



Investigation of the effect of mechanical pressure on the performance of negative lead accumulator electrodes during partial state of charge operation[☆]

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ABSTRACT

In the present work, our attention has been focused on the desired prevention of irreversible sulphation of negative test electrodes during cycling under simulated high-rate HEV duty. To this end, the negative active material was doped with carbon and, for comparison, with titanium dioxide as a nonconducting powdered additive, and the negative as well as positive electrodes were subjected to a defined pressure. Accelerated cycling revealed that electrodes doped with carbon in laboratory VRLA cells perform, in the first run, better than those doped with TiO₂ since they reached about 30,000 cycles regardless of the applied pressure. However, the electrode performances were almost equalized in the second run. Mechanical pressure of 4 N cm⁻² has a pronounced favourable effect on the cycle life of negative electrodes with expanders. Higher pressures are not recommended. Electrodes doped with carbon but without standard expanders are capable of long-life cycling at elevated pressures around 6 N cm⁻². Their cycle life is comparable to that of the electrodes with expanders.

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1. Introduction

We employed our experience gained earlier by investigating the positive [1] as well as negative [2] accumulator electrodes in the deep cycling regime (see Ref. [3] for details) using a special cell enabling the pressure to be measured and indicated in N cm⁻² (equivalent to 10 kPa) units.

The basic circuit of the work station has been shown in our earlier ALABC Project [4].

The measuring program operated under MS Windows XP operation system using the Agilent VEE 8.0 Professional program. All data were stored in Microsoft Excel XLS. To simplify the control of the program and the output of basic data for the measurement, a special control panel was constructed. The output data were: time, cycle number, voltage, current, electrode potential, pressure applied to the electrode system, and state of charge. These values are measured at intervals, put into XLS tables, visualized graphically, and stored as text files. Thus, the automation enabled long-term experiments to be carried out without regular service.

2. Experimental

2.1. Electrodes and cells

We employed pasted negative electrodes of dimensions 55 mm × 20 mm × 7 mm placed between two pasted positives of the same dimensions from a commercial station battery with AGM separators of the type BG260 EB170 (1.7 mm in thickness). The lead grid with parallel insulated ribs was of the composition Pb Ca0.2 Sn0.5%. The grids were pasted with a negative and a positive standard paste from Johnson Controls Autobaterie s r.o. Česká Lípa. The negative paste with standard expanders (“expanders” in further text) was doped either with 1% of milled N134 carbon black (S.D. Richardson Co., Acron, OH) or with 1% of powdered TiO₂ (1–3 μm, Lach-Ner Co., Neratovice, Czech Republic).

For comparison, six electrodes were prepared without any expander, only with 1% N134 carbon black. The initial capacity of the negative electrodes with additives was around 3 Ah. After formation, the electrode packs were placed into hermetically sealed cells. The density of the sulphuric acid electrolyte was 1.28 g cm⁻³. The electrode potentials were measured against a Cd reference electrode. The hermetically sealed cells were designed earlier [1,3] to ensure application of pressure to the electrode system. The pressure values were measured by tensometric sensors connected in the form of a wheatstone bridge. A detailed schematic cross section of the last variant of the cell, taken from our earlier report [3], is shown in Fig. 1.

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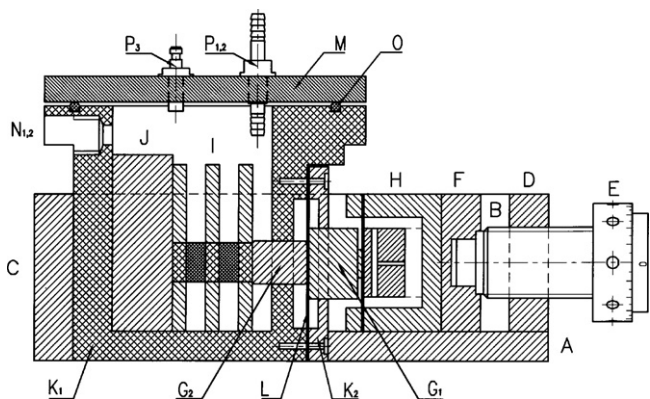


Fig. 1. Equipment for hermetically sealed cells under defined pressure. K_1 polypropylene pressure chamber, M organic glass lid, I electrode pack with central test electrode, K_2 separating plate, L rubber membrane, O rubber O-ring, $P_{1,2}$ bushes for electrolyte inlet and outlet, P_3 bush for connection with pressure sensor, $N_{1,2}$ bushes for current leads, J spacer, A base plate, B lateral strut, C fixed back plate, D fixed face plate with thread, E thrust screw, F movable plate, H force sensor and $G_{1,2}$ pressure transferring elements.

2.2. Formation

The cells were in the vented state allowed to stand for an hour and then subjected to 23 formation cycles including 4 h charging at 0.2 A, 2 h standing on open circuit, and again, in total 92 h charging and 44 h standing. Thus, they obtained 6-fold the assumed capacity.

2.3. Conditioning (refreshing) cycles

Several conditioning cycles were performed before the electrodes were subjected to accelerated cycling: discharging at 0.7 A until the voltage at the end of discharge dropped to 1.6 V, charging at 0.7 A with voltage limitation to 2.45 V for about 20 h, *i.e.* one cycle a day.

2.4. Accelerated PSoC cycling

After the conditioning cycles, the excess electrolyte from the cells was sucked off and the cells were hermetically closed. A pressure of 2, 4, and 6 N cm⁻² was set and the cell capacity was then determined by one conditioning cycle, the cells were discharged to 50% capacity and cycled as follows.

The cells were alternately charged and discharged at 2.5 A for 25 s and 3 s stand. Cycling continued until the voltage at the end of discharge dropped below 1.0 V. When the last cell collapsed, the cells were subjected to several conditioning (refreshing) cycles and another PSoC cycling run began. Usually three such runs were carried out.

