

CURRENT DISTRIBUTION OVER THE PLATE SURFACE IN LEAD-ACID CELL IN THE COURSE OF DISCHARGE

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ABSTRACT

Impact of fast cycling in partial state of charge (PSOC) regime was determined mathematically by using equivalent circuit method. The dependence of the internal cell resistance on the current and charge passed was determined by measurements on a laboratory cell. The results are presented in the form of 3D diagrams at various states of discharge.

1 INTRODUCTION

The decreasing amount of mineral raw materials brings about globally an ever-increasing endeavor of government and nongovernmental organizations toward a stronger exploitation of alternative source electric energy. Considerable attention is paid to electric vehicles and in last time especially to the transient step between a car with classic combustion engine and an electric vehicle – hybrid electric vehicles (HEV). This vehicle will be driven by an electric motor fed by relatively small battery continuously charged by a small combustion motor, working in the regime of optimum cruising speed with minimum emission.

A possible source for HEV might be the economically advantageous lead-acid battery. If we want a battery for the HEV to be able to receive el. charge at high rate charging (e.g. at recuperative brake), it must work in partial recharge regime (PSOC), because the ability of a lead-acid battery to receive the charge in charged conditions is rapidly decreasing. At the state of recharge about 50 %, the battery is receiving el. charge very well even at high rate of charging. Positive and especially negative electrode mass are, however at the same time, predisposed to a degenerative mechanism till the cell is no more capable to respond to charging with acceptable effectiveness. Long-term regime PSOC applied to lead-acid battery gives rise to a new mechanism of disturbances, whereby it is necessary to elaborately understand it and to remove it. Currently these mechanisms of disturbances are brought into the relation with irreversible sulphation, especially of negative electrode. Efforts toward the remedy are generally directed to a new type of additive active mass, optimization of current

collector (placement tab), prevention of temperature instability, optimization of oxygen cycle ratio and pressure effect.

2 RESEARCH OF THE IMPACT OF FAST CYCLING IN THE PSOC REGIME

In order to analyze the impact of fast cycling in the PSOC regime on use properties of negative electrodes, we have in the first phase dealt with the monitoring of the influence of carbon in the form of graphite added to the negative active mass. We have acquired a relatively wide choice of graphite from a domestic producer – Maziva Týn Ltd. in Týn nad Vltavou. On the basis of this information, we chose for the initial experiment the graphite with grain size 400, 40 and 4 μm . We manufactured a set of 8 negative electrodes differing in the size and quantity of graphite added to the negative active mass; the last one (No. 9) served as a comparative electrode without added graphite. Dimensions and the method of production of experimental electrode system was identical as that described in the previous chapter. The separator was made from glass fiber BG089GB056 supplied by Hollingsworth & Vose (89 g/m², thickness 0,56 mm). Electrolyte: H₂SO₄ solution with density 1,28 g/cm³. Formation: cycle for 4 h by 0,2 A charging current + 2 h idling, on the whole 72 h charging + 36 h idling. After finishing the formation, 10 start-up cycles were carried out. Regime of formation cycling: discharge current 0,5 A, charging constant current 0,5 A with voltage restriction 2.45 V for 8 h, i.e. 2 cycles every day.

Before the cycling experiment in the PSOC regime was started cells were discharged to 70 % capacities determined in the previous cycle and wired in series. Discharging and charging current was pre-set identically to 2.5 A, charging time 15 s, discharge 10 s (charging to 150 %). During the experiment we recorded total voltage both at the end charging and at the end of discharge. Total number of cycles was about 14 000. Best results were observed for electrodes with the addition of graphite with the grain size 4 μm . These electrodes exhibited at the end of charging the minimum voltage and, on the contrary, at the end of discharge the biggest voltage. Moreover, after finishing the experiment, active masses from these electrodes exhibited the smallest amount of sulphate. On the contrary, the worst results were exhibited by electrodes with the addition of graphite with grain sizes 40 μm and 400 μm .

