INFLUENCE OF TITANIUM DIOXIDE ON THE LIFE OF LEAD ACID BATTERIES WITH APPLIED PRESSURE

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Abstract: Hybrid electric vehicles use lead acid batteries operating under partial state of charge. The battery life of these batteries is dependent on the speed of growing of lead sulphate crystals ($PbSO_4$) on the electrode surface. The battery lifetime is affected by a variety of admixtures. This work deals with the influence of titanium dioxide on the negative active material in lead acid battery. This paper mainly devoted to the influence of the applied pressure.

Keywords: Lead-acid accumulator, hybrid electric vehicle, titanium dioxide, electrochemical cell, charging, discharging, applied pressure.

1. INTRODUCTION

Batteries in hybrid electric vehicles operate in PSoC mode (Partial State of Charge), which is good known as a partial charge mode. Operating area for battery charge is defined between 30-70 % SoC. If the charged value is less than 30 %, the battery is not capable of delivering the required power and electrode is sulphated (irreversible damaged). If the battery is charged over 70 %, accumulator retains less energy. It occurs with a drying of electrolyte (because of the electrolysis) and the system is also unable to recharge the battery during regenerative braking. [1][4]

2. BASIC PRINCIPLES

The cell consists of positive electrodes, negative electrode and separator. The positive electrodes are not manufactured by BUT. They are supplied by Akuma Mladá Boleslav company. The negative electrode is produced for laboratory experiments with discontinuous system of ribs. Six negative electrodes have been used for the measurement, as an additive has been used TiO_2 in negative active mass with the same concentration of 0.78 wt.%. The negative electrodes were limiting in our measurements. This is because the composition of the cell. The cell includes a negative electrode inserted into the separator of glass-fiber and two counter positive electrodes.[2]

Electrodes have to be formed after composition of the cell. Formation is the first slow charge. It is a process in which the negative electrodes reach the operating conditions. DoD cycles are following at the end of the formation. DoD cycle means Depth of Discharge. DoD completes the formation and maximizes active surface of the electrodes. Excess electrolyte was removed after the formation cycles and DoD cycles. Only the separator contained the electrolyte, it was approximately 50 ml. Cells were discharged to 50%. Pressure was applied to the individual electrodes. [3]

The electrodes with applied pressure 2 N/cm^2 (1 and 2) are marked in blue, with pressure 4 N/cm^2 (3 and 4) as green and pressure 6 N/cm^2 (5 and 6) pink. It has made 70 000 cycles in three PSoC cycle sets. 20 000 cycles in the first cycle set, 27 000 cycles in the second and third had 23 000. 20 000 cycles takes approximately 14 days. The PSoC experiments lasted about 49 days.

Modified Power Assist ALABC scheme used in the laboratory FEEC BUT:

Charging: - a current of 2.5 A for 25 seconds.

Standing: - for 3 seconds.

Discharging: - current 2,495 A for 25 seconds.

Standing: - for 3 seconds.

Cycling: charge - standing - discharge - standing.

2.1. CHARGING

It is desirable that the charging voltage reached a minimum, mainly because the voltage is higher than 2.45 V, more cells can "gas out" and also hold less charge. The battery life is influenced negtively. When the voltage at the cell is lower during charging, the electrode has better properties.

The figure No. 1 compares the voltage at the beginning of each PSoC cycle; this figure gives information about the total internal resistance of the cells. If the voltage is higher from beginning PSoC, internal resistance is higher as well. For all electrodes at each cycle was approximately voltage 2.3 V. This means that the internal resistance of the cells did not change extensively during the PSoC cycles.

Cells with the highest pressure demonstrated between the first and second PSoC during a significant reduction of the charging voltage.

Cells with the lowest pressure achieved the highest voltage in all cycle sets.