In each PSoC run, the cell voltage, the electrode potentials, the applied pressure, and the gas pressure in the cell were measured every 100 cycles. The contact resistance, R_k , and the active mass resistance, R_m , were measured at the beginning of the run in the charged state, in the 50% discharged state, at the last phase and at the end of the run in the discharged state.

Some authors recommended the application of slightly asymmetrical current pulses [5,6] to eliminate the necessity of using refreshing cycles. According to our experience, such cycling regime brings another obstacle, namely that the state of charge of the tested electrodes gradually increases. However, in a later stage of our work, we began to study the behaviour of electrodes containing no standard expanders (only 1% of N134 carbon black) and we decided to use this mode of cycling. We used six cells with three pairs of negative electrodes for pressures of 2, 4, and 6 N cm⁻². The cells were discharged at 2.495 A (2.45 A in the first PSoC run) for

Table 1
Evaluation of the sixth conditioning cycle.

| Cell No. | Charge to attain 2.45 V, %Q | I_{end} , A | Charge to attain 2.45 V, %Q |
|---------------------------|--------------------------------|---------------|--------------------------------|
| 1 (2 N cm ⁻²) | 68.03 | 0.0155 | 77.34 |
| 2 (2 N cm ⁻²) | 73.46 | 0.0327 | 75.55 |
| 3 (4 N cm ⁻²) | 71.23 | 0.0203 | 74.77 |
| 4 (4 N cm ⁻²) | 71.83 | 0.0155 | 71.95 |
| 5 (6 N cm ⁻²) | 68.11 | 0.0319 | 77.13 |
| 6 (6 N cm ⁻²) | 76.50 | 0.0217 | 79.84 |

25 s with 3 s stand and charged at 2.50 A for 25 s with 3 s stand. Thus, the electrodes got a charge higher by 0.2% (respectively, 2% in the first run) than they delivered in discharge during the given PSoC cycle. One PSoC run lasted for 20,000 cycles (about 14 days). After finishing the run, the cell capacity was measured and its state of charge was recovered.

After three PSoC runs, some cells showed interelectrode short-circuits. Therefore, they were flooded with electrolyte, the separators were replaced and the whole process repeated.

3. Introductory measurements

3.1. Electrodes containing carbon but no expanders

In the absence of expanders, there were practically no differences between the course of formation. Five cells out of the six attained the voltage of 2.5 V during the eighth cycle and the last one during the ninth cycle. On attaining the second charging step, the cells obtained a charge corresponding to about 2 C. The end voltages of the experimental cells read after 140 h were between 2.66 and 2.69 V corresponding to our recent results [7]. Although another carbon type was used, the drop in the cell end voltage is similar in both the cited and the present work.

The conditioning cycles showed a systematic capacity drop from cycle to cycle. A similar behavior has been observed in our preceding paper with electrodes containing more than 0.15% carbon [7] as well as with the carbon-doped electrodes in Fig. 3. In Table 1 are summarized some data measured in the sixth conditioning cycle. Owing to the voltage limitation by 2.45 V, the final charging current was equal to 15–30 mA only.

The last column shows the data after replacement of the separators before the start of the fourth PSoC run. Compared to the start of the experiment, the charge acceptance of the cells improved: the cells attained 2.45 V on acceptance of 72–80% charge.

3.2. Electrodes with additives and expanders

With the electrodes containing expanders and doping agents, it was found that the rate of formation of the negative electrodes under test was not equal. The time necessary to finish the formation was characterized by the moment when the cell voltage passed the limit of 2.55 V, thus attaining the second charging step. No correlation was found between the time necessary for full formation (around 47 h) and the type of admixture. The end voltage of the electrodes with carbon additive is somewhat lower compared to the electrodes with titanium dioxide except for one case; the measured data are given in Table 2.

In the course of conditioning cycles, the electrode capacities were measured. The results are shown graphically in Fig. 2. With electrodes containing TiO₂, the capacity shows an increasing trend, apparently related with a perfecting of the formation. In contrast, the capacity of electrodes containing carbon shows a decreasing trend in accord with our recent work [7] where the capacity of electrodes containing more than 0.1% carbon decreased moderately during conditioning cycling. A similar behaviour was

Table 2
Evaluation of formation and conditioning cycles.

| Electrode | Time of formation, h | End voltage, V | Charge to attain 2.45 V, %Q |
|---|----------------------|----------------|-----------------------------|
| C, 0 N cm ⁻² | 52 | 2.591 | 80.3 |
| TiO ₂ , 0 N cm ⁻² | 49 | 2.671 | 60.5 |
| C, 2 N cm ⁻² | 44 | 2.582 | 76.4 |
| TiO ₂ , 2 N cm ⁻² | 43 | 2.756 | 62.6 |
| C, 4 N cm ⁻² | 45 | 2.644 | 80.6 |
| TiO ₂ , 4 N cm ⁻² | 48 | 2.616 | 64.8 |
| C 6 N cm ⁻² | 52 | 2.609 | 81.5 |
| TiO ₂ , 6 N cm ⁻² | 45 | 2.671 | 63.5 |

observed with the electrodes containing only carbon without further additives.

It is interesting that the electrodes containing TiO₂ attain the second charging step much sooner – at about 60% of the accepted charge – than the electrodes doped with carbon – at about 80% of the accepted charge (cf. Table 2). The higher charge acceptance may be caused by the favourable effect of graphite at cathodic potentials in contact with lead sulphate in the acid medium described by Pavlov et al. [8].

4. Results

4.1. Electrodes containing expanders and additives, first PSoC run

In Figs. 4 and 5 are shown the dependences of the cell voltage on the cycle number for the first run. It can be seen that the electrodes doped with carbon perform better than those doped with titanium dioxide since they reached about 30,000 cycles regardless of the applied pressure. The courses of the cell voltage correspond to the courses of the negative electrode potentials.

