NEW FINDING FROM STUDY OF INNER RESISTANCE OF LEAD-ACID BATTERY

P. Křivák, P. Bača

Department of Electrotechnology, Faculty of Electrical Engineering and Communication Technologies, Technical University of Brno, Czech republic

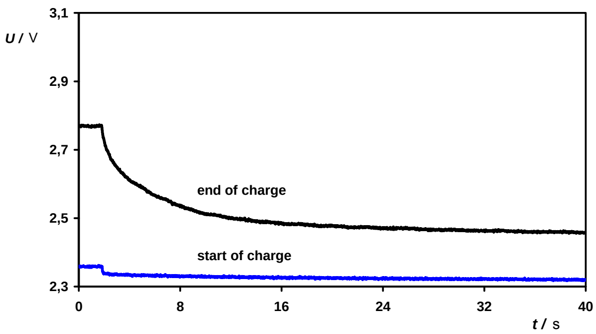
Corresponding author: Petr Křivák (krivak@feec.vutbr.cz)
Phone: +420 54114 6189
Fax: +420 54114 6147

Introduction

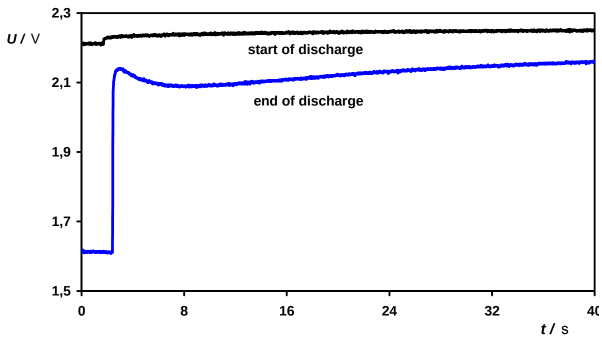
Aim of the work is to contribute to development of lead-acid batteries with better use properties with emphasis on research of inner resistance and it's changes depending on different parameters, conditions and regimes of cycling.

Experimental

Internal resistance is from definition given by equation $R_v=\delta U/\delta I$, where δU is increment of cell voltage and δI increment of current passing through the cell. Present differential method, based on jump change of passing current, where inner resistance is calculated according to the formula $R_v=\Delta U/\Delta I=(U_2-U_1)/(I_2-I_1)$, was rather inaccurate and unreliable especially at the end discharge and charge, when comes to rapid fall (growth) of cell voltage.



a)



b)

Fig. 1 *Course of voltage on experimental cell after disconnection of a) charge current and b) discharge current*

For better illustration of problem there are enclosed fig. 1a and 1b, where can be seen different courses of cell voltage during a period of 40 s after disconnection of charging (discharging) current. Internal resistance corresponds to the slope of the linear part of falling curve shortly after disconnection of current (less than 10^{-3} s). In next nonlinear part of curve is significant reactions of electrode double layer on interface active mass / electrolyte (10^{-3} s) and in later stage also diffusion processes (of a order seconds) [1].

From this reason it was designed and opened accurate and reliable method of measurement of inner cell resistance of lead-acid battery based on using of alternating current (AC), superimposed on direct current used to charge or discharge of tested cell. Amplitude of AC was adjusted on 0,5 A and frequence on 5 kHz. This method proved to be fast and reliable and suitable for automatic data measurement on PC.

Next interesting experiment was monitoring of inner resistance newly designed cell flooded with electrolyte and during resulting formation (charge). From fig. 2 a there is evident that in flooded state before formation there is a big value of inner resistence about 2 Ω. After start of formation it comes to rapid fall of inner resistance to about 0.1 Ω. It can be explained with help of theory AOS [2]. AOS model (abbreviation from English agglomerate of spheres) was developed in the year 1990 by Winsel. It comes from presumption that active mass of positive electrodes is composed especially from spheres interconnected by necks. This structure forms during formation of active mass when comes to vehement decrease of active mass inner resistence. It is related with generation of conductive connection (neck) among originally insulated particles (spheres) of active mass.