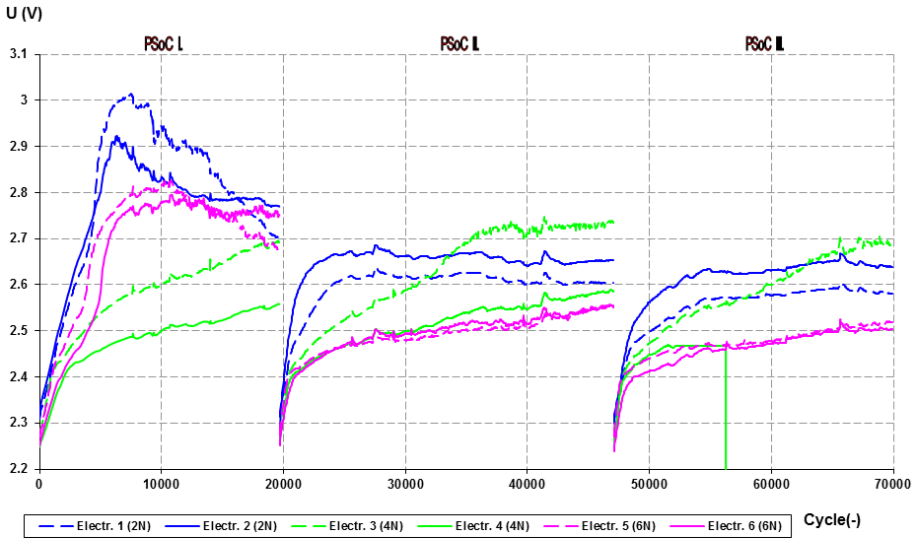

Figure 1: Dependence of the cell voltage during charging on of the cycle number

2.2. DISCHARGING

The first and second electrodes ended their life in the first cycle set, when the voltage dropped to 1.6 V. The applied pressure 2N/cm^2 for PSoC cycles are the least appropriate. Electrodes five and six (the highest pressure 6 N/cm^2) maintained the lowest voltage drop in PSoC cycle sets. The fourth cell ended its life in the last PSoC cycle set. There was a technical problem or error in measurement data logger.

The relation to the pressure size is reflected with discharging. In electrode is applied the lowest pressure (2 N/cm^2) and we can observe the steepest voltage drop. The figure No. 2 shows that the

electrode 1st and 2nd PSoC did not operate after the first cycle set. Higher pressure (4N/cm^2 or 6 N/cm^2) has no longer such an influence, but again it showed more ability to receive charge.

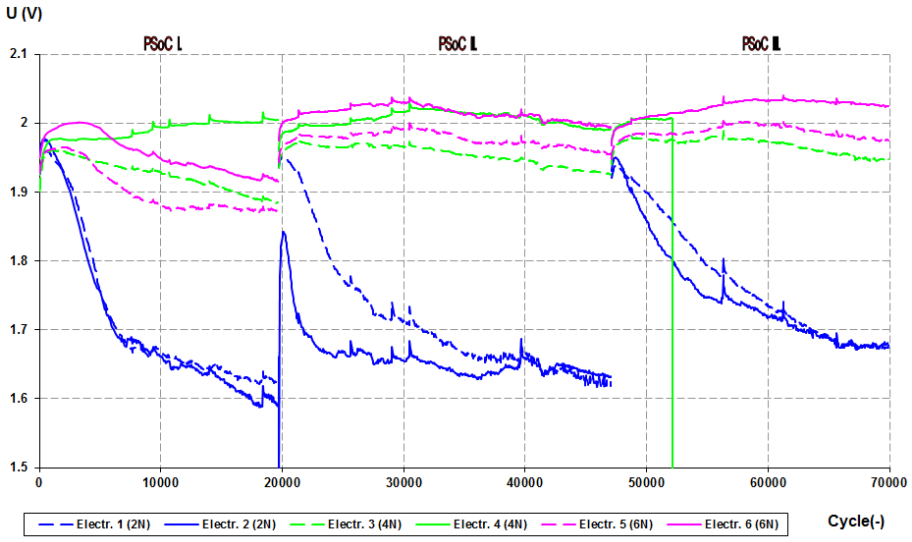

Figure 2: Dependence of the cell voltage during discharging on of cycle the number

2.3. CAPACITY

Capacities were measured in cells during DoD cycles. Identified capacities were plotted to figures. Electrodes 1 and 2 have due to wrong formation process the lowest capacity. The largest increase of capacity occurs in these electrodes. All electrodes lead to continuous increase up to approximately 12 cycles and then there is a slight decrease. The whole process is controlled by the charging and discharging in the voltage range from 1.6 V to 2.45 V, while it is used for discharging constant current of 0.7 A (down to a voltage of 1.6 V), and then charging the same current with the voltage limitations 2.45 V. 1 DoD cycle set was carried out between formations and 1st PSoC cycle sets. Other then between in PSoC cycle sets. 3 DoD cycle were performed each time was evaluated with the middle one. Measurements have not been taken due to time reasons after the last in PSoC cycle set.

The average initial capacity reached the value 59.11 mAh with standard deviation of 4.73 mAh. Maximum capacity, and were in the range 63.21 mAh of the fifth electrode and 81.5 mAh in the first electrode. Average maximum capacity was 72 mAh, with a standard deviation of 6.33 mAh.

