IN SITU INTERNAL RESISTANCE MEASUREMENT IN LEAD-ACID CELL

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ABSTRACT

Simultaneous measurements inernal resistance, R_I, of a lead-acid battery cell have been carried out during the charge and discharge of the cell, owing to an original experimental set-up devised in the laboratory providing real-time analog signals. It was shown that R_I depended on the state-of-charge in a non-linear way, with a significant increase at low state-of-charge. The R_I variations were explained by the blocking effect of insulating $PbSO_4$ crystals whose morphology and size depend on both state-of-charge and (dis)charge rate. It was also shown that the resistivity of the bulk electrolyte, measured above the plates, had no influence on the R_I value.

1 INTRODUTION

Value of the internal resistance in lead-acid cell is the sum of all his components such as the collector resistance, the collector - active mass transition resistance, the active – mass resistance, the active mass – electrolyte transition resistance, the electrolyte resistance in electrode pores, the electrolyte resistance, the separator resistance, the connection resistance between cells and the polarization resistance

Till the end of seventies, a.c. bridges and lock-in amplifiers were used for resistance measurement. From 1977[2], most investigations were performed with frequency response analyzers based on harmonic analysis. In the literature, other electrical parameters, more or less related to the electrochemical impedance are also employed. The terminology is rather fluctuating, and. sometimes, it is hard to understand which quantity is actually measured.

The conductance is defined as the real part of the reciprocal of the impedance. If the phase angle ϕ is low. the conductance, which is given in Ω^{-1} or Siemens, is the reciprocal of the high-frequency resistance R_I. Several definitions of the internal resistance have been reported, each depending on the measurement technique. This resistance is usually measured either with a milliohm-meter or with the period-of-rest technique or with the current-pulse technique. In the former case, a high frequency (typically 1 kHz) sinusoidal signal is employed and the milliohmmeter gives the real part of the complex electrochemical impedance.

Among the various parameters investigated, the ohmic resistance R_I is perhaps the more attractive since its measurement may be performed in short times with simple instrumentation.

2 EXPERIMENT

We have measured the internal resistance of experimental cell made from the cut out parts of lead – acid accumulator plates. The electrodes were separated and flooded by the lotion of 1.24 g/cm^3 H_2SO_4. After finishing the formation several start-up cycles were carried-out.

Fig. 1 presents the typical evolution of R_I, U and I . The experimental cell was discharged by the current 0.2 A until voltage dropped at 1V. Then the cell was charged up by current 0.2 A with voltage restriction 2,45 V. The end of the discharge was due to the negative plate exhaustion, as shown by the sharp U drop before current interruption. R_I changed very little during the first part of the discharge, then it increased, following the progressive screening of the plate surface by insulating $PbSO_4$ deposits. Beyond 75% of the total supplied charge, R_I increased rapidly till the end of the discharge. 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. After the current break, the relaxation of R_I exhibited in Fig. 1, from 0.34 Ω towards 0.05 Ω

In the next experiment cell was discharged by the current 0.2 A until voltage dropped at 1 V. Then the discharge current was switched off see Fig. 2. After the switching off the current R_I has stabilized at 0.13 Ω The value of R_I at low state of charge, might be associated to the redissolution of the $PbSO_4$ crystals formed locally at high current densities at the end of the discharge, or to the increase in the concentration of ions diffusing back from the electrolyte bulk towards the pores of the active mass.

Fig. 3 represents the situation in which the experimental cell was discharged by the double current 0.4 A until voltage dropped at 1 V. Then the cell was charged up by double current 0.4 A with voltage restriction 2,45 V. The evolution of R_I is similar like in Fig. 1. But the experimental cell was more rapidly discharged. The screening of the plate surface was more aggressive. Amount of sulphate in active mass is lower at the end of discharge. Final value R_I is lower then in first experiment - about 0.25 Ω.

Fig. 4 represents the situation in which the experimental cell was discharged by the half current 0.1 A until voltage dropped at 1 V. Then the cell was charged up by double current 0.1 A with voltage restriction 2,45 V. The evolution of R_I is similar like in Fig. 1. But the experimental cell was discharged later. The growth of $PbSO_4$ crystals was much slower at smaller discharging currents. Amount of sulphate in active mass is higher at the end of discharge. Final value R_I is higher then in first experiment - about 1.1 Ω.

