ELSEVIER

Journal of Power Sources 78 (1999) 94–98

JOURNAL OF POWER SOURCES

A study of the effects of compression on the performance of the positive active mass in lead–acid cells using absorptive glass mat separators

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Abstract

A new electrochemical cell was designed and constructed to enable in situ measurements of the performance and internal resistances of lead–acid test electrodes in a vertical position during cycling at well-defined degrees of compression. The AGM separators used were combined with microporous paper separators to prevent short-circuiting by conducting bridges of lead dioxide. The test cells were subjected to pressures in the range 0–8 N/cm^2; the compression decreased the positive active mass resistance and increased its cycle life.

Keywords: Lead–acid battery; Positive electrode; Active mass resistance; Compression

1. Introduction

The present work is a continuation of our previous studies [1], where an important step was the construction and testing of an electrochemical cell enabling reliable in situ measurements of the active mass resistance, interphase resistance, and capacity of test electrodes during cycling under sustained compressive force. Whereas negative test electrodes showed a weakly pronounced maximum of cycle life at a pressure load of 0.4 kg/cm^2, no such effect has been found with positive test electrodes, whereas a similar investigation at CSIRO, Melbourne [2] revealed a distinct positive effect. These unexpected results may be due to the fact that the electrode-separator packs were placed in a horizontal position causing gradual accumulation of gas bubbles, i.e., transport hindrance, in the fritted glass separators of 22% porosity. These were, during measurements of negative test electrodes, combined with three layers of a 1-mm thick AGM fabric providing more space for the gas bubbles; this provision led to the observation of the mentioned optimum at 0.4 kg/cm^2.

Our further work was devoted to construction of a new measuring cell permitting measurements of the effect of compressive force on the performance and resistances of test electrodes in vertical position. Detailed measurements on positive test electrodes form the subject of the present work.

2. Experimental

2.1. Pressure apparatus

A new measuring cell permitting measurements of the effect of compressive force on the performance and resistances of test electrodes in vertical position was developed, where the force acting on the electrodes is due to a screw (Fig. 1). Thus, it was possible, besides an exact and currently measurable pressure setting, also to follow the changes of the electrode pack thickness/compression in the course of cycling. The force sensors **H** worked reliably in the initial phase of the experiments. However, difficulties occurred after about 10 weeks owing to penetration of the electrolyte into the sensor body. After disassembling, we observed corrosion of the silicon rubber membrane close to the screws joining the sensor casing with the covering frame, and, moreover, corrosion of the internal parts of the sensor. Therefore, the cycling was interrupted after the 144th cycle for 14 days, during which period the sensors were completely reconstructed and the silicon rubber membrane was replaced by a polyethylene foil, tightened with a G 250 silicon cement. The sensors thus modified performed very well since then.

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0378-7753/99/$ - see front matter
PII: S0378-7753(99)00018-X

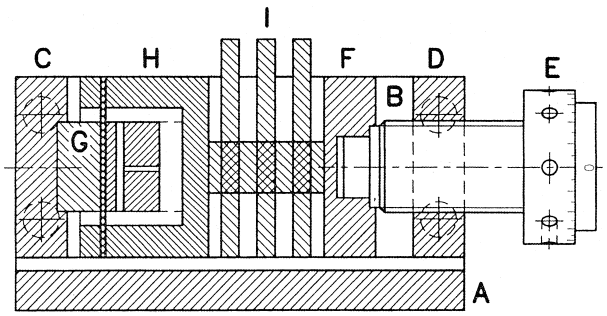

Fig. 1. Schematic cross-section of the pressure cell. **A** Base plate, **B** lateral strut, **C** fixed face plate, **D** fixed face plate with turns, **E** thrust screw, **F** movable plate, **G** flexible coupling element, **H** force sensor, **I** electrode pack with the test electrode in the middle.

2.2. Cycling regime and apparatus

Constant-current discharging and constant-voltage charging with current limitation was used at a frequency of two cycles per day, as shown schematically in Fig. 2. Sections **A** correspond to discharge with constant current that was set so as to reach the cut-off voltage of 1.6 V after about 4 h. Sections **B** correspond to charging with constant current, and **C** to constant voltage. A short stand, **D**, after every second cycle was used for resistance measurements. The initial constant charging current in section **B** could be varied within rather broad limits. The constant charging voltage in section **C** was set equal to 2.45 V. The time dependence of the charging current and the charge passed (at constant voltage limit of 2.45 V) at three different limitations of the current is shown in Fig. 3. The charge passed is given in percent of that obtained during the preceding discharge. It can be seen that, after 8 h of charging, the charge passed corresponds to about 110% regardless of the value of the initial charging current.

