

STUDY OF THE PRESSURE CHANGES OF POSITIVE AND NEGATIVE ELECTRODES IN LEAD-ACID CELLS

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Abstract

Measurements of pressure changes in test cells with lead sheet counter electrodes showed that the volume changes of positive test electrodes follow the expected course, i.e. expansion on discharge and vice versa. The volume increase of the negatives, which may be attributed to the expander, can be prevented or even overcompensated by the applied mechanical pressure.

Introduction

To investigate the pressure effects on the parameters of lead-acid test cells, the test electrode was placed between two counter electrodes. The counter electrodes were replaced by thin lead sheets. The pressure changes were then given by volume changes of the test electrodes. The lead sheets were corroded to some extent during cycling (cf. Planté formation process), but the corrosion was not important during the first 20 cycles, to which the results presented below refer.

The test electrodes of dimensions 20 mm x 55 mm x 7 mm were prepared by spreading the industrial paste material on to current collectors consisting of 10 insulated parallel ribs [4 and 5] in the factory AKUMA (Czech Republic). The ribs were taken from grids of the composition Pb Sb 2.19 Sn 0.20 wt.%.

The electrodes were mutually separated by very little compressible separators that were newly developed by DARAMIC Inc. (Germany) and AMER-SIL S.A. (Luxembourg). The thicker Daramic separators contacted (from both sides) the active region of the test electrode and copied closely its surface, thus, ensuring uniform pressure load. The Amer-Sil separators, placed between the Daramic separators and the counter electrodes, surpassed the active electrode surface, thus, preventing the formation of electrically conducting bridges. The electrode system was placed in an equipment that produced a defined pressure on the electrode surface. All that was immersed into a large excess of electrolyte of 1.24 g/cm³ density in a polypropylene vessel, thermostated at 35°C. The equipment produced a defined pressure on the active electrode surface by means of a thrust screw [5 and 6]. The pressure was measured by using tensometric sensors connected with a measuring apparatus and a personal computer.

Pressure changes during cycling

The results of measurements on systems with lead sheet counter electrodes (enabling the "net" behavior of a particular electrode to be followed) are shown in Fig. 1-4 for positive electrodes and pressures of 1, 4, 6 and 8 N/cm². The course of the cell voltage, U , is included for orientation; its dramatic drop at the beginning of discharge to negative values is caused by the negligible capacity of the counter electrodes. It can be seen that the pressure increases during discharging (Section A) and decreases rapidly during charging (Section B) down to roughly the starting value. This is in accord with the formation and subsequent reduction of the voluminous lead sulphate. Our finding is in support of that of Pavlov and Bashtavelova [12] and other authors (cf. [1 and 4]), but at variance with the (not very clear) results of Bashtavelova and Winsel [13]. The relative (in percent) pressure increase during discharging is highest at the lowest pressure (about 40%, Fig. 13), as could be expected, and moderate at higher pressures (8–10%, Fig. 2-4).

With negative electrodes, the values of the pressure changes during cycling are appreciably higher than for the positive electrodes (Fig. 5-8). After a small transitory increase at the start of discharge, probably due to lead sulphate formation, there is a steep pressure decrease, probably due to dissolution and softening of the dendritic lead skeleton. This is followed by a pressure increase till the end of discharge (Fig. 5-7), which may be ascribed to the voluminous lead sulphate. However, if the applied pressure is too high, the pressure increase does not take place (Fig. 8). During charging (Section B), the pressure passes through a minimum,

presumably due to reduction of PbSO_4 , followed by a maximum that may be ascribed to the effect of the expander.

The final pressure value is indicative of the stability of the negative electrodes. It can be seen from Fig. 5-8 that at an applied pressure of 1 N/cm^2 the electrode has a tendency to expand after one cycle, at 4 N/cm^2 it preserves its volume and at still higher pressures it contracts. In accordance with Fig. 5, Pavlov and Ignatova [14] found a volume increase of non-compressed negative plates on discharge, stating that the results depend on the expander used. From the practical point of view, it is noteworthy that there exists a pressure value (close to 4 N/cm^2) at which the volume changes of the negative electrodes are suppressed and thus their capacity preserved.