In 1981, Yahchouchi [4] and Gabrielli et al. [5] showed that the impedance of a large capacity lead-acid battery cell (2 V, 390 A h) increased when discharged. The increase of R_I was attributed to decreasing electrolyte conductivity and increasing surface coverage of the electrodes by insulating crystallized lead sulphate. The increase of R_1, which depends on the porosity of the electrodes, was likely caused by a blocking of the pores by lead sulphate crystals and by bubbles when overcharging. Yahchouchi [35] thought that R_{HF} could inform on the battery for continuous discharges not interrupted by short recharges which could dissolve the insulating crystals on the electrodes. Indeed, since R_{HF} includes the resistance of internal connections, ohmic resistance increases might enable detection of internal damages due to corrosion. He concluded that it might be possible to define an upper limit of the ohmic resistance for each type of battery and control the battery health periodically by comparing the measured value of R_{HF} to this upper limit.

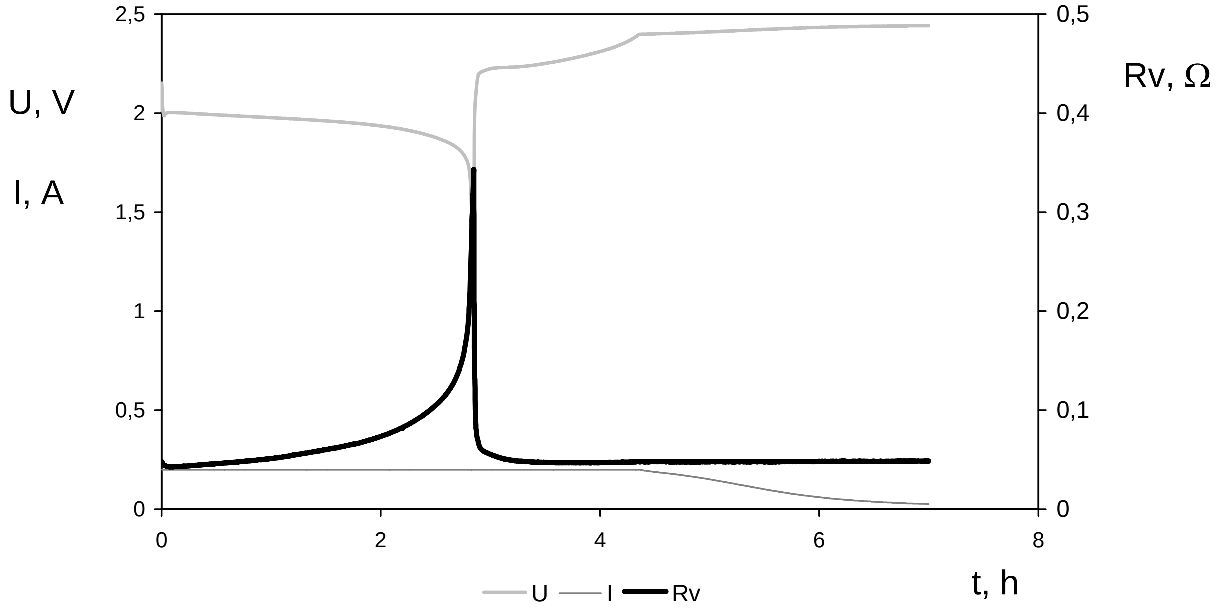

Fig. 1: *Evaluation of resistance characteristics during discharging and charging. I = 0,2 A.*