The voltage courses measured during discharge half-cycles (Fig. 3) show that the cycle life increases with increasing pressure. The cycle life of the electrode doped with TiO₂ without pressure was only 6000 cycles whereas a slight compression of 2 N cm⁻² caused an increase to 11,000 cycles. At 4–6 N cm⁻² this increased further to 17,000 cycles. The electrodes doped with carbon, in contrast, maintained the cell voltage between 1.76 and 1.44 V, well above the limit. (It should be noted that the cells “without pressure” were, in reality, subject to a small pressure given by assembling the cells.) The positive influence of carbon is, in the first run, doubtless; it is better than with titanium dioxide. The positive effect of compression of the active mass is also conspicuous, even if the difference between 4 and 6 N cm⁻² is not very large.

When the voltage is measured during charge half-cycles, the diagram looks more optimistic. Fig. 4 shows the corresponding dependences of the cell voltage for the first run. The electrodes doped with TiO₂ show a marked increase of the cell voltage with a

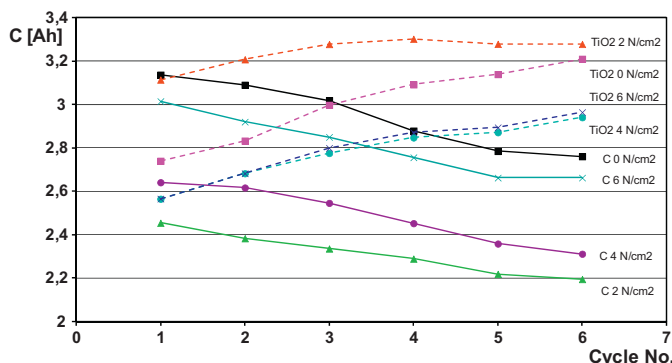


Fig. 2. Capacities of cells during conditioning cycling.

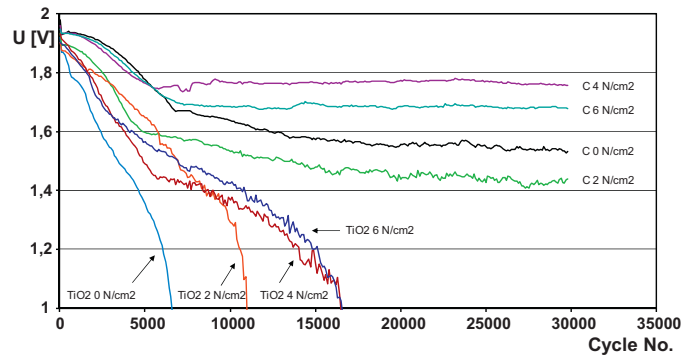


Fig. 3. Dependence of cell voltage on the discharge half-cycle number for the first run.

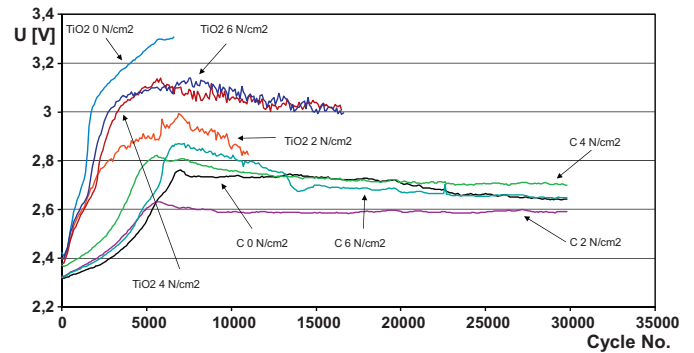


Fig. 4. As Fig. 3 but dependence on the charge half-cycle number.

maximum at about 6000 cycles followed by a moderate decrease. The increase is largest with the noncompressed electrode (up to 3.2 V). The electrodes doped with carbon show a less marked increase of the cell voltage (2.6–2.8 V) which, after passing through a maximum, again decreases. The decrease may again be related to the effect mentioned above [8]. The voltage courses for all the carbon-doped electrodes are similar and the values at the end of the first run are between 2.60 and 2.70 V.

The positive influence of carbon is, also here, doubtless. During the charging PSoC half-cycle, an important role of the additive consists in delaying the start of the second charging step, thus improving the charge acceptance (cf. Section 2.2).

4.2. Changes of the pressure

The pressure acting on the cells showed some fluctuations whose magnitude, however, was relatively moderate and could not markedly influence the experimental results (Fig. 5). Since the

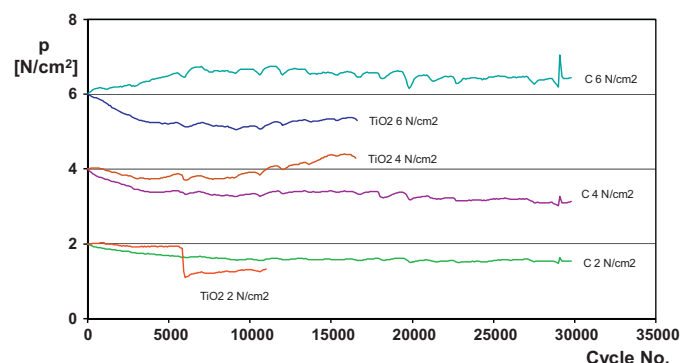


Fig. 5. Course of the mechanical pressure in the first PSoC run.

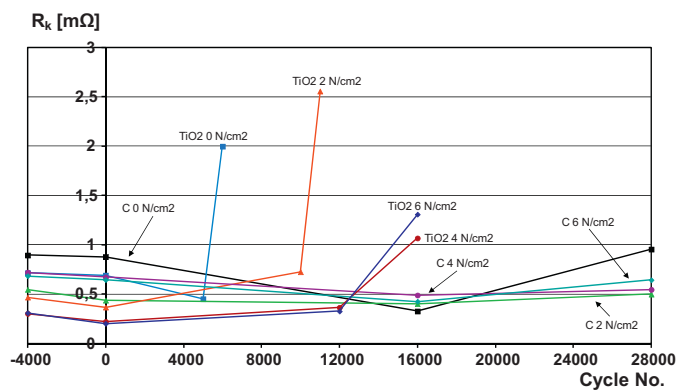


Fig. 6. Schematic evolution of the contact resistance for the tested electrodes.

character of these fluctuations is not uniform, their unique interpretation cannot be presented. The anomalous dependence for the electrode with TiO_2 at 2 N cm^{-2} was probably caused by a defective separator causing end of the cycle life.