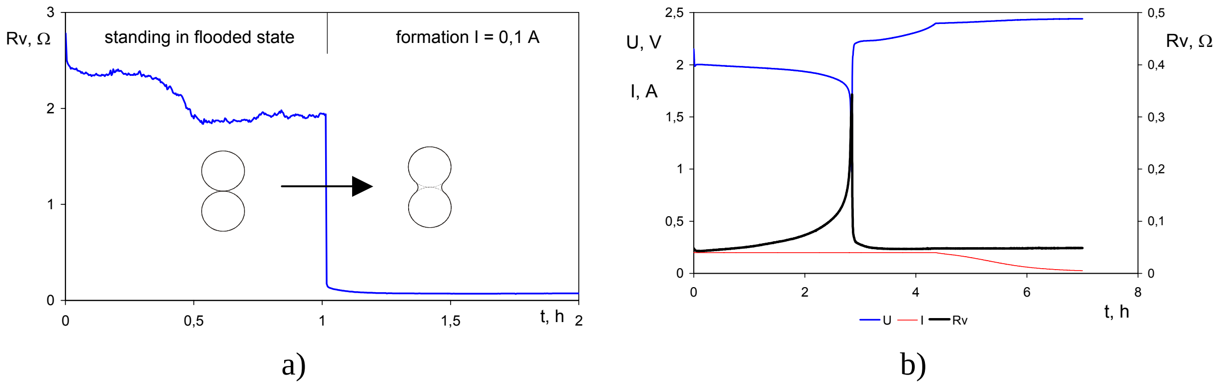


Fig. 2 *Dependence of inner resistance of a newly designed cell of lead-acid battery during standing in flooded state and resulting formation with current I = 0,1 A (a) and during discharge and charge.I = 0,2 A, 20-th cycle (b).*

Next aim of the research was monitoring of changes of lead-acid battery cell inner resistance in the course of it's life. On fig. 2 b it can be seen dependence of inner resistance during discharge and subsequent charge of the cell in 20-th cycle and on fig. 3 in 320-th cycle. It's clear from these figures, that course and value of inner resistance at the end of life does not change (when comparing with beginning of life), difference is only in much smaller capacity compared to state at the beginning of life. Hence value of inner resistance do not seem to be applicable like indicator of aging of electrodes. Cause of end of life of experimental cells can be different. Among most frequent cause of aging is sulphation of aktive mass, corrosion of positive electrode grid, shedding of positive electrode active mass, short-circuit or combination of these factors.

It is clear from previous experiments that course of inner resistance depends especially on generation and backward solution of crystals $PbSO_4$ in active mass especially inside positive electrode, which used to be mostly limiting (because of it's lower capacity in comparison with negative one) and also it has higher order resistance than negative one. A considerable influence on this course has also rate discharge (charge), because this parameter controls the shape and size of the $PbSO_4$ crystals in active mass.