Owing to the rather high porosity of the lead "sponge" skeleton, the electrode can absorb most of the lead sulfate in its pores. The pressure drop during discharge suggests a drop in the mechanical strength of the porous lead skeleton with its resulting slight compression. This may be related with the fact that the discharge capacity of the negative electrodes decreases unexpectedly with increasing pressure. It is noteworthy that this anomaly was not observed in our preceding work [1] where soft, easily compressible AGM separators were used (allowing the volume changes of the lead electrodes to be well accommodated) and where the measurement results corresponded to combined changes in thickness of both positive and negative electrodes.

Acknowledgement

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Figures

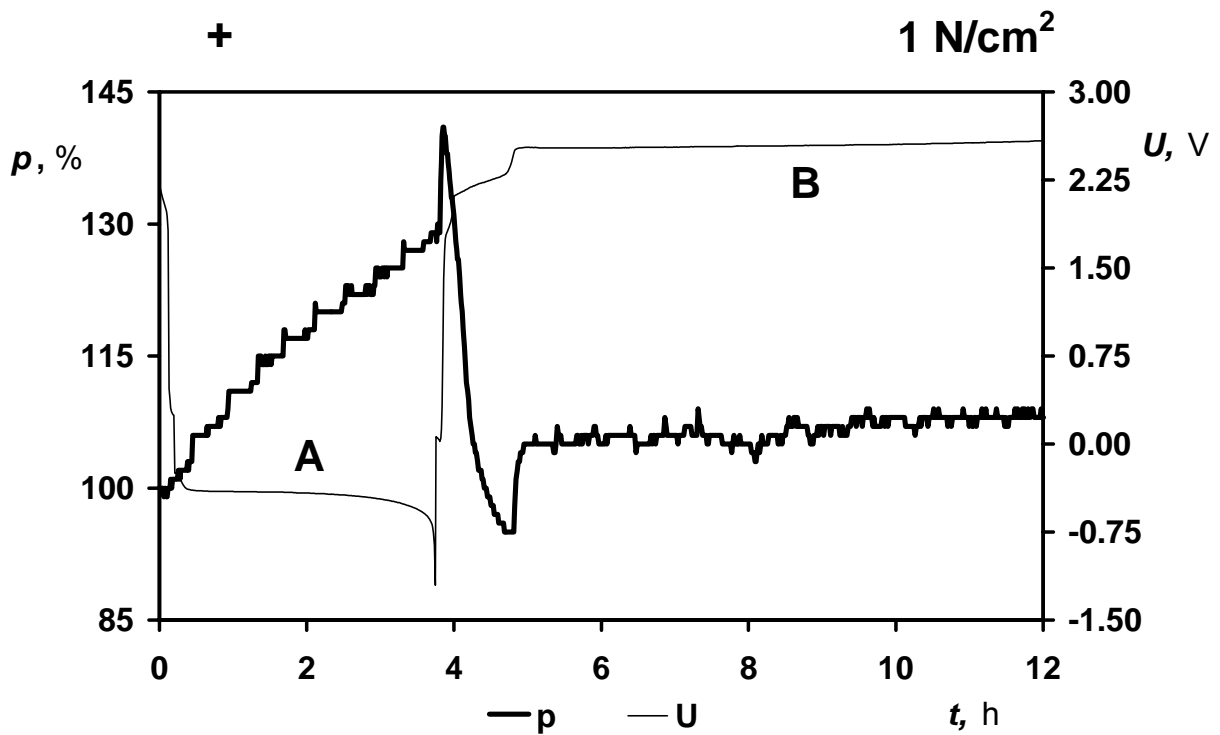


Fig. 1. Time dependence of cell voltage and pressure during discharging and charging. Positive test electrode, lead foil counter electrodes; cell compressed at 1 N/cm².

