IN SITU STUDY OF THE INTERNAL RESISTANCE IN A LEAD-ACID BATTERY CELLS

P. Křivák, *P. Bača*

Institute of Electrotechnology, Technical University of Brno, 602 00 Brno

Introduction

Total internal resistance of lead-acid battery cell is given as the sum of all its components, which for both positive and negative electrode involves resistance of the collector, of the collector - active mass inter-phase, of the active mass itself and finally of the active mass - electrolyte inter-phase. Further components of the total internal resistance comprise resistance of the electrolyte in the electrode pores, of the electrolyte itself, of the separator and again finally resistance of the inter-cell wiring and of polarisation resistance.

Experimental

The internal resistance of the cell is by definition expressed by the formula $Ri = \delta U / \delta I$, where δU is derivative of the cell voltage and δI is the derivative of the current passing through the cell. The difference method that has been used so far, based on the jump change of the current (internal resistance is calculated according to the formula $Ri = \Delta U / \Delta I = (U_2 - U_1) / (I_2 - I_1)$), is not sufficiently precise and not reliable enough especially at the end of discharge and charge where there is a sudden drop (increase) of the cell voltage.
Therefore there was developed device for measurement of the internal resistance based on the method of a.c. current, superimposed on the d.c. current used to charge or discharge the test cell. The a.c. current amplitude was set to 0.5 A and the frequency was set to 5 kHz. This method proved to be rapid, reliable, and suitable for automatic recording by using a PC.
We used experimental cells set up from cut-out parts of standard plates used for construction of starting lead-acid batteries. Electrodes were separated by separator and flooded by H_2SO_4 of 1.24 g/cm^3 density. After formation and several starting cycles they were subjected to some experiments with the aim of detailed exploration of inner resistance changes in situ.
Typical course of internal resistance is illustrated on Fig. 1. Cell was discharged with constant current 0.2 A to 1 V, then charged with current 0.2 A with voltage limitation 2.45 V. In the course of discharge owing to the increase of $PbSO_4$ content (insulating material) in the active mass there is evident growth of the internal resistance. Especially at the end of discharge there is rapid growth of the internal resistance. This behavior was related to the screening of the last accessible areas of active mass by $PbSO_4$ crystals, or to an increase in resistivity of the electrolyte in the pores of the active mass since the ionic concentration is strongly reduced there at the end of the discharge. At the beginning of charge there is a rapid drop of inner resistance of the experimental cell from value 0.34 Ω at the end of discharge to 0.05 Ω (value close to the beginning of discharge). This drop

Corresponding author: Petr Křivák
E-mail: krivak@feec.vutbr.cz

appears to be much more quick than growth of inner resistance at the end discharge.

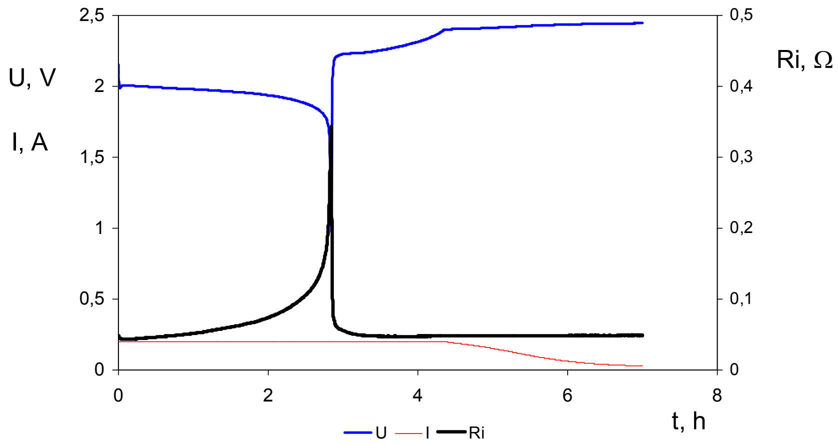

Fig. 1 *Dependence of the internal resistance during discharge and charge, I = 0.2 A.*

In the following experiment there was a cell discharged with constant current 0.2 A to 1 V, then the current was cut-off (see Fig. 2). There is evident from the Figure, that after cut-off of the discharge current there is a rapid drop of the internal resistance analogically as in the previous case. At the end of discharge there is created unstable layer of easily soluble crystals of $PbSO_4$ owing to the increase of local current density in areas of the active mass yet uncover by lead sulphate, which then, after disconnection of discharge current, quickly dissolves to the electrolyte especially in the area with local shortage of sulphate ions and causes a rapid drop of internal resistance. However, in contrast to the previous experiment, the value of internal resistance after disconnection of the cell will stabilize to the much higher value around 0.13 Ω (there was no charging of the cell).

