THE EFFECT OF PRESSURE ON THE ELECTRODE SYSTEM IN LEAD ACID BATTERIES WITH EXPERIMENTAL GLASS FIBERS ADITIVES IN NEGATIVE ELECTRODES

Daniel Fryda

Doctoral Degree Programme (1), FEEC BUT

E-mail: xfryda00@stud.feec.vutbr.cz

Supervised by: Petr Bača

E-mail: baca@feec.vutbr.cz

Abstract: This article discusses the effect of pressure-applied to a system of electrodes in lead acid batteries in hybrid electric vehicles. During the operation of these vehicles is adversely affecting the properties and battery's life. Experiments in our laboratories found that application of right pressure on the system of electrodes can improve some parameters lead acid accumulators and extend its lifetime.

Keywords: lead-acid accumulator, PSoC mode, glass fibers, pressure

1. INTRODUCTION

Lead-acid battery works in partial state of charge (PSoC mode) in hybrid electric vehicles. The battery operating in this mode is associated with different main degradation mechanisms. These effects are impulse for much research for many years. It was shown, that by changing some parameters of the battery can partially improve properties, for example by adding various additives to the negative active mass as glass fibers. Another modification, that positively influences the characteristics of the battery, is the application of a variety pressure on the electrode system.

2. THEORETICAL

Degradation mechanisms in PSoC occur as a result of changes in the structure and electrical properties of the battery during cycling. These effects are called PCL effects (Premature Capacity Loss) can be classified into 3 groups according to the site of action. PCL - 1 operating on interface of the grid and the active material, PCL - 2 in the positive active mass, it is the increase of mass discharging and PCL - 3 are effects occurring in connection with the negative active mass. Based on theoretical and experimental data have been proposed methods for suppressing PCL effects to avoid these premature losses of capacity. These methods can be divided into two groups. The first group is associated with the production technology and the second group of parameters of the proposed cell. [1][2][4]

Pressure applied to the electrode system is trying to suppress the effects associated with the degradation of the positive active mass and the sulfating of the negative electrodes. The volume of positive active mass is changing during discharge PSoC mode. Influence of the increase might be interrupted conductive contacts in the active mass. It is necessary to find the suitable pressure, because insufficient pressure cannot get any changes. Conversely high pressure can damage parts of the experimental cell, such as the structure of the active masses or separators. Excessive compressions of separators reduce the size and number of available pores and may reduce the intensity of the oxygen cycle. [2][3]

3. EXPERIMENTAL

Six negative electrodes were created for the experiment with a discontinuous system of parallel ribs. Negative active mass was applied on electrodes. Lead dust was main component, it was formed 41.645 g. The other dry ingredients formed a borosilicate (0.105 g), vanisperze (0.042) and the mixture expander STB 17.2 (1.165 g). Expander contained an admixture of glass fibers (0.39 g). Liquid ingredients were formed demineralized water (4.543 g) and (2.5 g) sulfuric acid with a density (1.28 g/cm3). Weight of negative active mass was 50 g. The mixture was applied to the exposed ribs. The process of curing was performed. [4]

The active area of the electrodes had dimensions of 55 x 20 x 7 mm. The negative electrodes were along with the positive electrodes and AGM separators assembled into cells and stored in hermetically sealed containers. For the measurement of potential was used cadmium reference electrode. All sections were suffused H_2SO_4 concentration of 1.28 g/cm^3 and ready for measurement. Prepared samples were subjected to the formation and DoD (depth of discharge) cycling. [1]

Formation is a process, where the cell was first charged slowly and it got gradually to operating conditions. Formation was created mixture of oxides and lead sulphates from the active mass to highly porous lead. 24 cycles was carried on each cell during formation. One cycle consisted of charging (4 h) and standing (2 h). DoD cycling consisted of several charge and discharge cycles $I_{charging} = I_{discharging} = 0.7$ A. Charged cells were discharged after formation down to the voltage drops below the value of U = 1.6 V. At this time, charging had started with voltage limiting U = 2.45 V. One cycle charge / discharge it took 24 hours. A total of 16 DoD cycles in a flooded condition was done in our experiment.