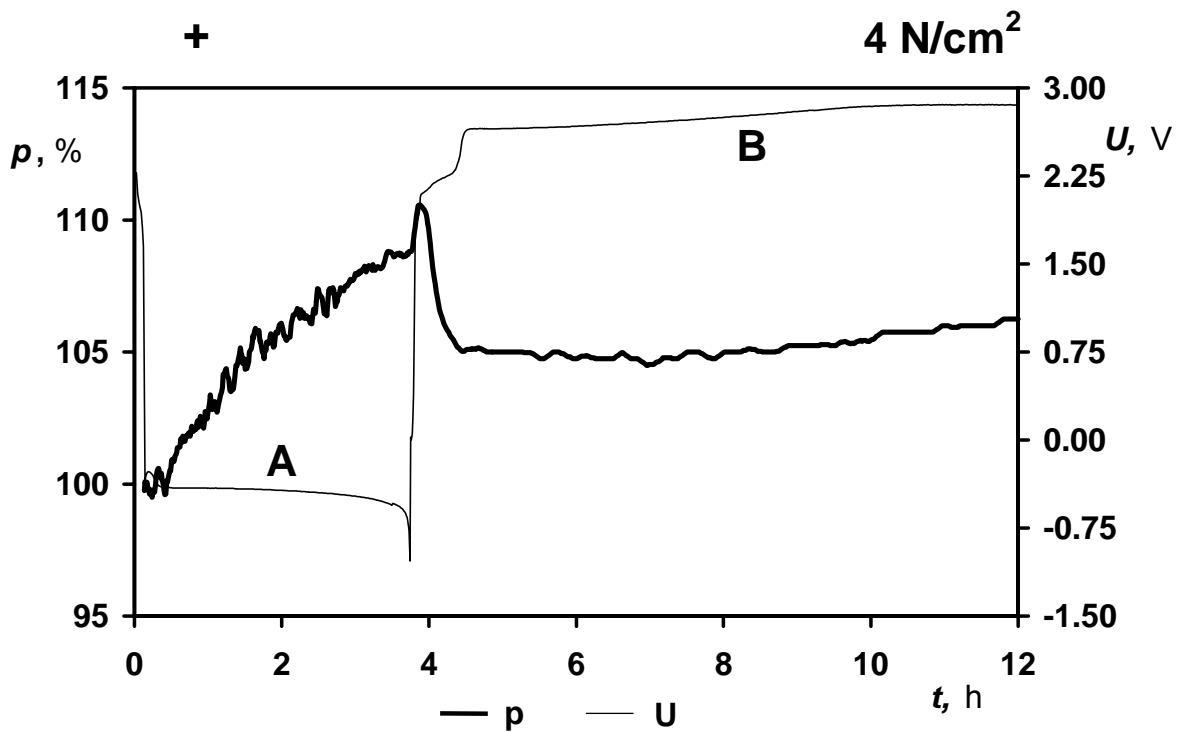


Fig. 2. Time dependence of cell voltage and pressure during discharging and charging. Positive test electrode, lead foil counter electrodes; cell compressed at 4 N/cm².