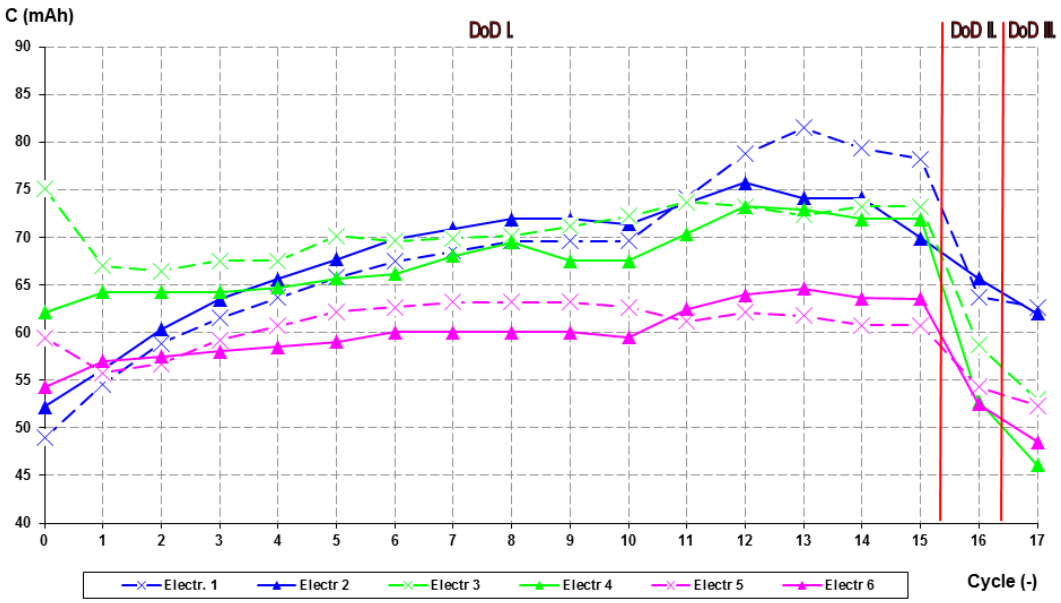

Figure 3: Dependence of the NAM capacity per gram on the cycle number

2.4. PRESSURE DECREASE

The figure No. 4 shows changes of pressure, which were irregularly, adjusted to the specified value throughout all PSoC cycle sets. Manual adjustment of pressure is always accompanied by a stepper increasing the value of pressure. The figure shows that, especially at the beginning of a large decrease pressure, this drop is greater, the applied pressure is greater. For 2 N/cm^2 is a drop of approx. 0.5 N/cm^2. For 4 N/cm^2 decreases the value by 1 N/cm^2. It is 6 N/cm^2 for decreasing pressure up to 2 N/cm^2.

We assume that this effect is caused because of the compressibility separators, which absorb a certain amount of pressure. How to stabilize the structure of the separator and the electrode active mass of both pressure decreases in the cycles after the first cycle set PSoC decreased. In the second and third cycle set is a decrease compared to the first half PSoC cycle set.

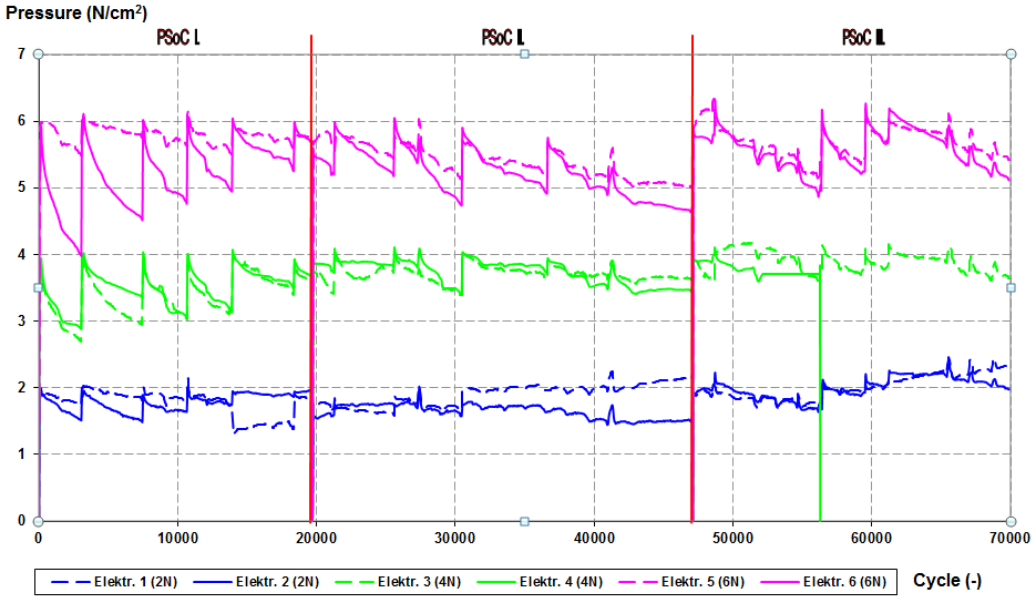

Figure 4: Dependence of the applied pressure during charging of all PSoC cycle sets

3. CONCLUSIONS

The paper is focused on the influence of pressure applied to cells. From this perspective, the lowest applied pressure 2 N/cm^2 shows the worst. Of course PSoC cycle sets can be concluded that the higher pressure has a positive effect on the lifetime of the electrodes, the longest lifecycle of the electrode with the applied pressure 6 N/cm^2. The effect of pressure can be observed in the discharge curves of PSoC cycles, the electrodes with the highest pressure achieved the minimum voltage drop. The effect of pressure on the contrary, is not in charge PSoC, which is more pronounced ability to take charge of the electrode. The disadvantage of applied pressure 6 N/cm^2 is a big drop during the PSoC cycle sets, change of the pressure reached 2 N/cm^2 from the beginning of the cycling. It is therefore impossible to determine whether the preferable applied pressure should be 4 N/cm^2 or 6 N/cm^2.

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