4.3. Contact resistance and active mass resistance

During the first PSoC run, the cycling was interrupted at 10 min intervals to measure the electrode resistances by our original method [9]. Four measurements were presented graphically for each electrode: (i) in the charged state (“cycle –4000”), (ii) in the 50% state of charge (“cycle 0”), in the course of PSoC cycling, and at the end of life (Figs. 6 and 7). The first two values of the two resistances, R_k and R_m , were practically stable in the range between 0.2 and 0.7 $\text{m}\Omega$, evidence that the negative electrode structure was in a good condition during the corresponding time period. However, the end of life of the electrodes doped with titanium dioxide was visualized by a marked increase of the both resistances due probably to sulphation of the pores close to the electrode surface. On the other hand, the resistances of the carbon-doped electrodes are nearly constant and below 1 $\text{m}\Omega$ up to the end of the run, 30,000 cycles.

It should be noted that the mentioned method [9] is based on the assumption that the electrode active mass is macrohomogeneous. This is also usual in the theory of porous electrodes [10]. However, in the present work, the electrodes were polarized by relatively short, alternating current pulses that obviously caused conversion of a relatively thin layer of the active mass. Therefore, the resistance changes caused by this process were smaller than those observed in our past work [2] dealing with a rather slow cycling regime which, according to our theory [10], enables the electrochemical process to penetrate deeper. As pointed out already by Lam et al. [11], the

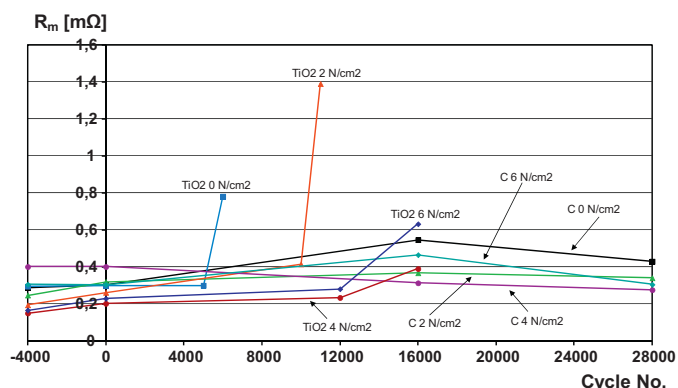


Fig. 7. Schematic evolution of the active mass resistance for the tested electrodes.

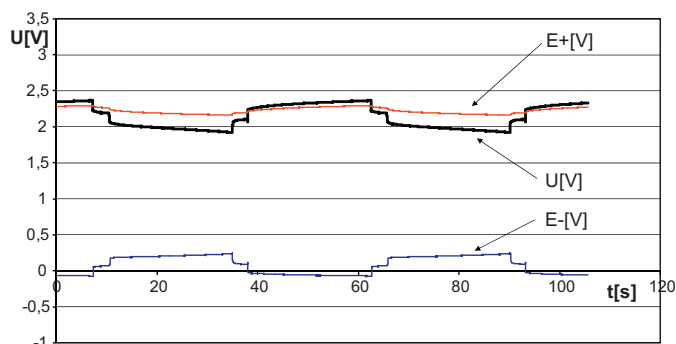


Fig. 8. Time courses of voltage and potentials in the PSoC regime for carbon-doped electrode at a pressure of 4 N cm^{-2} and cycle number 1000. Potentials measured against Cd electrode.

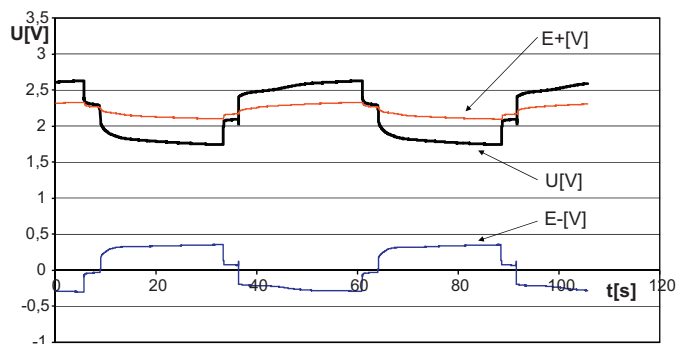


Fig. 9. As preceding but cycle number 6000.

high-rate PSoC regime causes accumulation of lead sulphate at the surface of the negative plates, thus hindering the transport of both mass and charge in the direction normal to the plate surface. Our measurements of active mass resistance, however, involve current lines parallel to the plate surface, i.e. parallel to the sulphate layer, so the results simulate lower resistance values.

4.4. Detailed course of a PSoC cycle

With some cycles, the course of the voltage and potentials was recorded during charge, discharge, and stand for about two subsequent cycles. In Figs. 8–10 are shown the diagrams for graphite-doped electrodes with expanders at a pressure of 4 N cm^{-2} at the beginning and at the end of the cycle life. Analogous diagrams for titanium dioxide-doped electrodes with expanders are shown in Figs. 11 and 12. Since the positive active mass was in excess, its potential was practically constant, hence the cell voltage follows the potential of the negative electrode.

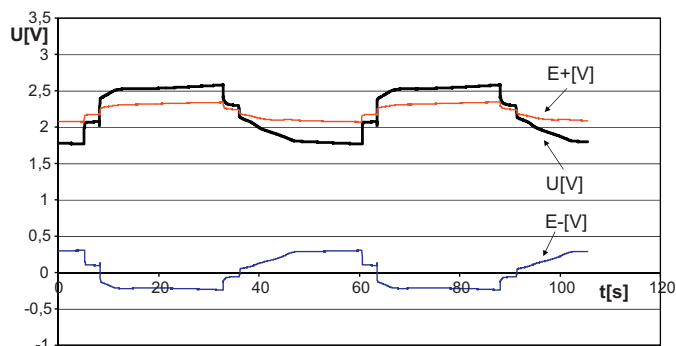


Fig. 10. As preceding but cycle number 24,400.