Therefore, in the next step, the additive to the active mass of the negative electrode was chosen to be the graphite with grain size 4 μm . We manufactured four pairs of negative electrodes; each of them contained 5, 2.5, 1 and 0.5 % of graphite with the above-mentioned grain size. We also had the last comparative electrode No. 9 without any graphite at all. These electrodes were this time just about 2.5 mm thick and had initial capacity around 1.5 Ah. Trial cells were manufactured in the same manner as in the previous case; separator and electrolyte were again identical. The formation was carried out in the same way as before. After finishing formation 10 start-up cycles were carried out. With electrodes prepared in this manner, we carried out 3 experiments aimed at the optimization of the cycling process. Before starting each experiment, characteristics of cells were made more uniform by performing several cycles comparable to formation cycles and cells was discharged at 50 % capacity determined in previous cycle.

Experiment 1

Cycling regime: Both discharging and charging current was 1 A, duration 10 s, charging was carried out without voltage restriction. Between charging and discharging electrodes were always kept for 2s in idle state. Altogether about 6000 cycles were carried out. In three

electrodes (those with 5 %, 2.5 % and 1 % graphite) the reversal of polarity in cells was found, caused by the crash of potential at negative electrode. At the end of charging, a sharp rise of voltage in cells with 1 % C was observed.

Experiment 2

Cycling regime: Both discharging and charging current was 1 A. Discharging period was 10 s, charging period 10.5 s with voltage restriction 2.46 V per cell. Between charging and discharging the electrodes were – as before – kept for 2 s in idle state. Altogether about 9000 cycles were carried out. After that the experiment was terminated, because of the discharge of negative electrodes. Electrodes with 5 % C added were disconnected after 3300 cycles (high voltage at the end charging) or after 6000 cycles (discharge of negative electrode).

Experiment 3

Cycling regime: Both discharging and charging current was 1 A. Discharging period was 10 s, charging period 20 s with voltage restriction 2.46 V per cell. Between charging and discharging electrodes were – as before – kept for 2 s in idle state. Before the start of the experiment one of the electrodes with 5 % C added was excluded because of its small capacity. This experiment has not been finished so far. Up to now about 50 000 cycles have been carried out and electrodes are in good conditions. Optimization of cycling process will further go on.

3 OPTIMIZATION OF CURRENT COLLECTOR

Current distribution over the electrode in a lead-acid battery during discharge was studied for different arrangements of supply (tab) placement. A part of the equivalent electric circuit used for the calculation of current distribution over the electrode surface is in fig. 1. Here R_{vk} is resistance between 2 corresponding elements of both electrodes. At the positive grid $R_{x+} = 1.6125 \text{ m}\Omega$ and $R_{y+} = 0.5375 \text{ m}\Omega$, at the negative grid (with negative active mass in charged state) $R_{x-} = 1.327 \text{ m}\Omega$, $R_{y-} = 0.327 \text{ m}\Omega$; grid: $R_{x0} = 0.5375 \text{ m}\Omega$, $R_{y0} = 0.3583 \text{ m}\Omega$.

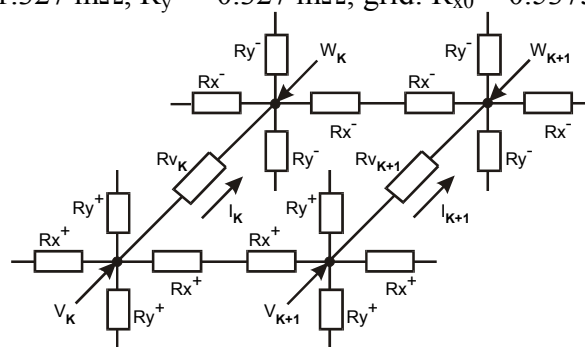


Fig. 1: Equivalent electrical circuit

In the case of the positive electrode, the active mass does not contribute significantly to the conductances of the grid. However, in case of a negative one, the grid conductances must be corrected for the conductances of the active mass. Our older papers contain the finding that the dependence of the conductivity of the negative active mass on time is in the course of discharge practically linear. The dependence of the resistance of individual components of