2.3. Electrodes and cells

The shape and dimensions of the test electrodes with current collectors of 10 isolated parallel ribs were similar

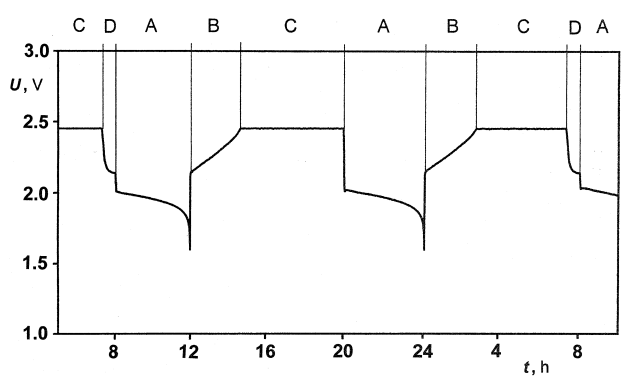

Fig. 2. Dependence of the cell voltage on the time during cycling. **A** denotes period of discharge with constant current, **B** constant-current charging, **C** charging at constant voltage of 2.45 V, and **D** period of stand.

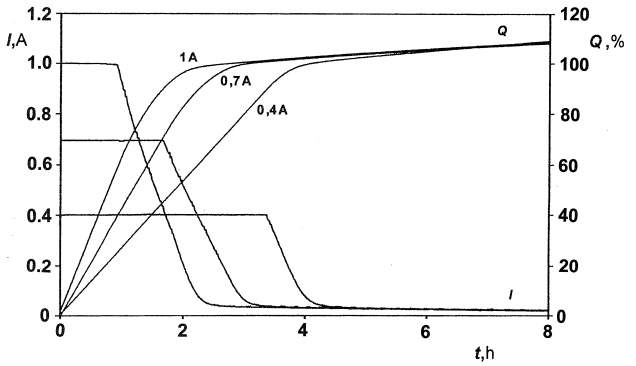

Fig. 3. Time dependence of the charging current and charge passed at constant voltage of 2.45 V. Labels indicate maximum current at the start of charging.

to those used in our previous work [1]. The ribs were taken from grids of the composition Pb Sb 2.19 Sn 0.20, and they were fixed in place by two strips of epoxy resin. Each rib was provided with current and voltage leads connected with a 20-pole plug, enabling the electrode to be connected either to the cycling equipment or to the resistance measuring apparatus. The electrodes were pasted with positive active mass in the AKUMA factory, Mladá Boleslav (Czech Republic). The negative counter electrodes were manufactured analogously, except that their ribs were mutually interconnected and provided with a single current lead and a single voltage lead.

After curing and drying, six cells were assembled from one positive and two negative electrodes; these were subjected to formation with constant current in a large excess of electrolyte of 1.24 g/cm^3 density. The current was disrupted for 2 h at 4-h intervals; the formation lasted for 72 h and the total length of the stand periods amounted to 32 h.

After formation, the electrode systems were inserted into the pressure cells; the quantity and the density of the electrolyte were preserved. The cells were subjected to pressures equal to 0, 1, 2, 4, 6, and 8 N/cm^2 (i.e., 0, 10, 20, 40, 60, and 80 kPa). These values were checked every day during cycling and deviations were corrected.

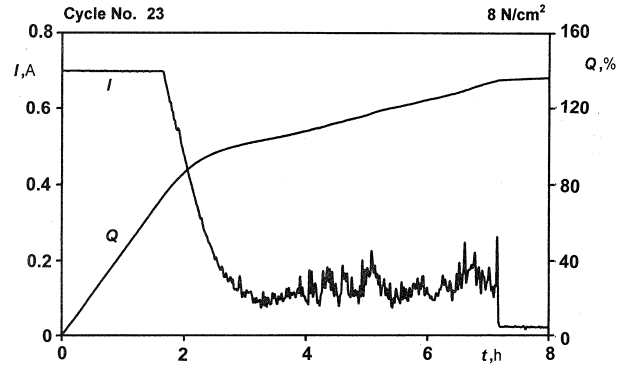

Fig. 4. Time dependences of current and charge passed during charging, with distortion due to shorts in the separator. Cell compressed at 8 N/cm^2.