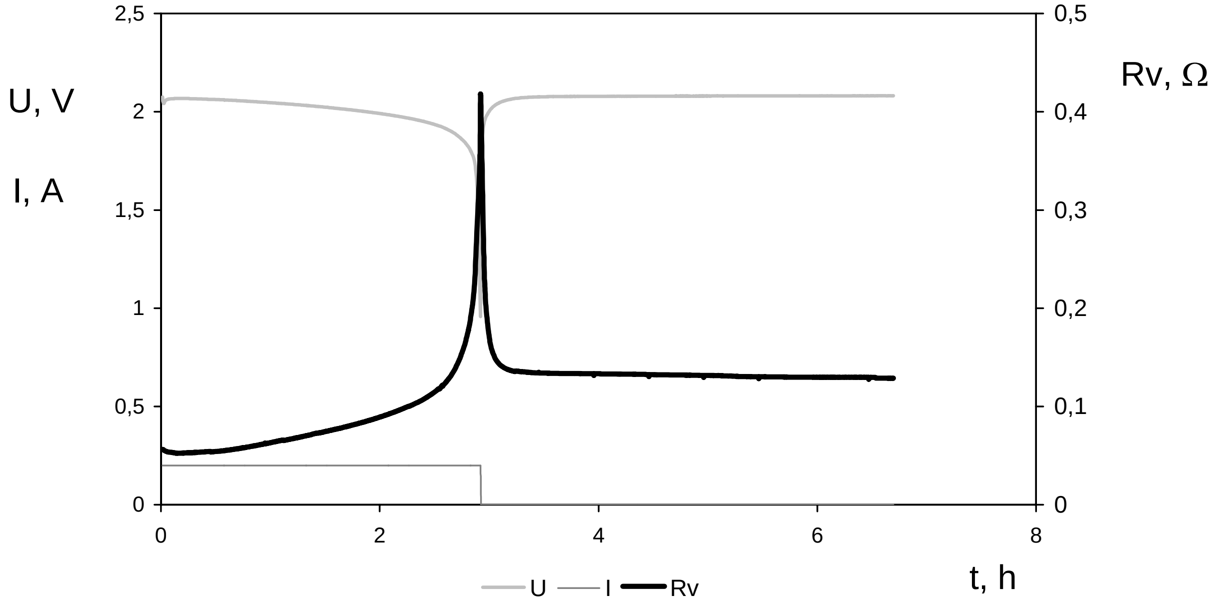

Fig. 2: *Evaluation of resistance characteristics during discharging and switching off the current. I = 0,2 A.*

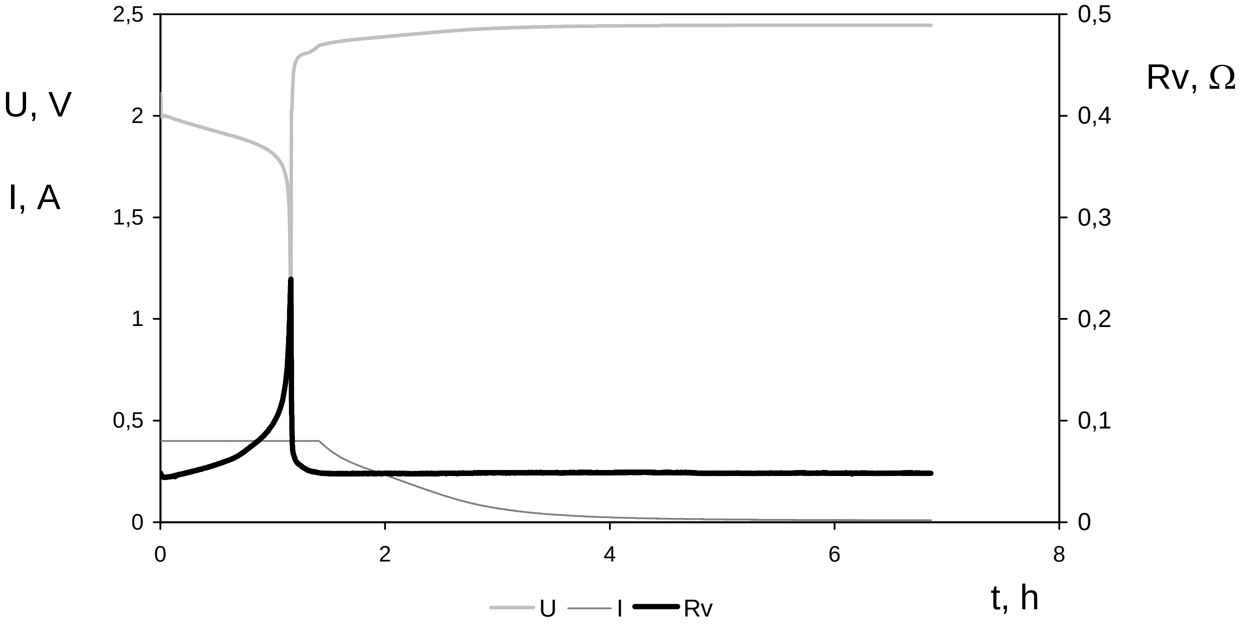

Fig. 3: *Evaluation of resistance characteristics during discharging and charging. I = 0,4 A.*