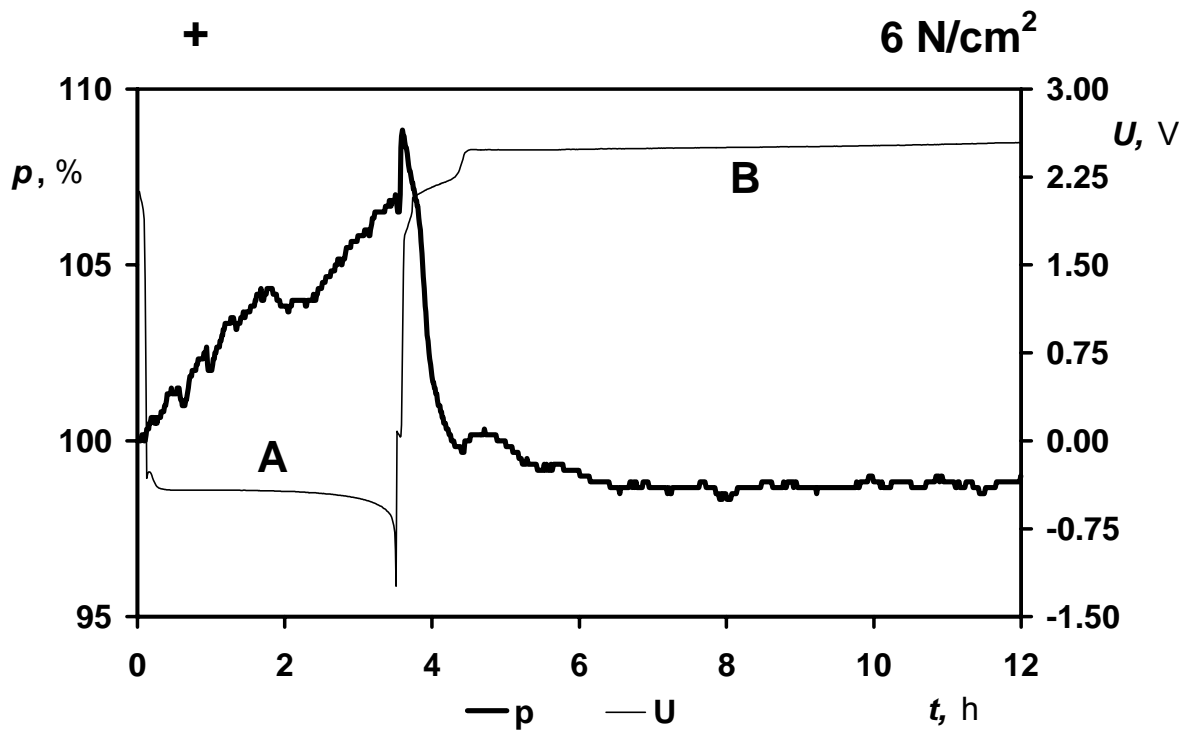


Fig. 3. Time dependence of cell voltage and pressure during discharging and charging. Positive test electrode, lead foil counter electrodes; cell compressed at 6 N/cm^2 .

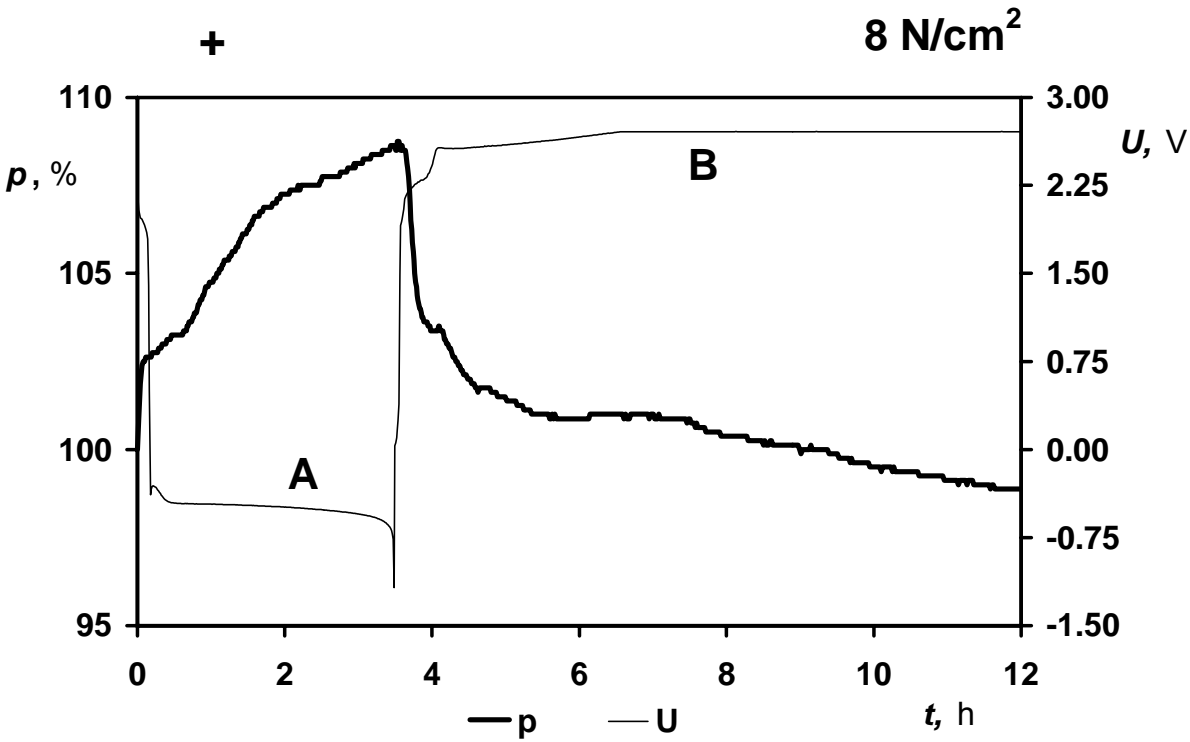


Fig. 4. Time dependence of cell voltage and pressure during discharging and charging. Positive test electrode, lead foil counter electrodes; cell compressed at 8 N/cm^2 .