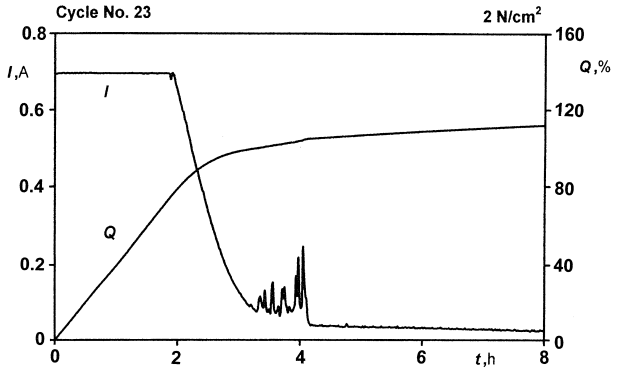

Fig. 5. Time dependences of current and charge passed during charging, with distortion due to shorts in the separator. Cell compressed at 2 N/cm^2. Effect of shaking the cell after 4 h.

2.4. Separators

To separate the positive and negative electrodes, AGM separators of the type H&V IIP15 were employed in the initial stage of the experiments. They were placed on both sides of the negative electrodes and cut in size so that the pressure was only acting on the active area of the positive electrode. However, difficulties soon appeared, which were manifested by distortion of the dependence of the current and charge passed on the charging time, as exemplified by Figs. 4 and 5. The charging current at constant voltage often showed considerable fluctuations and the total charge passed at the end of charging was significantly higher (corresponding to more than 110%). This anomalous course could be amended by shaking the middle electrode during transitory relief of the pressure, as in the case illustrated in Fig. 5, after 4 h from the start of charging. Replacement of the separators was also helpful, although only for a limited time.

This phenomenon could only be attributed to the formation of electronically conducting bridges of lead dioxide in the separator. Therefore, after the 32nd cycle, an additional 5-mm thick AGM separator of the type BGE 84065 was inserted between the positive test electrode and the H&V IIP15 separator. This provision, however, proved well also only for a limited time.

Finally, a paper separator ARMORIB (Grace, Hamburg, FRG) for starting accumulators, with the rib spacers removed mechanically, was inserted between the separators H&V IIP15 after the 99th cycle. By this provision, the mentioned difficulties were durably removed. It should be noted that similar combinations of microporous separators with glass mats were used for compressed cells by earlier investigators [3–5]. The dependence of the compression (i.e., thickness decrement) of the resulting electrode pack on the applied pressure is shown in Fig. 6.

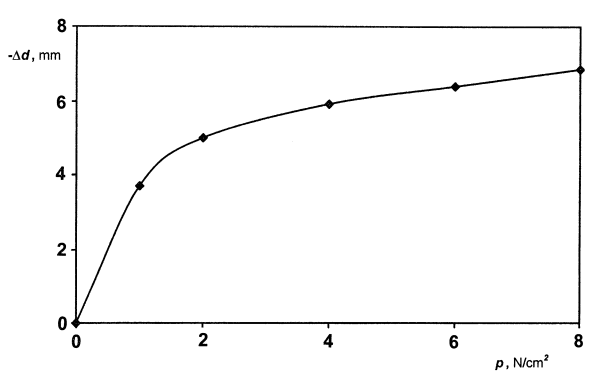

Fig. 6. Dependence of compression of the electrode pack on the applied pressure. The pack contained four 2-mm thick AGM layers (one at either side of the negative electrodes) and two 5-mm thick AGM layers (one at either side of the positive).

3. Results

3.1. Pressure changes during cycling

As already mentioned, the pressure apparatus used permits the pressure changes within the cell (due to volume changes) to be followed during operation. As an example, pressure changes in a cell, loaded with an initial pressure of 2 N/cm^2 (20 kPa), during one cycle are illustrated in Fig. 7. To obtain information about the state of charge, the time dependence of the voltage is shown by a thin line; section **A** corresponds to discharging, **B** to charging with constant current, and **C** to charging at constant voltage by analogy to Fig. 2. (The pressure characteristics were only recorded after the 244th cycle in order not to complicate the cycling experiments.)

It can be seen that the mechanical pressure in the cell decreases during discharge down to a minimum; initially it increases during charging and later it more or less decreases or remains constant. The pressure maximum occurs close to the instant at which the charging regime changes from constant current to constant voltage. (The somewhat rounded shape of the pressure minimum is due to the method of graph drawing.)