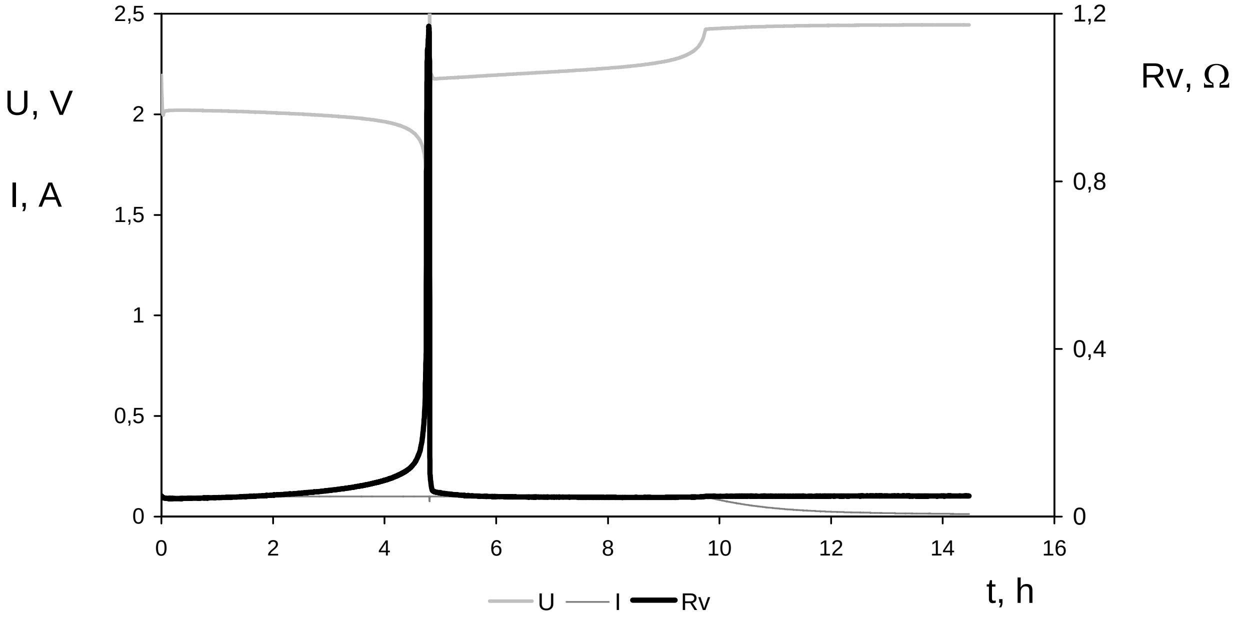

Fig. 4: *Evaluation of resistance characteristics during discharging and charging. I = 0,1 A.*

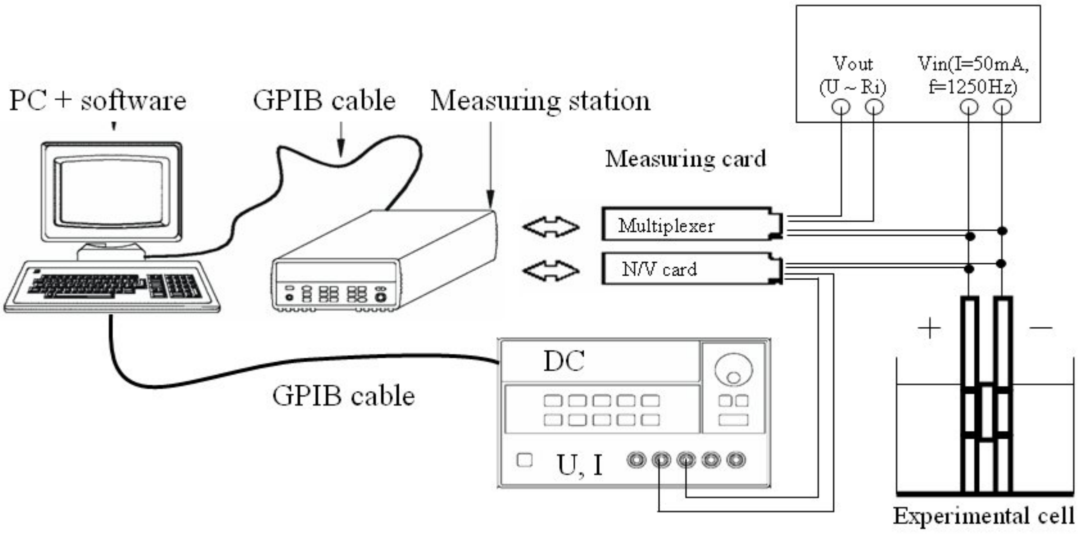

Fig. 5: *Measuring device for internal resistance measurement*

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