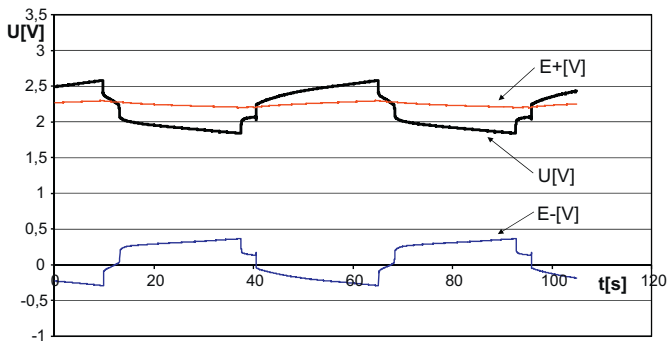


Fig. 11. Time courses of voltage and potentials in the PSoC regime for TiO₂-doped electrode at a pressure of 4 N cm⁻² (cycle number 1000). Potentials measured against Cd electrode.

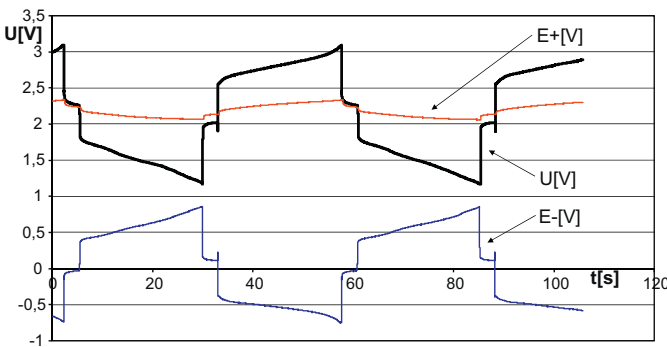


Fig. 12. As preceding but at cycle number 13,500 (end of life).

The discharge region of the PSoC cycle (e.g. Fig. 9) is for all cells similar and consists roughly from two sections:

- (1) Instantaneous drop of the cell voltage (measured from the horizontal 3 s stand section). Its magnitude corresponds to the internal resistance of the cell (ohmic potential drop). This drop increases in the course of the PSoC run, i.e. the internal cell resistance increases. Since the cell voltage drop corresponds to the potential drop of the negative electrode, the increase of the internal cell resistance corresponds to the increase of the negative electrode resistance. We have measured the instantaneous cell voltage drop at the beginning (cycle No 1000), ΔU_1 , and at the end (cycle No. 24,400), ΔU_2 , of the PSoC run; and the corresponding values in mV are given in Table 3. It can be seen that the initial internal cell resistance is relatively rather low for all the four cells under test and that it is practically independent of the applied pressure. The increase of the internal cell resistance, roughly proportional to $\Delta U_2 - \Delta U_1$, is lower for electrodes with higher applied pressure.
- (2) Subsequent slow potential drop (Fig. 9) related to the faradaic reaction (oxidation of Pb) combined with diffusion and double layer phenomena.

The resulting value of the cell voltage at the end of the PSoC run is influenced by the first section (the cell resistance, respectively, the

Table 3
Voltage drop at the beginning, ΔU_1 , and at the end, ΔU_2 , of the PSoC run.

| Electrode | ΔU_1 [mV] | ΔU_2 [mV] | $\Delta U_2 - \Delta U_1$ [mV] |
|------------------------|-------------------|-------------------|--------------------------------|
| C 0 N cm ⁻² | 109 | 331 | 222 |
| C 2 N cm ⁻² | 129 | 399 | 270 |
| C 4 N cm ⁻² | 117 | 137 | 20 |
| C 6 N cm ⁻² | 117 | 219 | 102 |

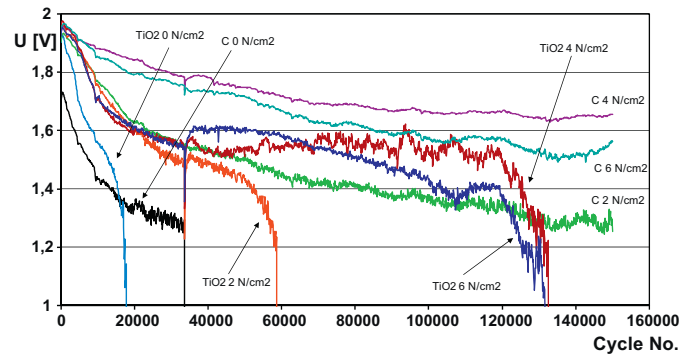


Fig. 13. Dependence of cell voltage on the discharge half-cycle number for the second run.

negative electrode resistance) and this is least affected at higher pressures. Thus, it can be assumed that the applied pressure stabilizes the structure of the negative electrode.

The charging region of the PSoC cycle involves again an instantaneous ohmic potential step followed by a subsequent potential step due to double layer charging and faradaic reaction (reduction of sulphate) causing activation polarization. Thus, the cell voltage increases above 2.5 V (Fig. 9).

For electrodes doped with TiO₂, the discharge region of the PSoC cycle is similar with all cells (Figs. 11 and 12) and consists again of two sections:

- (1) Instantaneous drop of the cell voltage (ohmic potential drop) at the beginning of the PSoC run was about 177–201 mV, nearly twice as large compared with the carbon-doped electrodes. Since the values of R_k and R_m for electrodes with different additives were comparable, we assume that the increase of the internal resistance must have been caused by the activation polarization which is in this case higher since the favourable effect of graphite on the reduction of lead sulphate mentioned above [8] was missing. The quantity ΔU_2 defined above (cf. Table 1) was at the end of the cycle life in the range of 310–511 mV and hence comparable with the values given in Table 1. Although the internal resistance of the negative electrodes increased sensibly in the course of their cycle life (cf. Figs. 6 and 7), it cannot be considered as the reason for their end of life.
- (2) Approximately linear, decreasing portion of the discharge curve in Figs. 11 and 12 is related to the electrochemical reaction. Its slope is higher than with the carbon doped electrodes, an unfavourable feature for high-rate discharge. In the stand period, the voltage of electrodes with TiO₂ is, after discharge, by about 30 mV lower than in the case with carbon.