Excess electrolyte was aspirated from accumulators before first PSoC cycle set and the electrolyte must be soaked only in glass separators. Then the cells were discharged to 50% capacity and pressure was set at electrode system. Blue electrodes 1 and 2 were applied pressure 2 N/cm^2, the green electrodes 3 and 4 was applied pressure 4 N/cm^2 and 6 N/cm^2 on pink electrodes 5 and 6. PSoC cycle set simulated operation of the hybrid electric vehicle starting after the preparatory phase.

1) Charging: - a current of 2.5 A for 25 seconds.
2) Standing: - for 3 seconds.
3) Discharging: - current 2.495 A for 25 seconds.
4) Standing: - for 3 seconds.

Three PSoC cycle sets were at total of 61.000 cycles. DoD cycles were performed after finishing PSoC cycle set. The reason was determining the status of changes the parameters of electrodes.

3.1. PSoC – CHARGING CHARACTERISTICS

According to the experiment, the best performance was attained during charging in II. and III. PSoC cycle sets. Voltage on cycles grew slowly. For these electrodes is started intensive oxygen cycle, which becomes intensified further. In I. PSoC cycle set voltage is increasing almost all cells rapidly to a maximum and then declined slightly. More oxygen over time causes a negative electrode sulfated, which reduces potential of the negative electrode and thus the voltage of the whole cycle. Over time, the increasing resistance of the entire cell, which are confirmed by measuring the resistance the negative active mass. The resistance of the entire cell is increasing over time. Measurement of the resistance the negative active mass confirmed it.

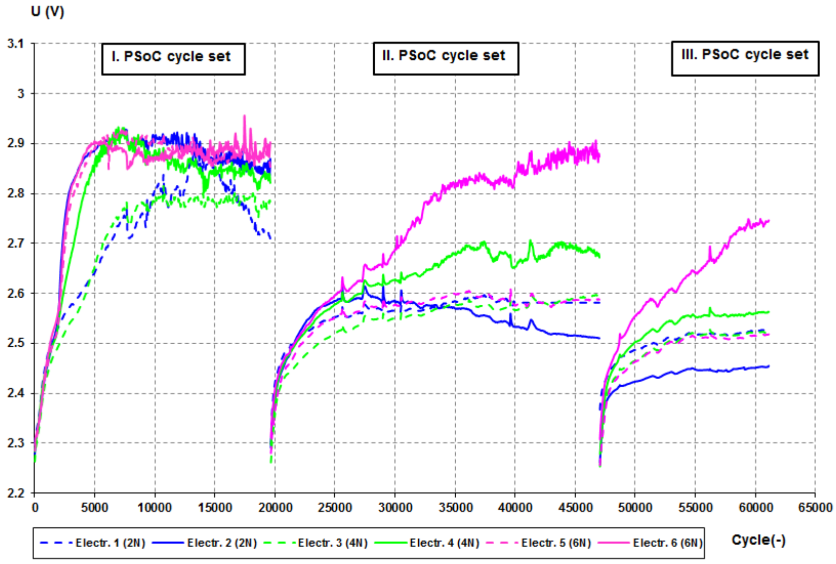

Figure 1: Dependence of voltage on all PSoC cycle sets (charging).

3.2. PSoC – DISCHARGING CHARACTERISTICS

Voltage dropped at experimental cells in the first PSoC mode. It is remarkable that the electrode 3 with pressure (4 N/cm^2), retains a slightly decreasing trend. We can tell that after the II. PSoC cycling, the process was significantly improved in all cycles. In addition to electrode No. 1, this exhibited the worst characteristics during the measurement and moved to the end of lifetime. The main reason is probably a combination of the effects of low pressure and an impaired ability to absorb the charging current.