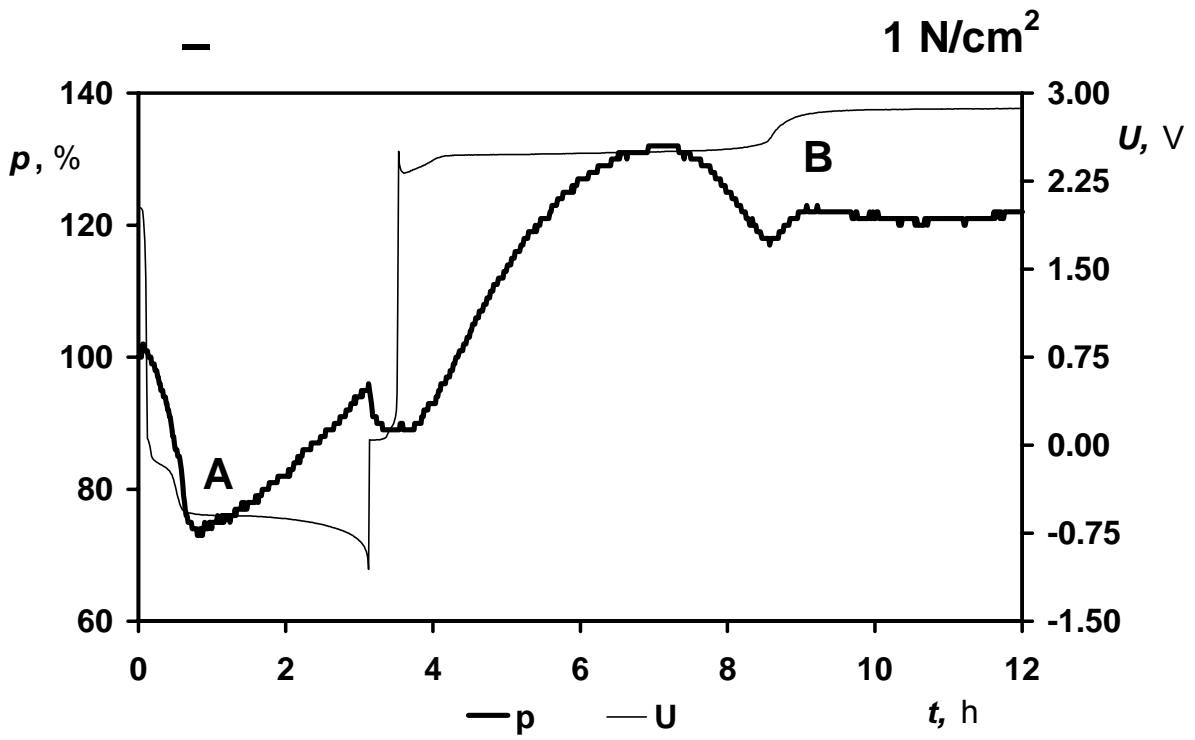


Fig. 5. Time dependence of cell voltage and pressure during discharging and charging. Negative test electrode, lead foil counter electrodes; cell compressed at 1 N/cm^2 .

