STUDY OF THE EFFECTS OF COMPRESSION ON THE PERFORMANCE OF POSITIVE ELECTRODES IN LEAD-ACID CELLS

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Abstract

Optimum mechanical pressure was found to be close to 4 N/cm^2, at which the cycle life of positive test electrodes exceeded 600 cycles at 100% DOD.

Introduction

To investigate the pressure effects on the parameters of lead-acid test cells, the test electrode was placed between two counter electrodes in the usual configuration [1]. The 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.%. Both counter electrodes were of the same size and design as the test electrode. 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/cm^3 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.

The systems described enabled measurements of the changes of capacity and resistances of the test electrodes. In contrast to the test electrodes, the counter electrodes with excess capacity were only partially utilized.

Pressure control and cycling regime

In order to follow the pressure effects, six cells with positive and six cells with negative test electrodes were subjected, by a suitable setting of the thrust screw, to sustained pressures of 0, 1, 2, 4, 6 and 8 N/cm^2 (corresponding to 0, 10, 20, 40, 60 and 80 kPa). After several formation cycles, the electrode systems were subjected to a computer-controlled cycling regime. The cells were discharged at a 4 h rate (0.4–0.5 A) to 1.6 V cut-off voltage and then charged for 8 h with a current of 0.4 A with voltage limitation to 2.45 V. Thus, two cycles daily could be carried out. Prior to the start of every cycle, the resistances of active masses (R_m) and the interphase (contact) resistances between the current collector and active material (R_k) were measured by our method [7 and 8]. In addition, the values of the scatter criterion (K_{rel}) for the contact resistances were calculated [9]. Eventually, the pressure settings and the 4 h rate discharge currents were corrected. During cycling, the terminal voltage and the current values were recorded at 1 min intervals for all the cells under test with the aid of a computer and used to calculate the capacity, the charge passed during charging and the state of charge. The 4 h rate discharge current for the subsequent cycle was also calculated.

Changes of capacity and resistances of positive electrodes during cycling

The dependences of the capacity, C, active mass resistance, Rm, contact resistance between the current collector and the active mass, Rk and its scatter criterion, Krel, on the cycle number for positive electrodes under mechanical pressures of 0, 1 and 4 N/cm^2 are shown in Fig. 1, Fig. 2 and Fig. 3. Only every

10th point was recorded for better readability. The end of the cycle life was given by the cycle at which the capacity decreased to 66 % of its value (indicated by the horizontal dashed line) corresponding to the 10th cycle. The diagrams for 2, 6 and 8 N/cm^2 were similar to those at 4 N/cm^2. For comparison, the capacities are summarized for all pressure values in Fig. 4 and the active mass resistances in Fig. 5. It can be seen that the capacity, after several formation cycles, shows practically no correlation with the pressure in accord with our previous findings where either AGM [1] or fritted glass separators [9] were used. In contrast to these, however, the capacity is now much more reproducible and rises slowly with the cycle number up to a flat maximum (Fig. 4) except for the electrode operating without pressure, whose capacity passes through a conspicuous maximum and falls down after about 150 cycles. The active mass resistance of this electrode is somewhat higher than that for the other ones and rises steadily after some 150 cycles (Fig. 5). This behavior is probably due to the expansion of the active mass: the rising porosity causes initially a capacity increase but later the interparticle contacts deteriorate considerably, resulting in a capacity drop (compare [1]).

It should be noted that with compressed electrodes, the values of R_m begin to rise later than the interphase resistance (in contradistinction to non-compressed electrodes [8]), since the interparticle contacts are more or less stabilized.

In Fig. 6 is shown the dependence of the cycle life on the applied sustained pressure. It is of practical interest that the optimum mechanical pressure appears to be close to 4 N/cm^2. The highest pressure of 8 N/cm^2 caused (together with corrosion) mechanical damage to the lead grid after about 570 cycles.