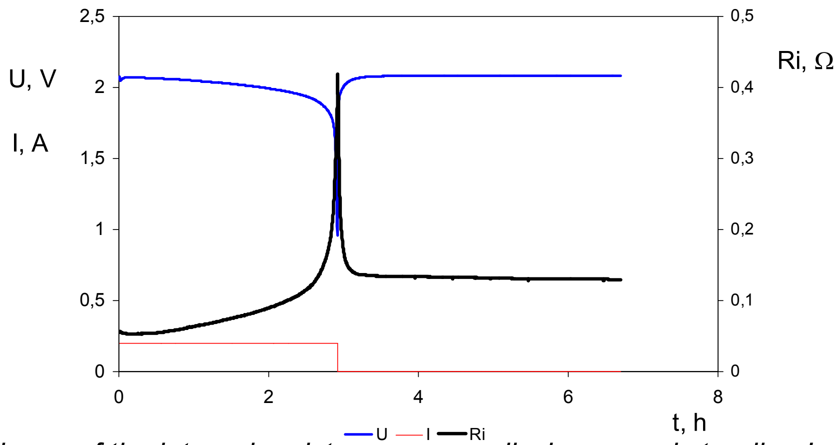

Fig. 2 *Dependence of the internal resistance during discharge and standing I = 0.2 A.*

In 3rd experiment the cell was discharged with constant current 0.4 A to 1 V, then charged with current 0.4 A with voltage limitation 2.45 V. The course of the internal resistance is similar as in 1st experiment. In contrast to that, however, the cell is discharged much earlier (the cell indicates less capacity). At higher discharge currents there is quicker creation of screening layer of lead sulphate, that hinders to more deep discharge, lead sulphate content in active mass at the end discharge is less and that is why also the final value of the inner resistance at the end of discharge is less (approx. 0.25 Ω) - see Fig. 3.

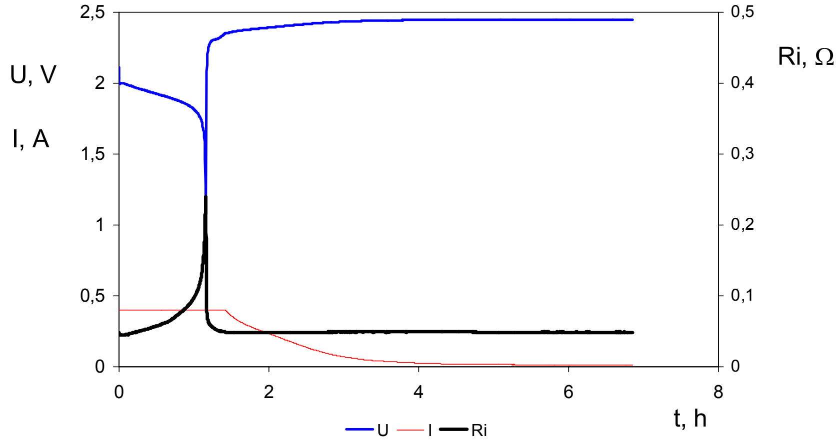

Fig. 3 *Dependence of the internal resistance during discharge and charge, I = 0.4 A.*

In 4th experiment the cell was discharged with constant current 0.1 A to 1 V, then charged with current 0.1 A with voltage limitation 2.45 V. The course of the internal resistance is again similar as in 1st experiment. In contrast to that, however, the cell is discharged much later (the cell indicates bigger capacity). At lower discharge currents there is slower growth of $PbSO_4$ crystals, chemical reaction of lead sulphate formation proceeds more deeply in active mass, sulphate content in active mass at the end discharge is bigger and that is why also the final value of the inner resistance at the end of discharge is bigger (approx. 1.1 Ω) - see Fig. 4.