active mass on charge Q passed can then be expressed by the following approximate equations:

$$R_{x-} = 0.5 / (376.67 - 1142.9 Q) \quad (1)$$

$$R_{y-} = 0.5 / (1530 - 10286 Q) \quad (2)$$

Values of the internal resistance of individual cell element R_{vk} include the electrolyte resistance, the contact resistance between the grid and the active mass, the active mass resistance and the polarization resistance. The course of their changes during the discharge for a number of discharge currents was identified experimentally on a miniature cell. These changes are a function of the current I passing through the cell and the charge Q passed. The results were expressed by the following regression function calculated by the least squares method:

$$R_{vk} = 0.32 + 4.2 Q + 2.6 \times 10^{-5} \exp Q + 100 I - 14 \quad (3)$$

By applying the first and second Kirchhoff laws to the nodes and loops of the whole equivalent electric circuit, a system of linear equations is obtained, whose solutions gives the requested distribution of the potentials and currents. To take into account the system changes with the time, the calculations were carried out in steps as follows.

Step 1 ($i = 1, t_1 = 1 \text{ s}, \Delta t_1 = 1 \text{ s}$): The initial value of $R_1 = 0.32 \Omega$ is introduced into all elements representing the internal resistance R_{vk} and the potential distribution in the nodes of equivalent circuit is calculated. The node potentials of k -th element V_{kl} and W_{kl} , are used to calculate the corresponding voltage and current

$$U_{kl} = V_{kl} - W_{kl}, I_{kl} = U_{kl} / R_{kl} \quad (4)$$

The charge passed through the k -th element can be calculated as

$$Q_{kl} = I_{kl} \times \Delta t_1 \quad (5)$$

Step 2 ($i = 2, t_1 = 30 \text{ s}, \Delta t_1 = t_2 - t_1$): The internal resistance corresponding to the k -th element is calculated from Eq. (1). Afterwards, the node potential distribution is again calculated and the corresponding voltage and current values are found as in step 1. The charge passed through the k -th element is calculated as

$$Q_{k2} = Q_{k1} + I_{k2} \times \Delta t_2 \quad (6)$$

The procedure continues step by step until $t_n = 12000 \text{ s}$. The chosen value $\Delta T = 30 \text{ s}$ is suitable since the resulting error in the linearization is negligible. Higher values of ΔT cause increasing errors in the linearization, lower values lead to a considerable increase of the calculation time.

The current distribution over the electrode surface during the discharge was calculated for 7 variants differing in the location of current tabs over the electrode Figs. 2 and 3 show the results only for the case of biggest and smallest current in-homogeneity and for 0, 40, 60, 80, 90, and 100 % discharge. In cases where tabs of positive and negative electrodes are close to each other (Fig. 2), most-loaded areas are at the beginning of the discharge those closest to the tabs. Therefore, these areas are quickly discharged and their internal resistance considerably increases. According to this, if the total discharge current over the electrode is constant, the current fall in these regions, incurred by the resistance growth, leads in the course of discharge to load growth in other region of the electrode, originally less loaded. It leads during the discharge to a gradual exploitation of other regions of the electrode. In spite of the increasing uniformity of the current distribution during the discharge, this tab arrangement is

not suitable for battery operation.

The in-homogeneity of the exploitation of the active mass decreases with the increasing distance between positive and negative electrodes. As it seems, the best configuration is the system with planparallel equipotential current tabs placed on opposite ends of both electrodes, see fig. 3. In such a case is the current distribution over the electrode surface in the course of discharge virtually quite uniform. Small differences are brought about only by the higher conductivity of the thicker upper and lower horizontal grid rib.