Acknowledgement

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References

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Figures

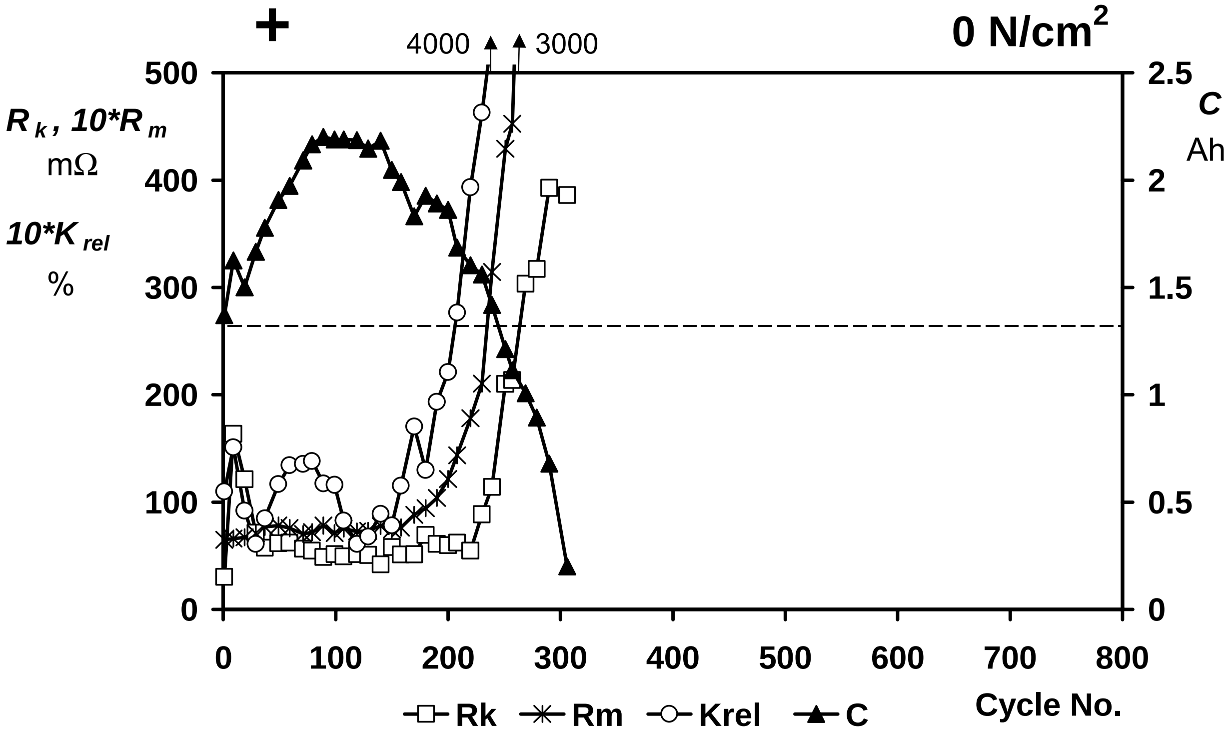

Fig. 1. *Evolution of capacity, C, active mass and interphase resistances, R_m and R_k, and scatter criterion, K_{rel}, during cycling. Positive test electrode, cell without compression.*