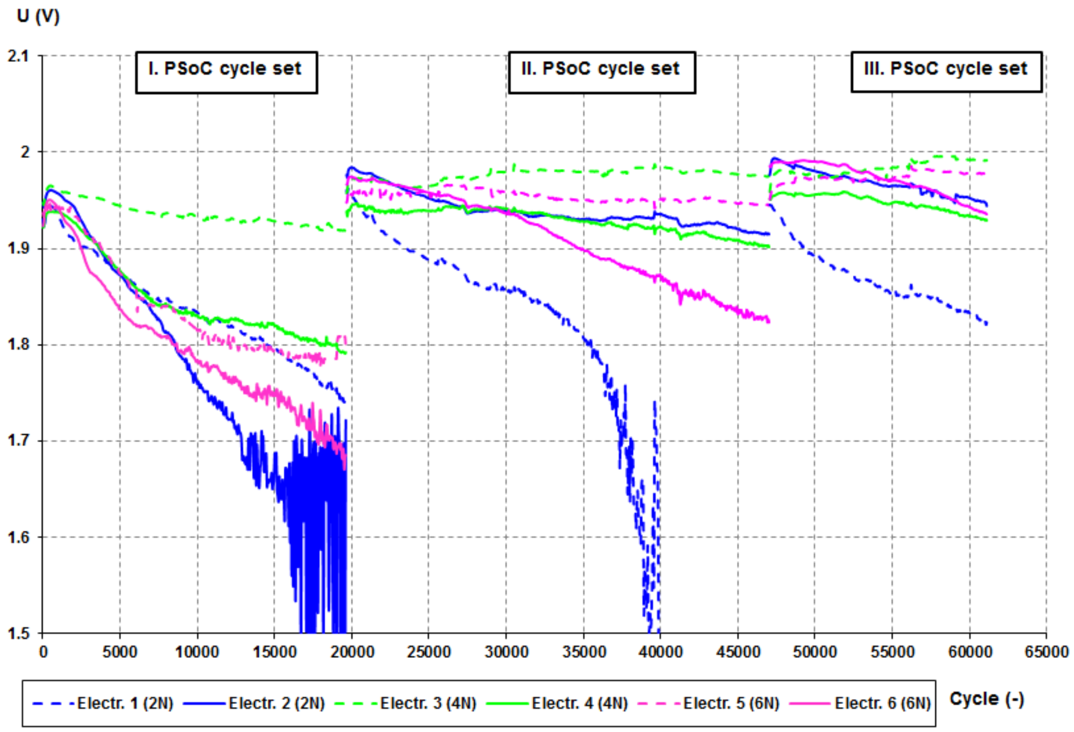

Figure 2: Dependence of voltage on all PSoC cycle sets (discharging).

3.3. PRESSURE CHANGES DURING PSOC CYCLING

Figure 3 shows the pressure which the system exhibited during the experiment. At the beginning of PSoC regime occurs to large drops in pressure which is most pronounced at the electrodes 5 and 6 with the highest applied pressure (6 N/cm^2), up by 2 N/cm^2.For electrodes 3 and 4, "medium" pressure is exerted by the decrease of 1 N/cm^2. We assume that this effect is caused by compression of cells higher pressure with AGM separators compressed and then partially absorb the pressure, and thus decreases their thickness. This effect in cells 1 and 2 with pressure 2 N/cm^2 is not as noticeable because the pressure on the electrode system does not reach such values. II. and III. PSoC cycle set was already quite a stable pressure. The biggest decrease occurred in cells with pressure (6 N/cm^2) in the second run PSoC cycle set. Cells with pressure (4 N/cm^2) were relatively constant. The cells with pressure 2 N/cm^2 had the best properties. Cells with applied pressure 2 N/cm^2 had a slight increase of pressure on the contrary. The applied pressure probably does not lead to stabilization of the active materials structure, active mass started to expand.