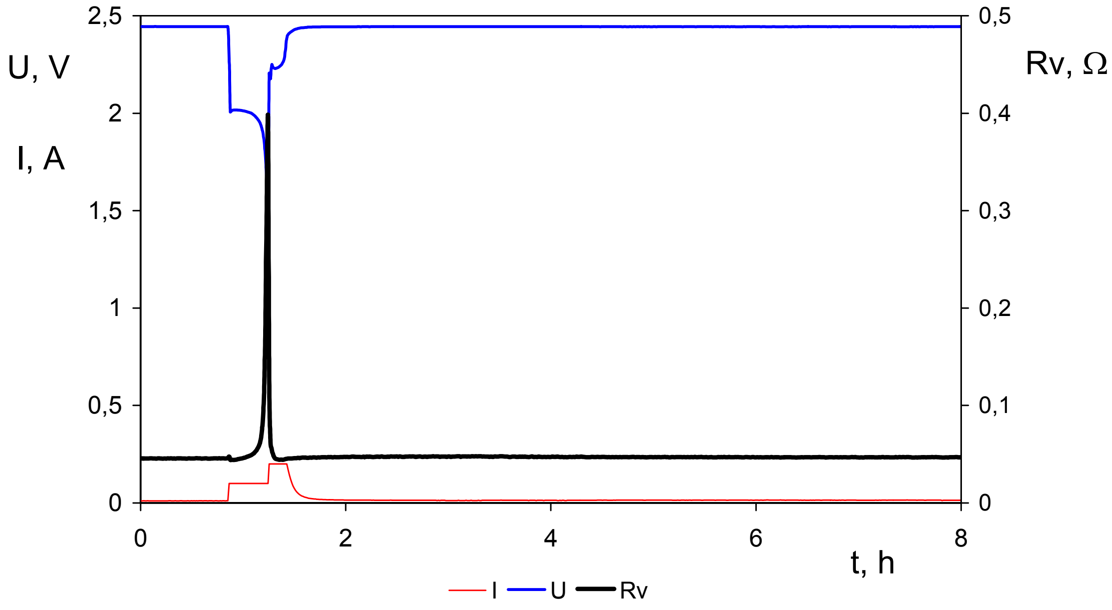


Fig. 3 *Dependence of inner resistance during discharge and charge, I_V = 0.1 A, I_N = 0.2 A, 320-th cycle.*

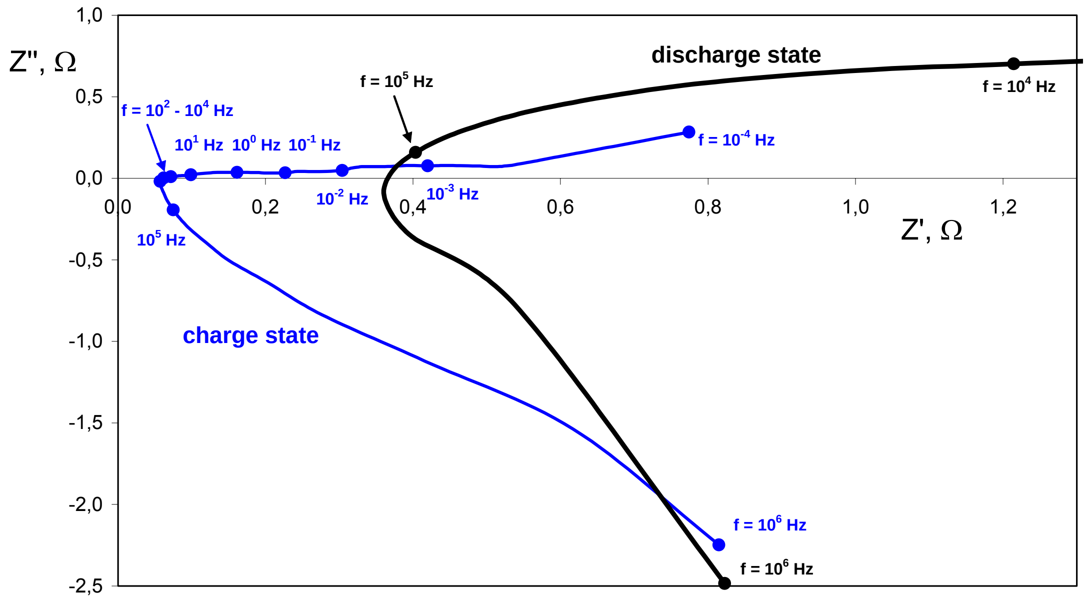


Fig. 4 *Frequency dependence of real and imaginary part of impedance of experimental cell for frequency range f = 10^{-4} – 106 Hz (in charge state) and for frequency range f = 10^{-4} – 106 Hz (in discharge state).*

In so far last phase of research there was made an impedance measurements on experimental cell of lead-acid battery in wide frequency range from 10^{-4} to 106 Hz both in charge and discharge state. Measurements was made with help of potenciostat (firm Autolab) and resulting dependencies presented in the form of Nyquist diagram, where on x-axis is real part of complex impedance and on y-axis imaginary part of complex impedance of experimental cell. Diagram includes inductive part (below x-axis) for high frequencies and capacitive part (above x-axis) for low frequencies. Inner resistance of the cell can be readed from a minimum value of real parts of impedance, when at the same time imaginary part of impedance equals to nought. It is clear from fig. 4 that correct value of inner resistance of experimental article could be read in charged state at frequences 103 – 104 Hz (0.05 Ω), while in discharged state as far as at frequences around 105 Hz (0,4 Ω). This finding somewhat complicates an optimum setting of frequence dutiny measurement of inner resistance of experimental cells of lead-acid battery.

Acknowledgements

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