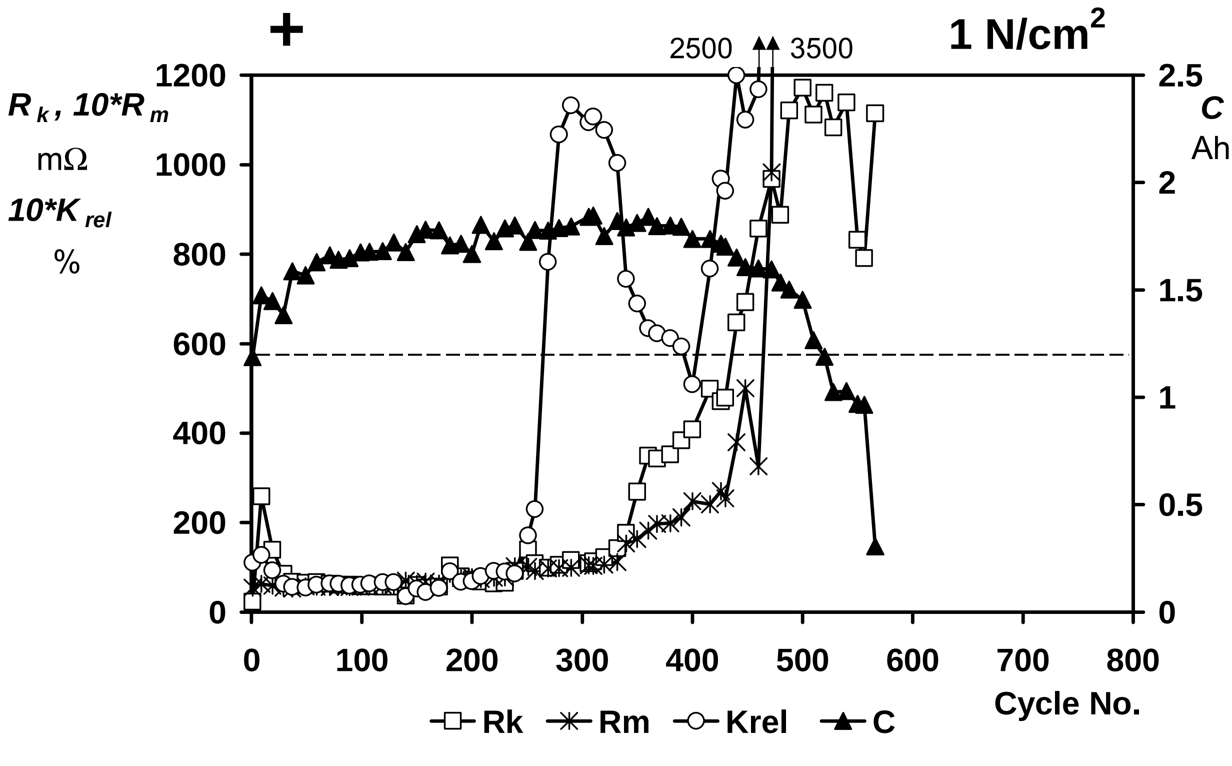

Fig. 2. *Evolution of capacity, C, active mass and interphase resistances, R_m and R_k, and scatter criterion, K_{rel}, during cycling. Positive test electrode, cell compressed at 1 N/cm^2.*

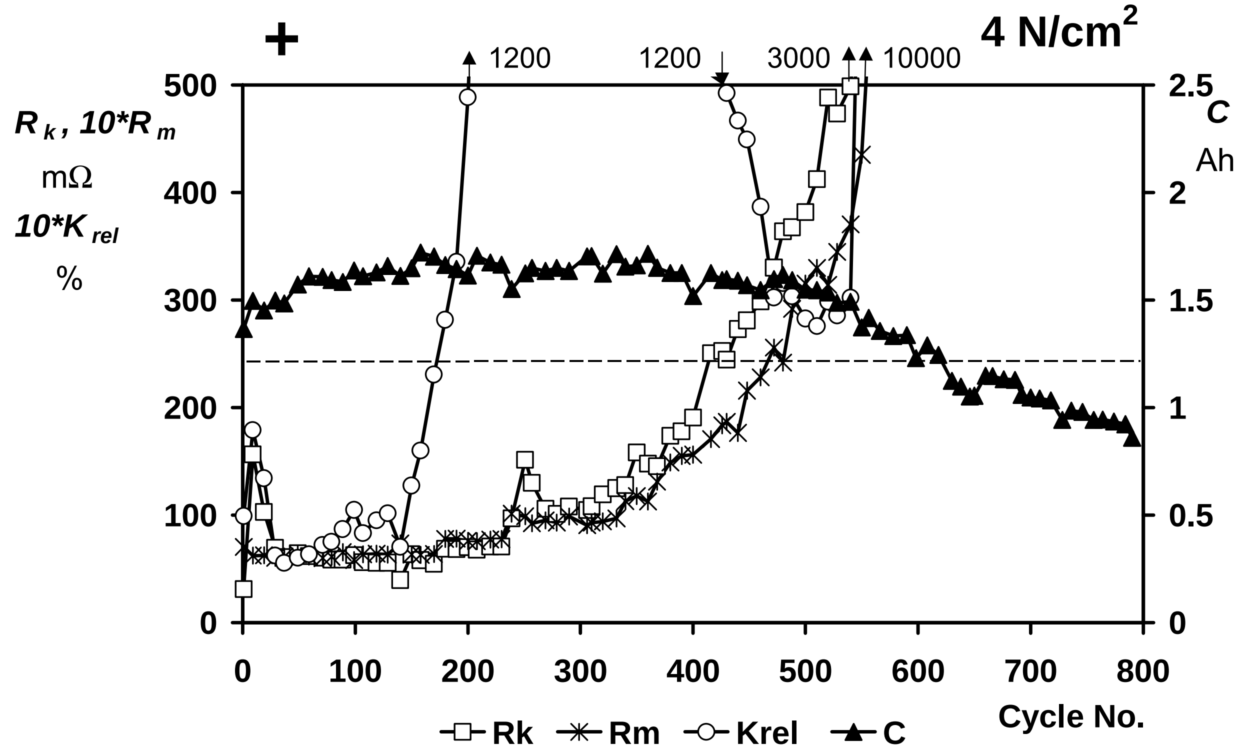

Fig. 3. *Evolution of capacity, C, active mass and interphase resistances, R_m and R_k, and scatter criterion, K_{rel}, during cycling. Positive test electrode, cell compressed at 4 N/cm^2.*