The charging region of the PSoC cycle shows a more steep voltage increase than in the case with carbon. At the end of the charging region, the voltage exceeds 2.5 V after 1000 PSoC cycles, hence the evolution of hydrogen cannot be excluded. This finding can be compared with Fig. 4.

4.5. Electrodes containing expanders and additives, second PSoC run

The courses of voltage during the discharge half-cycles are shown in Fig. 13. Here, all electrodes with the titanium dioxide additive attained an appreciably longer cycle life than in the first PSoC run. The end of life is marked with a steep voltage drop caused apparently by a sulphate layer at the electrode surface.

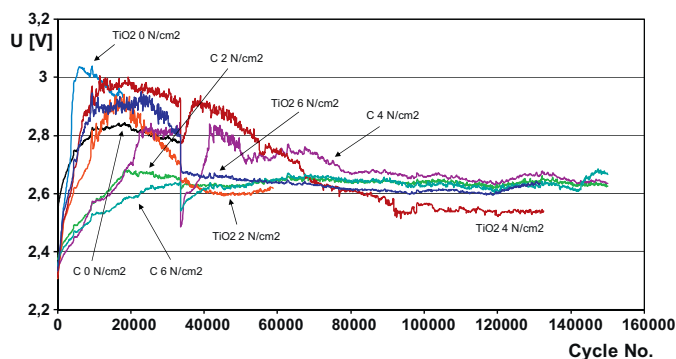


Fig. 14. As Fig. 13 but dependence of voltage on the charge half-cycle number.

The compressed electrodes with graphite additive did not show a voltage drop under 1.0 V up to the end of the second run (150,000 cycles); the electrodes compressed at 2, 4, and 6 N cm⁻² kept their end voltage at 1.3, 1.65, and 1.55 V, respectively.

The initial voltage of the carbon-doped electrode without pressure was by about 200 mV lower than with the other three, evidence for an elevated internal resistance of the cell. This was substantiated by a detailed record of the PSoC cycle No. 15,000 where the instantaneous voltage drop at the start of discharge was nearly twice that measured for the other test electrodes. The increased internal resistance was obviously the primary reason for the end of life of this cell.

The courses of voltage measured in the charging half-cycles and shown in Fig. 14 are analogous to those in the first PSoC run. The electrodes doped with TiO₂ show, in the first phase, a marked increase of voltage (limited charge acceptance). The increase is slower and the highest voltage is lower than in the case of the first run, indicating an improvement. A detailed record of the PSoC cycle No. 15,000 shows that as soon as the charging starts, the voltage increases to about 2.4 V to reach about 2.9 V at the end of the half-cycle. After very many cycles, however, the voltage attained a slightly lower level than the electrodes with carbon (Fig. 14). In comparison to the first run, the cycle life in the second run was markedly higher.

The abrupt drop of voltage at the cycle No. 33,000 is due to a change of the glass fiber separator to remove short-circuiting. An overview of the results according to Fig. 13 is given in Table 4.

The electrodes under test show the best characteristics (cycle life and potential) at a pressure close to 4 N cm⁻². A similar optimum pressure value was found in our work concerning compressed negative electrodes [2] where the reason for this optimum was attributed to volume changes of the negative electrodes which tend to expand at lower pressures whereas they tend to constrict at higher pressures. The authors concluded that compression causes loss in porosity and hence loss in capacity, whereas expansion causes loss in mechanical strength leading to eventual disintegration. These findings referred to electrodes containing expanders. In the next section, we shall turn our attention to electrodes containing no expanders but only 1% of carbon N134.

Table 4
Cycle life of the tested electrodes.

| Pressure | Additive C | Additive TiO ₂ |
|----------------------|------------|---------------------------|
| 0 N cm ⁻² | 33,000 | 18,000 |
| 2 N cm ⁻² | >150,000 | 58,000 |
| 4 N cm ⁻² | >150,000 | 132,000 |
| 6 N cm ⁻² | >150,000 | 130,000 |

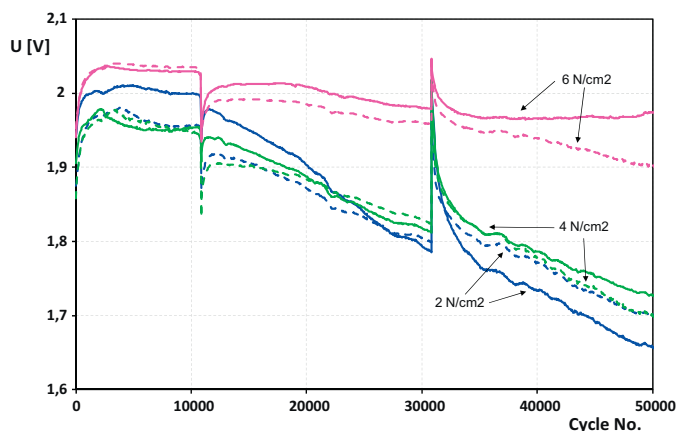


Fig. 15. Dependence of voltage on the discharge half-cycle number for the first three runs. Electrodes doped with carbon N134 without standard expanders.