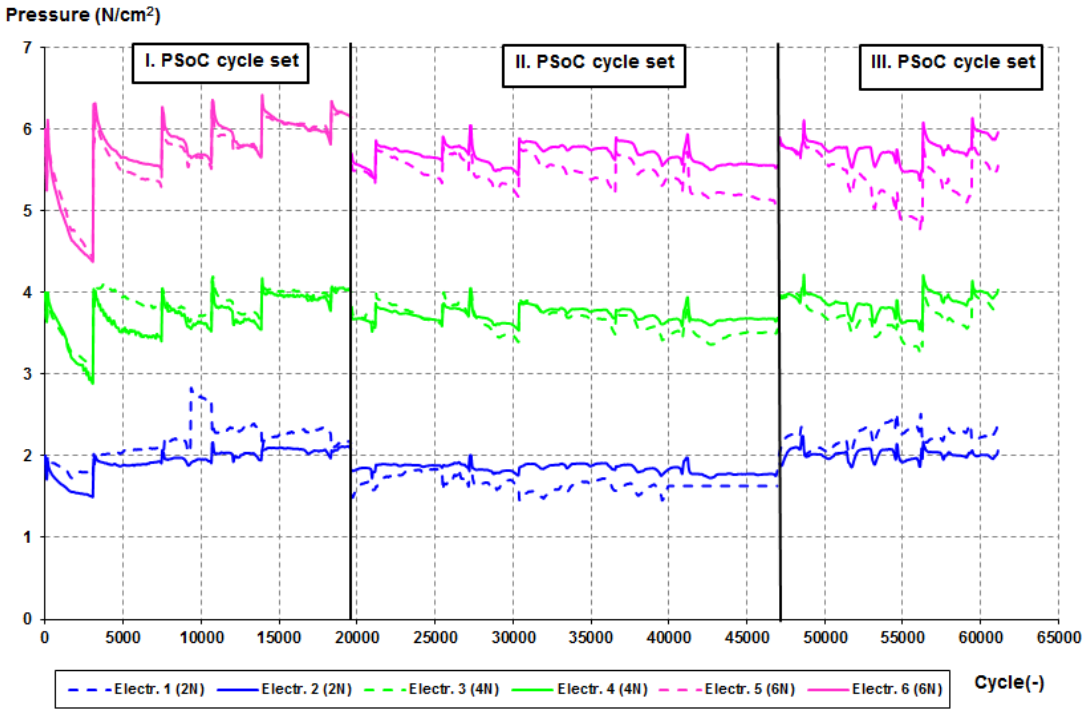

Figure 3: Dependence of the applied pressure during charging all PSoC cycle sets

3.4. RESISTANCE OF THE ACTIVE MASS

The initial increase of resistance can be observed in Figure 4 for cells 1 and 2 with the lowest pressure (2 N/cm^2). This increase is down to local maximum. We assume that the low pressure on the electrodes causes a slow expansion of the negative active mass (NAM) with the result of the increase in resistance NAM. The negative active mass expands further after reaching the maximum space for expansion (given configuration of the internal space cell and the compressibility of the separator). The electrodes 3, 4 and 5 (with the higher applied pressure 4 and 6 N/cm^2) exhibit a constant resistance value of the active mass. The electrode 6 with pressure (6 N/cm^2) showed differences on the resistance of the mass and charging characteristics from the other electrodes. The increase in resistance at the end PSoC cycle set is due to increased cell voltage starting intensive oxygen cycle with the consequence of progressive sulphation NAM down to deep structures and thus a measurable increase in the resistance of the active mass.