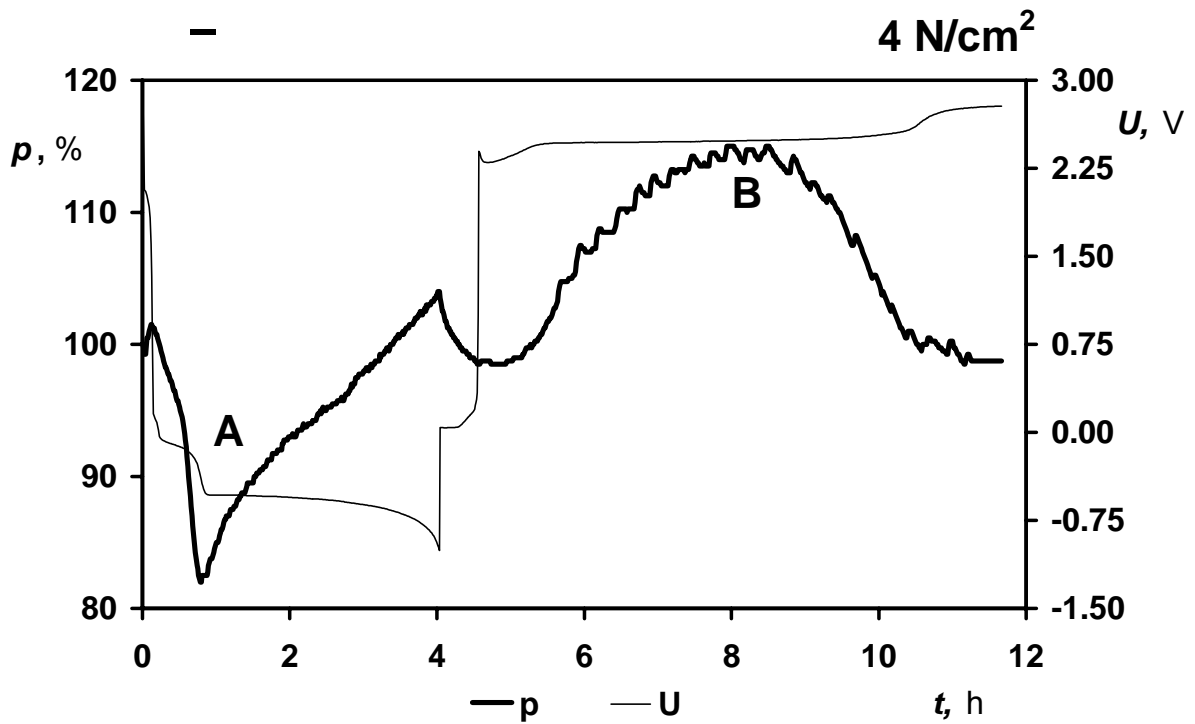


Fig. 6. Time dependence of cell voltage and pressure during discharging and charging. Negative test electrode, lead foil counter electrodes; cell compressed at 4 N/cm^2 .