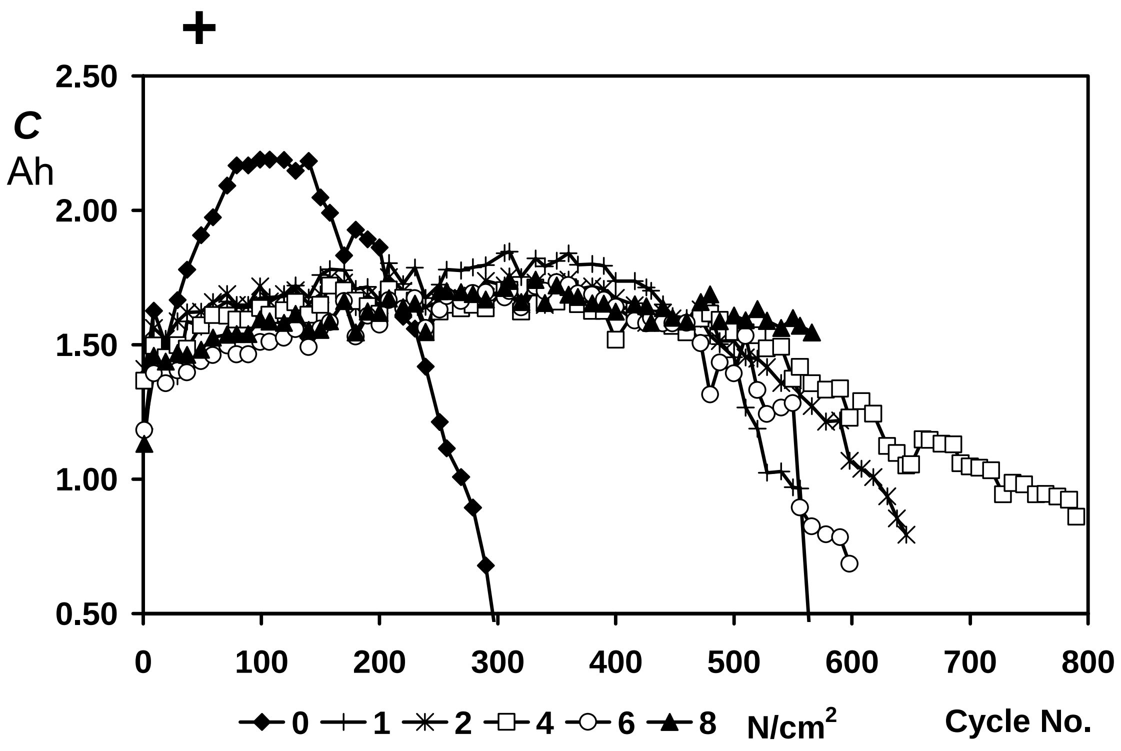

Fig. 4. *Evolution of capacity of the positive test electrodes during cycling at pressures from 0 to 8 N/cm^2.*