The same apparatus can be used to follow the thickness changes of the electrode pack during cycling. In this case,

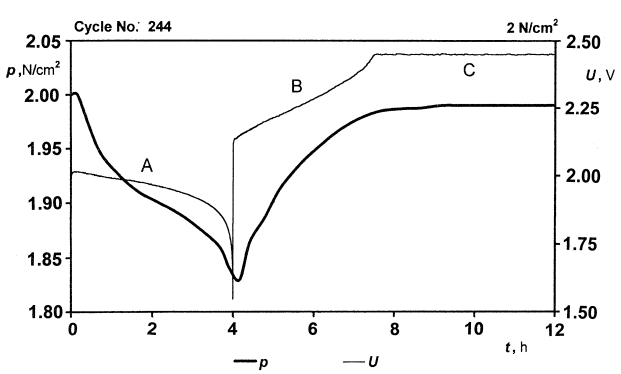

Fig. 7. Time dependence of cell voltage and pressure during discharging and charging. Cell compressed at 2 N/cm^2.

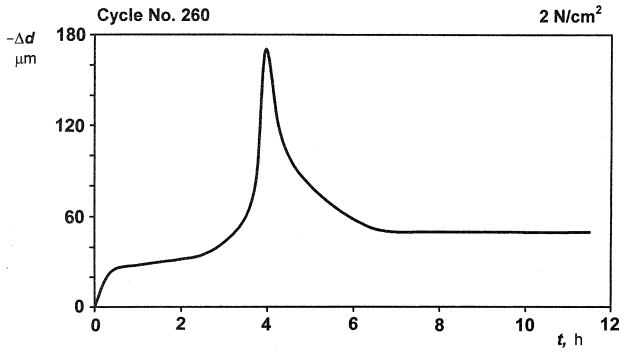

Fig. 8. Thickness changes of the electrode pack during discharging and charging at constant pressure of 2 N/cm^2.

the force acting on the electrodes is maintained constant by turning the thrust screw, and the thickness changes of the electrode pack are read from the scale on the head of this screw. As an example, the thickness changes of an electrode system compressed at 2 N/cm^2 are shown in Fig. 8.

Our pressure measurements are in accord with those of Bashtavelova and Winsel [6], but at variance with those of Takahashi et al. [3], who observed pressure increase in their cell during discharge, and vice versa. Alzieu et al. [4] investigated thoroughly the pressure changes during cycling and found an important temperature effect: charging causes an increase of the cell temperature with a resulting pressure increase (and vice versa). Depending on the magnitude of the Joule heat, heat capacity of the cell, and heat conduction in the cell, the results of pressure measurements may be more or less distorted. The relevant literature was reviewed and discussed by us earlier [7].

3.2. Changes of capacity and resistances of positive electrodes during cycling

Typical results of measurements of the capacity, C, active mass resistance, R_m, interphase resistance, R_k (both in the charged state), and scatter criterion, K_{rel}, at pressures from 0 to 8 N/cm^2 are shown in Figs. 9–11. The

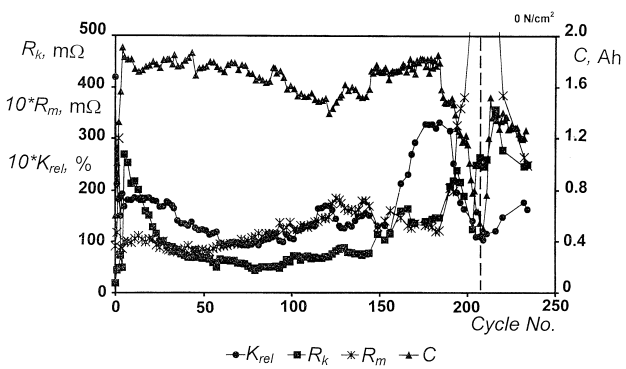

Fig. 9. Evolution of capacity, C, active mass and interphase resistances, R_m and R_k, and scatter criterion, K_{rel}, during cycling. Cell initially without compression. Vertical dashed line indicates application of 4 N/cm^2 pressure.