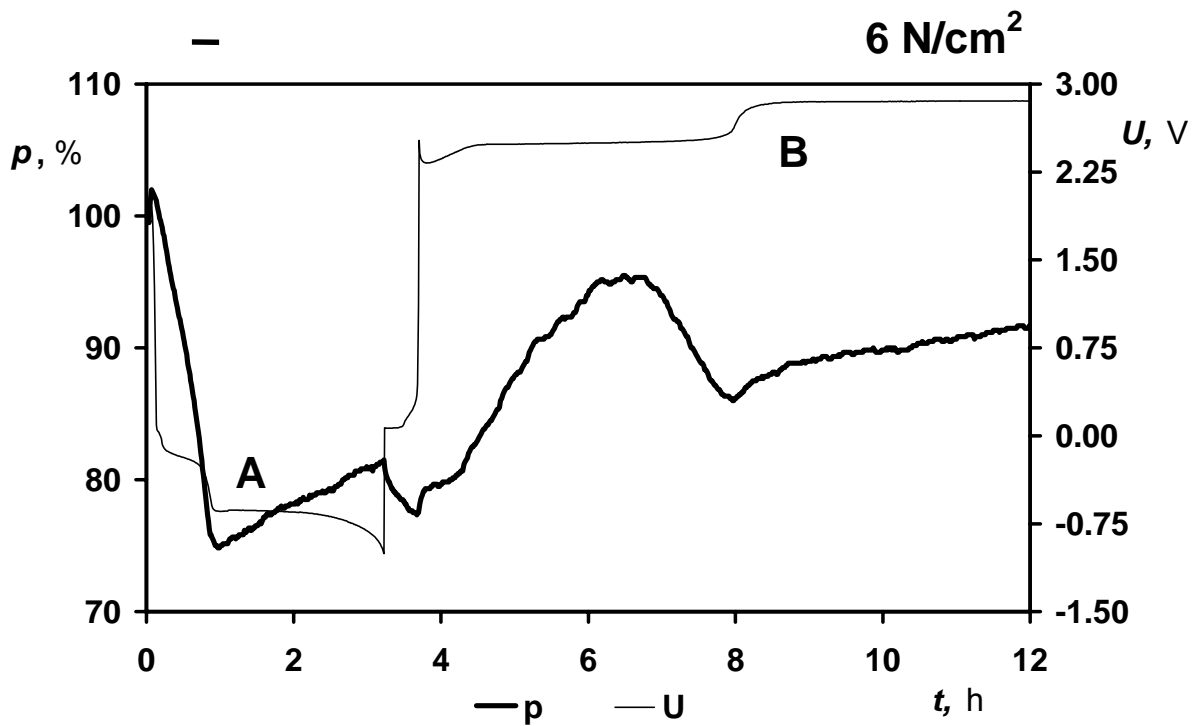


Fig. 7. Time dependence of cell voltage and pressure during discharging and charging. Negative test electrode, lead foil counter electrodes; cell compressed at 6 N/cm^2 .

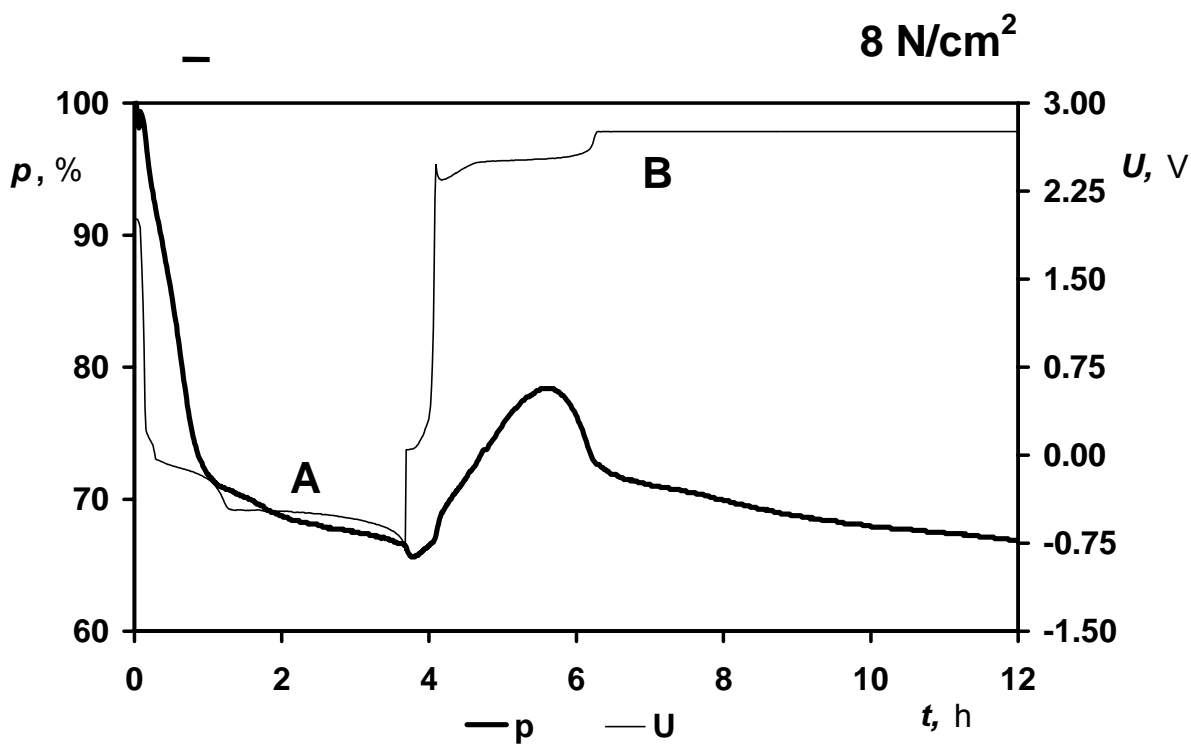


Fig. 8. Time dependence of cell voltage and pressure during discharging and charging. Negative test electrode, lead foil counter electrodes; cell compressed at 8 N/cm^2 .