V to -0.80 V recorded at cycle 40; (b) X-ray diffractograms for Pb electrode after the voltammetry test stopped at -1.20 V (reduced state).

Hydrogen evolution reaction on Pb electrode

Figure 3 presents the Tafel dependences for the hydrogen evolution reaction on Pb electrodes in electrolyte solutions obtained by the voltammetry measurements for the two types of cells. Looking at the potential-current dependences recorded on Pb electrodes in the cells with the two different separators, it is clearly evident that the organic substance released by the PE separator in the electrolyte reduces the hydrogen overvoltage on the Pb electrode and thus accelerates the hydrogen evolution reaction. The lower hydrogen evolution overvoltage in the presence of PE separator may negatively affect the lead-acid negative plate charge reaction and increase the Pb electrode self-discharge reaction.

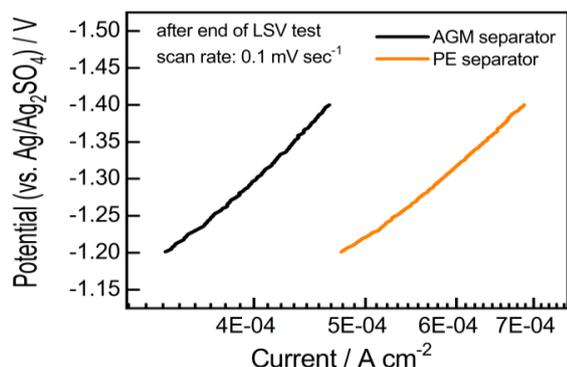


Figure 3. Tafel plots of the hydrogen evolution reaction for Pb electrodes.

Pb/PbSO₄ electrode - open circuit and charge acceptance tests

The test electrodes were left on open circuit for 65 h in 1.28 g cm⁻³ sulfuric acid solution. During the open circuit stay, cathodic reactions of hydrogen evolution and oxygen reduction proceed, and the coupled anodic oxidation of lead to lead sulfate or lead oxide takes place at a slow rate. The

longer time of open circuit stay permits the slow processes, such as formation and recrystallization of lead sulfate, to proceed.

Figure 4a presents the potential vs. time curves for the two types of electrodes. After switching off the circuit, the potential has a value of -0.97 V, i. e. the reversible potential of the Pb/PbSO₄ electrode. The potential remains at this value until a narrow pore membrane layer of sulfate is formed on the electrode surface, which separates the lead from the bulk electrolyte solution. In the narrow pores, the solution is more diluted and a concentration difference exists between the mouth and the bottom of the pore, which is reflected in a change of potential to about -0.70 V measured between the lead and the reference electrodes in the bulk solution. The rate of formation of the membrane layer is determined by the rate of dissolution of lead and the mode of lead sulfate deposition. If the deposit is rather two-dimensional (thin layer) and covers quickly the lead surface, this time will be short; if it is more like three-dimensional (thicker), the time will be longer. It can be seen from Fig. 4a that this characteristic time is about 30 h for the cell with AGM separator and less than 1 h for the cell with PE separator. Hence, it can be assumed that, in the PE cell, there is (are) some substance(s) that either change(s) the rate of lead dissolution and/or change(s) the mode of lead sulfate deposition.

After that, the samples were subjected to a potentiostatic pulse, with 50 mV overpotential vs. the Pb/PbSO₄ equilibrium potential, for 1 h and the obtained current transients are presented in Fig. 4b. It can be seen that in the first 20 s of the potentiostatic pulse the current values for the AGM and PE cells are similar. The current transient for the cell with PE separator is a simple falling one with initial value of about 4 mA, whereas that for the cell with AGM separator rises from 1.8 to 3 mA and both curves decline thereafter.

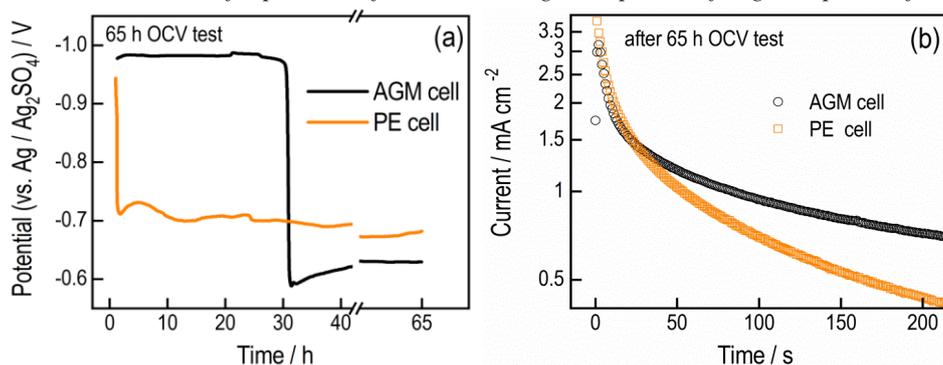


Figure 4. (a) Open circuit experiments (for 65 h) on cells with AGM or PE separators; (b) Potentiostatic reduction transients recorded at 50 mV overpotential after the OCV standing test.