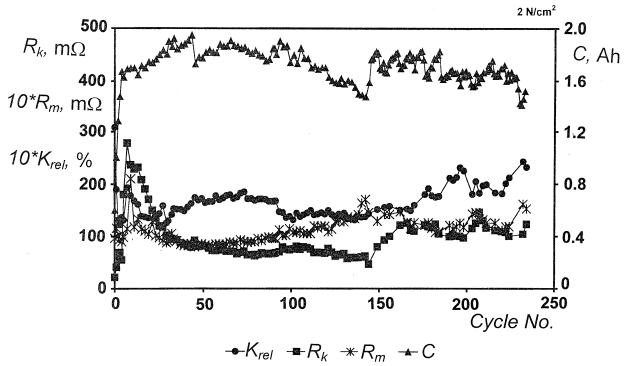

Fig. 10. Evolution of capacity, C, active mass and interphase resistances, R_m and R_k, and scatter criterion, K_{rel}, during cycling. Cell subjected to 2 N/cm^2 pressure.

R_m values are averages from seven measurements between neighbouring ribs, R_k are averages from eight measurements on individual ribs. The criterion K_{rel} is a measure of inhomogeneity of the interphase resistances [8]. The method of measurement of the two resistances, R_k and R_m, was described by us earlier [9].

It can be seen that the active mass resistance increases, more or less, with the cycle number up to the 144th cycle, with a corresponding capacity decrease, a phenomenon often observed in our earlier work. After the 144th cycle, the pressure sensors were reconstructed (cf. Section 2.1) and the electrolyte replaced by a fresh one. This provision resulted in restoration of the capacity and R_m values.

With the electrode operating without pressure (Fig. 9), the capacity began to drop beginning from the 183rd cycle with a conspicuous increase of the active mass resistance, manifesting the end of the cycle life. After the 209th cycle, a pressure load of 4 N/cm^2 was applied to the cell, as denoted by the vertical dashed line. This caused a pronounced decrease of the R_m values and partial restoration of the capacity in the course of a few cycles (Fig. 9). Hence, the preceding increase of the R_m values was apparently caused by loss of cohesion with resulting ex-

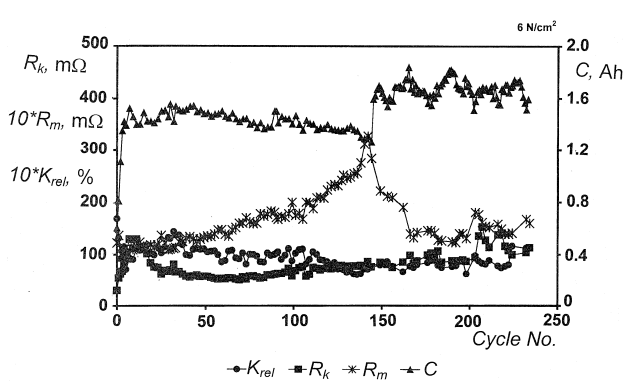

Fig. 11. Evolution of capacity, C, active mass and interphase resistances, R_m and R_k, and scatter criterion, K_{rel}, during cycling. Cell subjected to 6 N/cm^2 pressure.

pansion of the active mass. This experiment represents an illustrative evidence for the favourable role of the cell compression.

In conclusion, our assumption that the horizontal arrangement of the electrode pack used in the preceding project [1] caused some gas transport problems and thus limitation of the cycle life seems to be justified by the present work using the vertical arrangement: the number of cycles attained under similar conditions is now incomparably higher and the cycling experiments are still in progress. (In commercial VRLA batteries, the mentioned problems do not appear, thanks to 'gas recombination', i.e., quantitative reduction of any evolved oxygen.) Our work further implies that the selection of proper separators is of crucial importance for optimum functioning of cells with compressed electrode packs. In further work, we intend to repeat the cycling experiments with the separators selected in the later stage of the work and to investigate the behaviour of negative test electrodes.

Acknowledgements

The authors are indebted to AKUMA, Mlada Boleslav, Czech Republic, for providing pasting facilities, Dr. K. McGregor and Dr. A.F. Hollenkamp (CSIRO, Port Melbourne) for valuable discussions, and Mr. František Korínek and Mrs. Jaroslava Hlavsová for careful technical assistance. Samples of AGM separators were kindly furnished by George Zguris (Hollingsworth&Vose) and A.F. Hollenkamp. This work was supported by the Advanced Lead–Acid Battery Consortium (Project No. B-001.1), a program of the International Lead Zinc Research Organization, and by the Grant Agency of the Czech Republic (Grant No. 102/98/1170).

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