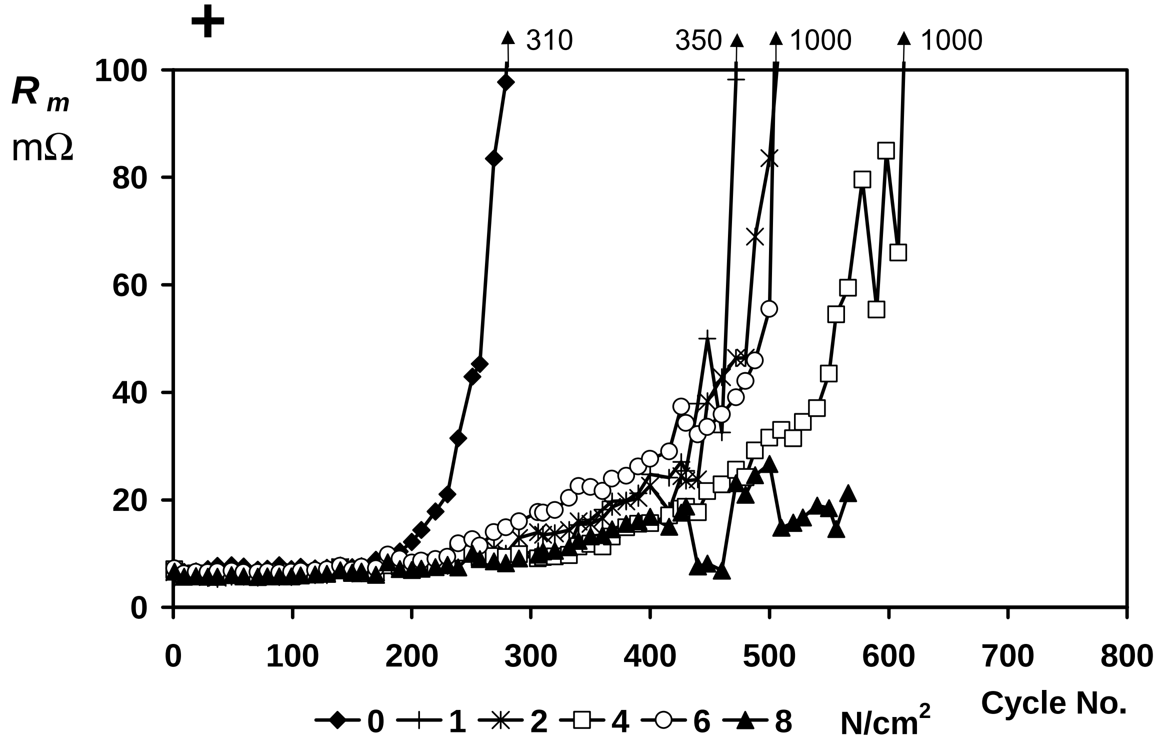

Fig. 5. *Evolution of active mass resistance of the positive test electrodes during cycling at pressures 0 - 8 N/cm^2.*

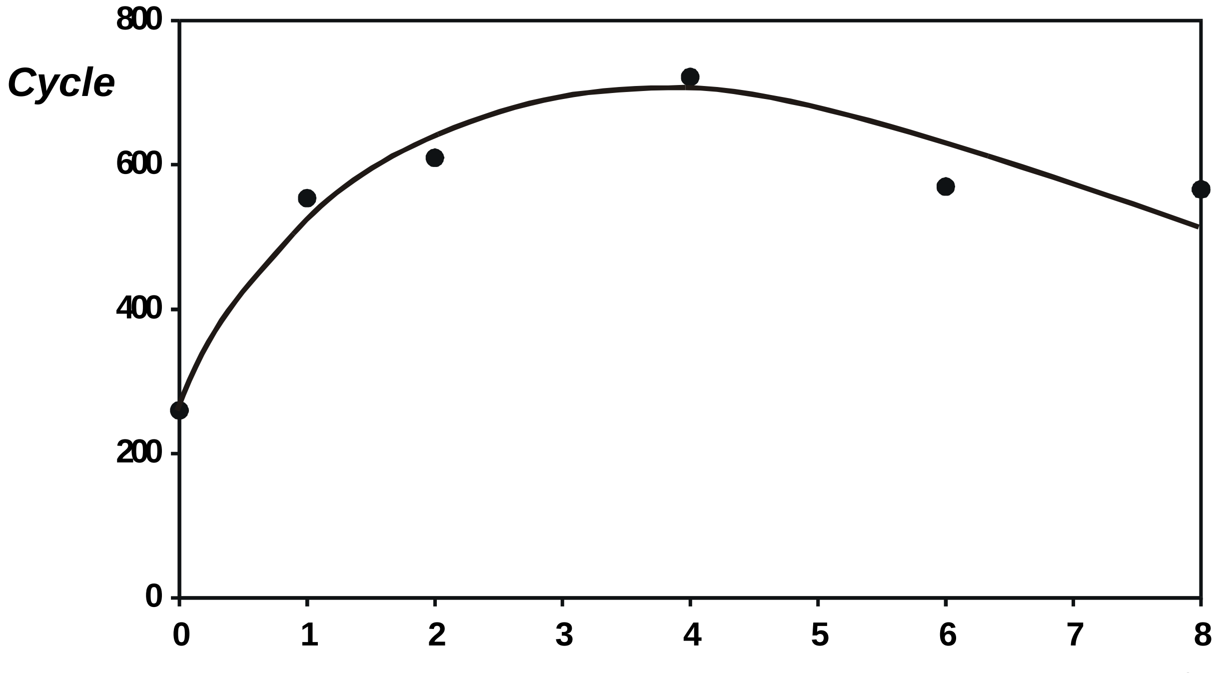

Fig. 6. *Dependence of cycle life of positive test electrodes on mechanical pressure. The point at 8 N/cm^2 corresponds to damage of the lead collector ribs.*