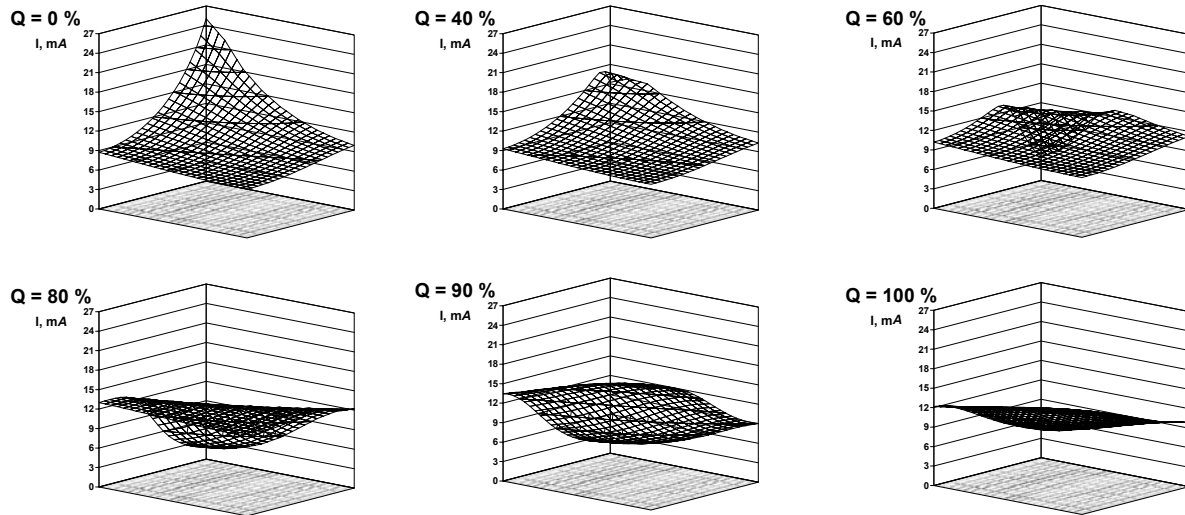


Fig. 2: *The biggest current in-homogeneity*

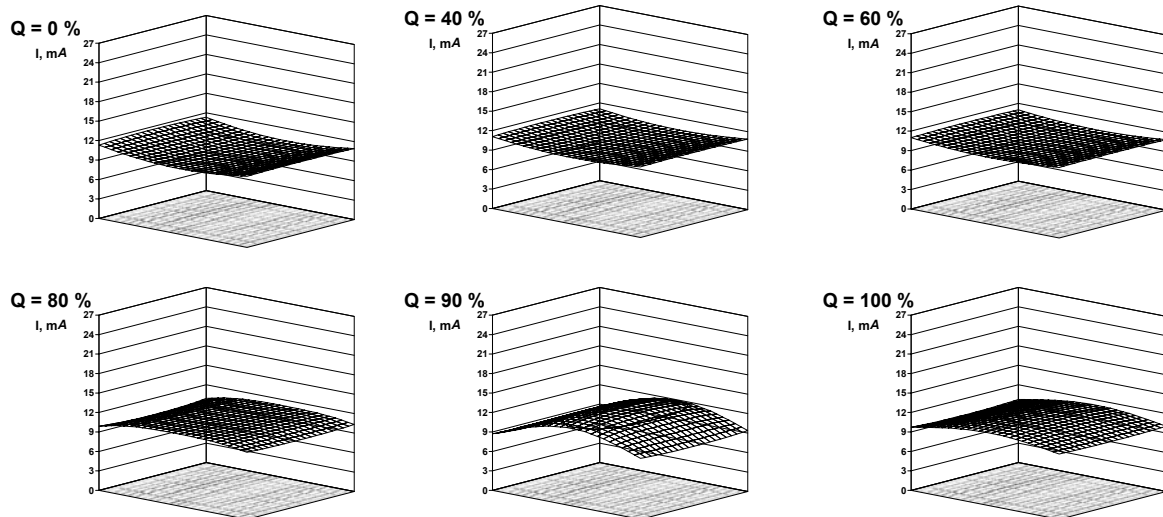


Fig. 3: *The smallest current in-homogeneity*