4.6. Electrodes with carbon without expanders; first three runs

In Figs. 15 and 16 are shown the courses of voltage in the first three runs taking, respectively, 10, 20, and 20 thousand PSoC cycles. The voltage was measured either in the charge half-cycles (Fig. 16) or in the discharge half-cycles (Fig. 15). In the first asymmetrical PSoC run, the cells obtained by 2% higher charge during charging than during discharging. The voltage at the end of charging (Fig. 16) increased rapidly above the gassing voltage; the voltage at the end of discharging (Fig. 15) was relatively high as well (1.96–2.03 V). This situation was obviously close to the full state of charge. Hence, the run was terminated after 10,000 cycles, a conditioning cycle was carried out in the flooded state, the excess electrolyte removed, the cells charged to 50%, and the asymmetrical cycling continued except that the charge supplied was only by 0.2% higher than that delivered by discharging. (The first and second PSoC run (Fig. 15) started with the separator saturated with the electrolyte, in contrast to the third run where apparently the separator was not saturated. This may elucidate the difference in the slope of the starting portions.)

According to Fig. 15, the positive effect of the pressure is obvious; the electrodes with the highest pressure (6 N cm⁻²) showed the best performance in all the three runs. This diagram suggests the influence of the cell internal resistance increasing with the age of the electrodes at lower pressures, especially apparent for the electrodes operating at 2 N cm⁻². However, the courses of voltage during charge half-cycles (Fig. 16) show that the final voltage is only little dependent on the applied pressure and so the cell

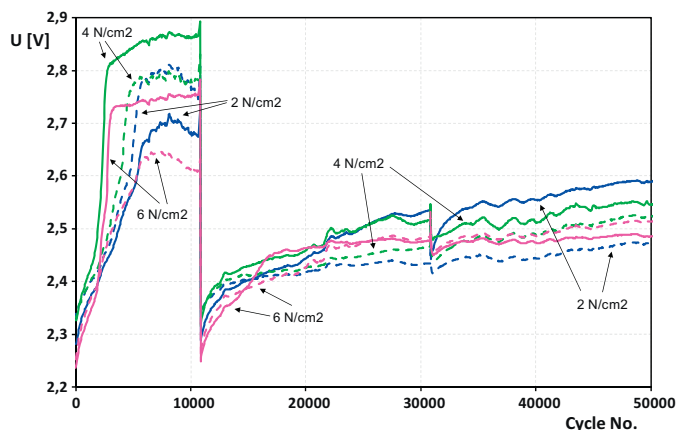


Fig. 16. As Fig. 15 but dependence on the charge half-cycle number (cf. text).

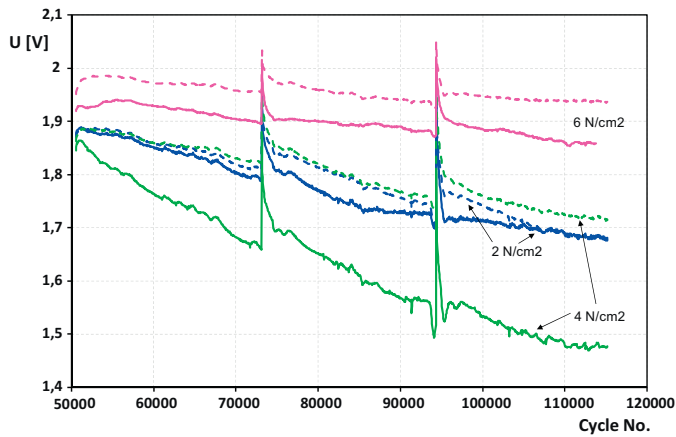


Fig. 17. Dependence of voltage on the discharge half-cycle number for runs No. 4–6.

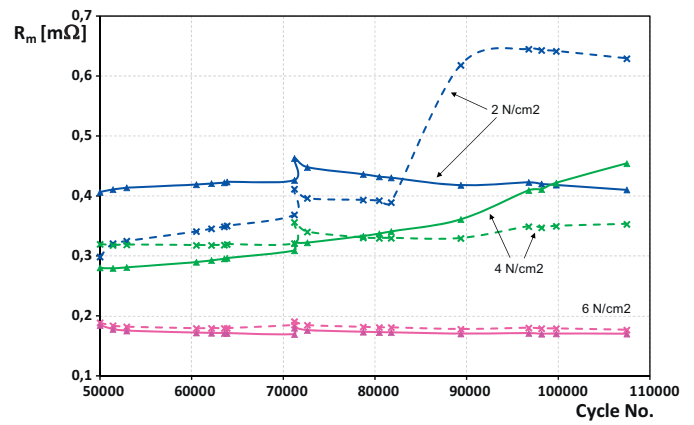


Fig. 19. Dependence of negative active mass resistance on cycle number for runs No. 4–6.

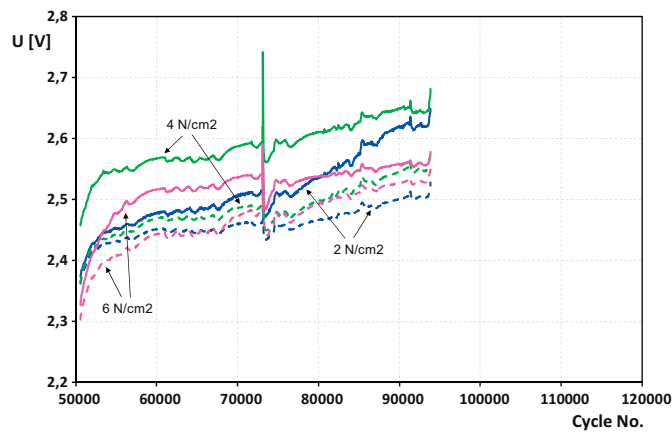


Fig. 18. As Fig. 19 but dependence on the charge half-cycle number.

internal resistance does not seem to be a factor in this case. A higher sensitivity of the anodic curves in Fig. 15 against pressure may be compared with a higher sensitivity of the anodic curves in Figs. 3, 13 and 17 in comparison with the corresponding cathodic curves in Figs. 4, 14 and 18 where the voltage is less affected by the pressure. In other words, the rate of the cathodic process is higher than that of the anodic one. This may be elucidated by the fact that the reduction of PbSO_4 particles proceeds simply by dissolution and electron acceptance, whereas the oxidation of lead is accompanied by the formation of a sulphate layer which is eventually complicated by an oxide layer. Thus, the transport of sulphuric acid to the lead/electrolyte interface may be more or less hindered.