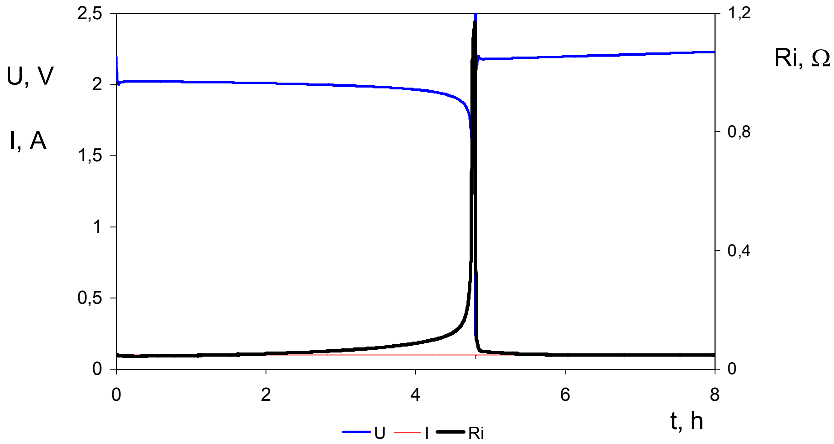

Fig. 4 *Dependence of the internal resistance during discharge and charge. I = 0,1 A.*

In final experiment the cell was subjected to overdischarging - see Fig. 5. At the beginning the cell was discharged with constant current 0.2 A. In the course of discharge there was a growth of internal resistance till the moment of polarity reverse of positive electrode (part 1). Then comes to sharp drop of inner resistance partly in consequence of dissolution of unstable $PbSO_4$ crystals on positive electrode and partly positive electrode begins to form to the negative one - Pb gradually generates from lead sulphate crystals (part 2). Next little growth of internal resistance happens when polarity of negative electrode is reversed, although growth isn't so strong as in positive one - from that is evident, that dominant effect on growth of the inner resistance has positive electrode (PbO_2 on positive electrode has much less conductivity than Pb on negative one). After reversion of polarity of negative electrode the negative electrode begins to form to the positive one - PbO_2 gradually generates from $PbSO_4$ crystals (part 3). At the end of overdischarge the current is switched to charge and it comes to backward reversion of polarity of both electrodes. In consequence of regeneration of lead sulphate crystals after reversion of polarity of electrodes it comes again to temporary growth of inner resistance. In the course of following charge $PbSO_4$ crystals transforms to the corresponding active masses (PbO_2 and Pb) and inner resistance again drops to its original value as at the beginning of discharge (part 4).

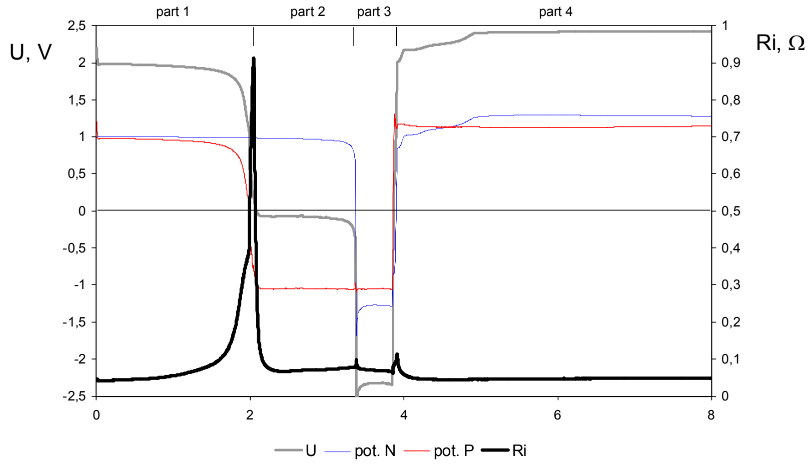

Fig. 5 *Dependence of the internal resistance during overdischarge and charge, I = 0,2 A.*

Conclusions

Internal resistance changes cannot be ascribed to the variations in resistivity of the electrolyte. The blocking action of insulating $PbSO_4$ crystals in the pores of the active mass is reflected in the inner resistance value and represents the main component of the inner resistance variations during the charge and discharge of lead-acid batteries. This component strongly depends on the (dis)charge rate because this parameter controls the shape and size of the $PbSO_4$ crystals.

Acknowledgements

This work was supported by the Grant Agency of the Academy of Sciences of the Czech Republic (Grant No. B2813305).

References

1. Calábek M., Micka K., Bača P., Křivák P.: J. Power Sources 95, 97 (2001)
2. Huet F., J. Power Sources 70,59-69 (1998)
3. Huet F, Nogueira R.P, Torcheux L., J. Power Sources 113,414-421 (2003).