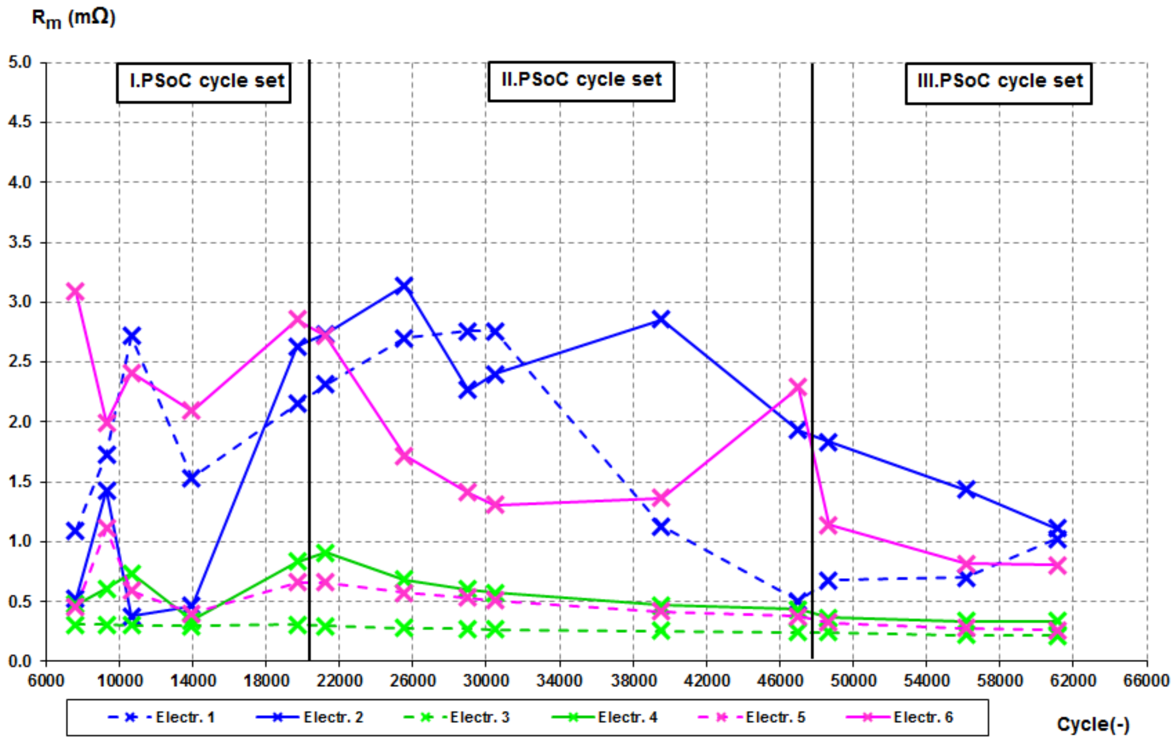

Figure 4: The resistance of the NAM during all PSoC cycle sets

4. CONCLUSIONS

From the measured values, we can consider that the least desirable was the lowest pressure (2 N/cm^2) applied to the first and second electrodes. These electrodes had the worst characteristics and there was a decrease of voltage in cells. Even the largest pressure 6 N/cm^2 (at the electrodes 5 and 6) was not suitable because there were unstable results during the measurement. Applied pressure 4 N/cm^2 (at the electrodes 3 and 4) showed the best results. Cycles were accompanied during the measurement the best properties and high stability.

ACKNOWLEDGEMENT

Author gratefully acknowledges financial support from the Centre for Research and Utilization of Renewable Energy under project No. LO1210 – „Energy for Sustainable Development (EN-PUR)“.

REFERENCES

[1] BAČA, P., *Studium jednotlivých forem předčasné ztráty kapacity bezúdržbových olověných akumulátorů VRLA*. Brno, 2007. 89 s. Habilitační práce. VUT v Brně.

[2] K. Nakamura, M. Shiomi, K. Takahashi, M. Tsubota *Journal of Power Sources,Volume 59*, March-April 1996, Pages 153–157

[3] MAREK, J., STEHLÍK, L.: *Hermetické akumulátory v praxi*. IN-EL, spol. s.r.o., 2004. ISBN 80-86230-34-4

[4] FRYDA, D. Efekt přítlaku vyvozovaného na elektrodový systém olověného akumulátoru s experimentálními elektrodami s příměsí skelných vláken. Brno: Vysoké učení technické v Brně, Fakulta elektrotechniky a komunikačních technologií. Ústav elektrotechnologie, 2013. 67 s., 0 s. příloh.