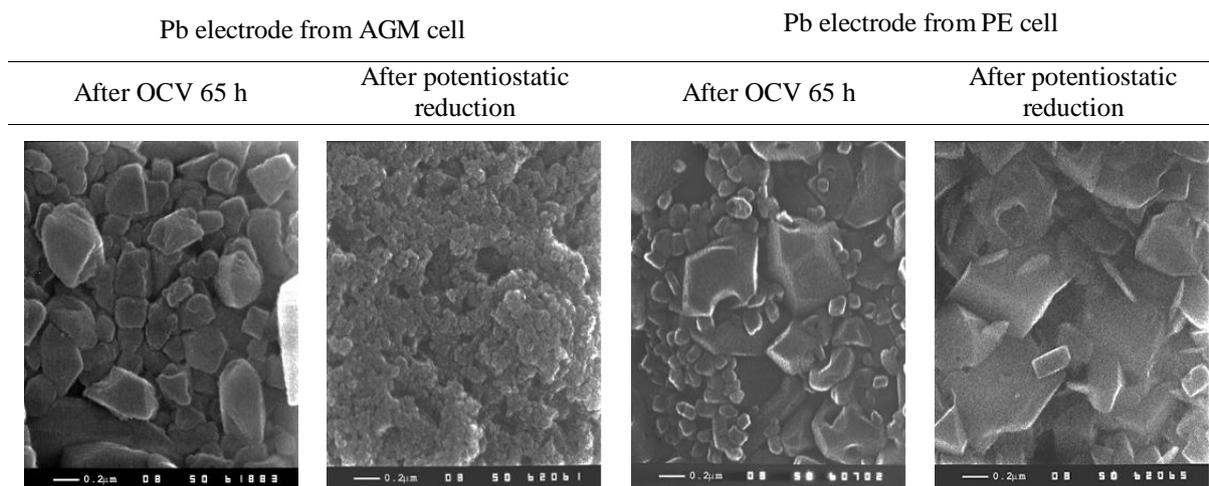


Figure 5. SEM pictures of electrodes AGM and PE after 65 h open circuit stay and after potentiostatic reduction tests

The simple transient means that the interface between the lead electrode and the solution is reactive from the very beginning and the falling part reflects the consumption of Pb²⁺ ions available in solution. The rising part means that initially the reactive interface is small and then its area increases. In contrast, after the first 20 s, the current of the PE cell abruptly decreases while the AGM cell exhibits about 65% higher current values. Probably, this effect could be attributed to organic additive molecules released by the PE separator in the electrolyte and then adsorbed on the electrode surface, thus reducing the active Pb surface area. In lead-acid battery terms, this is called “poor” or “good” charge acceptance of the lead electrode, respectively.

The morphology of the different lead electrodes after OCV stay for 65 h and after potentiostatic reduction, respectively, is illustrated by the SEM images in Fig. 5. It can be seen that well-shaped lead sulfate crystals, about 0.5 micrometer in size, occupy the surface of both electrodes after longer time of open circuit stay. In the case of the PE cell, the smallest crystals in the deposit are about 0.1 micrometer in size and are well separated from

each other. This means that, in the PE cell, they are stabilized by the adsorbed organic additive molecules and do not recrystallize easily. Some of the big lead sulfate crystals have defects on their surfaces, despite the fact that there are many small crystals within short distance and even grown over them. After potentiostatic reduction at 50 mV overpotential for 1 h, PbSO₄ is reduced to Pb in the AGM cell, while significant number of bigger and well-shaped PbSO₄ crystals still remain on the electrode surface in the PE cell. During the potentiostatic pulse, only the very fine PbSO₄ particles are converted back to Pb crystals. Probably, the organic substances released by the PE separator in the electrolyte are adsorbed on the PbSO₄ crystals and thus suppress the reaction of cathodic reduction.

CONCLUSIONS

The type of separator has significant impact on the electrochemical processes and charge acceptance of lead-acid battery negative electrode. Organic substances used in the production of the PE separator are released in the electrolyte. These substances most probably adsorb onto the surface

of the Pb and PbSO₄ crystals and thus impede the electrochemical processes that take place in the PE cells. The mechanism of action of organic substances in PE is to stabilize lead sulfate crystals in sulfuric acid solution, to suppress the rate of dissolution and therefore the rates of lead sulfate recrystallization and eventually the charge rate of lead-acid cell negative plate.

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