In Table 5 are shown the results of capacity measurements in the three PSoC runs mentioned. It can be seen that the asymmetrical PSoC cycling in the first run where the cell obtained a 2% higher charge than it delivered during discharge led to a relatively rapid increase of the electrode's state of charge (to 80% after 10,000 cycles). A similar situation where the cell obtained a 0.2% higher charge than it delivered during discharge (second and third run) caused a slower increase of the electrode's state of charge. This effect seems to be accentuated at higher pressures.

Table 5
State of charge, C (in %), measured at the end of the PSoC run.

| Pressure | 2 N cm ⁻² | | 4 N cm ⁻² | | 6 N cm ⁻² | |
|--------------|----------------------|-------|----------------------|-------|----------------------|-------|
| 1st PSoC run | 81.76 | 83.42 | 78.96 | 79.98 | 82.02 | 78.67 |
| 2nd PSoC run | 49.10 | 71.55 | 61.28 | 84.37 | 75.52 | 78.54 |
| 3rd PSoC run | 77.49 | 79.66 | 88.73 | 85.50 | 93.01 | 96.92 |

4.7. Electrodes with carbon without expanders; further three runs

Because of interelectrode shortages found between the third and fourth runs, the cells were flooded, the separators were replaced, and after a few conditioning cycles the excess electrolyte was sucked off. The cells were then discharged to 50% DOD and further three runs were carried out, 20,000 cycles each. The results are shown in Figs. 17 and 18.

Asymmetrical current pulses involved a 0.2% higher charging current as compared to the discharge. The negative electrode potentials correspond, again, to the course of cell voltages.

The voltage courses measured in the discharge half-cycles at the beginning of the fourth run (Fig. 17) show some drop as compared to the first run (Fig. 16), especially considerable at lower pressures. This suggests an increase of the internal resistance, possibly caused by manipulation during the replacement of the separators. However, the positive effect of the pressure is again apparent. The cell voltage at the end of the sixth run was scattered between 1.48 and 1.94 V.

The voltage courses in the charge half-cycles (Fig. 18) could only be measured during the fourth and fifth runs after which some defect occurred in the measuring station preventing the record of the sixth run. The presence of the internal resistance is again apparent at the pressure of 4 N cm⁻². The initial voltage of the other cells was in the range from 2.30 to 2.40 V with an increasing trend during the experiment, not related to the pressure.

4.8. Supplementary measurements

In Figs. 19 and 20 are shown the courses of the active mass resistance, R_m , and contact resistance, R_k , measured during the last three runs. The values of the former lie within 1–4 mΩ showing a pronounced influence of the magnitude of the applied pressure: the lowest resistance corresponds to the highest pressure. The contact resistances, which are bound to the quality of the collector/active mass layer, do not show such dependence; they are scattered in the interval from 0.5 to 1 mΩ. Both the two resistances did not change appreciably during the measurement except for two electrodes in the sixth run where their resistances increased considerably. These electrodes showed also a considerable drop in voltage in the discharge half-cycles (Fig. 15). (For a closer discussion of the active mass resistance, see Section 4.3 above.)

The courses of the individual PSoC cycles show a distinct similarity to Figs. 9–11 corresponding to an electrode with standard expander and carbon. The curves were not appreciably influenced by the state of charge of the electrode. Measurements of the state

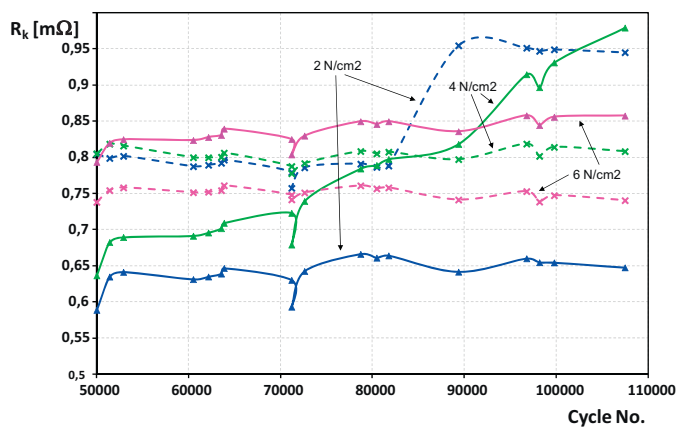


Fig. 20. Dependence of negative active mass/collector contact resistance for runs No. 4–6.

Table 6

State of charge, C (in %), measured at the end of the PSoC run.

| Pressure | 2 N cm ⁻² | 4 N cm ⁻² | 6 N cm ⁻² |
|--------------|----------------------|----------------------|----------------------|
| 4th PSoC run | 45.29 | 56.12 | 57.11 |
| 5th PSoC run | 102.06 | 99.05 | 100.64 |
| 6th PSoC run | 99.75 | 111.57 | 86.66 |

of charge revealed that this quantity increased slowly due to the asymmetrical current pulses as shown in Table 6.

5. Conclusions

- (1) Accelerated PSoC cycling carried out with laboratory VRLA cells revealed that electrodes doped with carbon perform in the first run better than those doped with TiO₂ since they reached about 30,000 cycles regardless of the applied pressure. However, the electrode performances were almost equalized in the second run.

- (2) Mechanical pressure of 4 N cm⁻² has a pronounced favourable effect on the cycle life of negative electrodes with expanders in the accelerated PSoC regime. Higher pressures are not recommended.
- (3) Electrodes doped with carbon but without standard expanders are capable of long-life cycling at elevated pressures around 6 N cm⁻². Their cycle life is comparable to that of the electrodes with expanders.
- (4) Experimental evidence showed that the cathodic reaction (charging) process at the lead electrode proceeds at a lower overpotential (higher rate) than the anodic one.

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