



Short communication

Study of the influence of carbon on the negative lead-acid battery electrodes

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ARTICLE INFO

Article history:

Received 26 August 2010

Received in revised form 14 October 2010

Accepted 7 November 2010

Available online 12 November 2010

Keywords:

Lead battery electrodes

Doping with carbon

Accelerated testing

ABSTRACT

Experiments were made with negative lead-acid battery electrodes doped with different concentrations of powdered carbon. It turned out that the rate of formation decreased with the rising concentration of carbon added into the active material. During accelerated cycling in the PSoC regime, the cycle life showed a maximum at a concentration of carbon near 1%, whereas at lower or higher concentrations the cycle life was profoundly lower. A marked increase of the active mass resistance with the cycle number was recorded at carbon concentrations above 2%. Orientation experiments showed that compression of the lead-acid laboratory cells caused an increase of the cycle life of the negative electrode in the studied regime.

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1. Introduction

The favourable effect of powdered carbon on the performance of negative lead-acid battery electrodes has attracted the attention of many investigators [1–9]. Especially much effort has been spent in the development of lead-acid batteries for various types of hybrid electric vehicles [2,4–6]. A probable mechanism of the action of carbon in the negative lead-acid battery electrodes, based on experiments and on thorough measurements including the active mass and contact resistances, has been proposed in our preceding publications [7,8]. Thus, it has turned out that the effect of carbon is due to steric hindrance of the sulphate crystallization rather than the electric conductivity of graphite. An interesting phenomenon has been discovered by Pavlov et al. [3] who observed that the electrochemical reduction of lead sulphate on certain (electroactive) carbons proceeds at a lower overvoltage than on lead. Our aim was to investigate what happens when the carbon concentration in the negative lead electrode is changed, since the results may be fruitful to see whether the proposed mechanism [7,8] is acceptable.

2. Experimental

2.1. Electrodes and cells

We prepared six experimental electrodes with a discontinuous system of parallel ribs, pasted with negative active mass according to the common industrial method. Their dimensions were

55 mm × 20 mm × 7 mm. The active mass was doped with various concentrations of graphite CR2996 (Graphite Týn, s.s. r.o., Týn nad Vltavou, Czech Republic). This was, in substance, finely ground natural graphite of 99.5% purity with particle size 3.5–5.5 μm, specific surface area of 13.0 m² g⁻¹, and square density of 160 g l⁻¹. The concentrations of its admixtures in the electrodes were chosen as indicated in Fig. 1. Each electrode was assembled with two positive ones (with excess active mass) and AGM separators of the type BG 260 EB 170 (1.7 mm in thickness) and mounted in a cell permitting hermetization. Electrode potentials were measured against a cadmium reference electrode. The cells were finally filled with a sulphuric acid solution of 1.28 g cm⁻³ density.

2.2. Formation

The process of formation consisted of 26 cycles, each consisting of charging with 0.2 A for 4 h and stand for 2 h. Thus, the whole process took 156 h and the electrodes received seven times the expected capacity. The results are shown in Fig. 1.

It can be seen that the negative electrodes with different graphite concentrations attained different final voltages (corresponding to the second charging step) as recorded after 66 h. The electrode with 0.15% graphite attained the highest value (2.752 V), while that with 5.15% graphite attained only 2.635 V. The dependence of the final voltage on the graphite concentration in the negative electrode is shown in Fig. 2. It seems that the final voltage shows a distinct tendency to drop with increasing concentration of graphite. This behaviour resembles the observation of Pavlov et al. [3] who found a distinct electrocatalytic effect of active carbon and carbon black on the cathodic reduction of lead sulphate.

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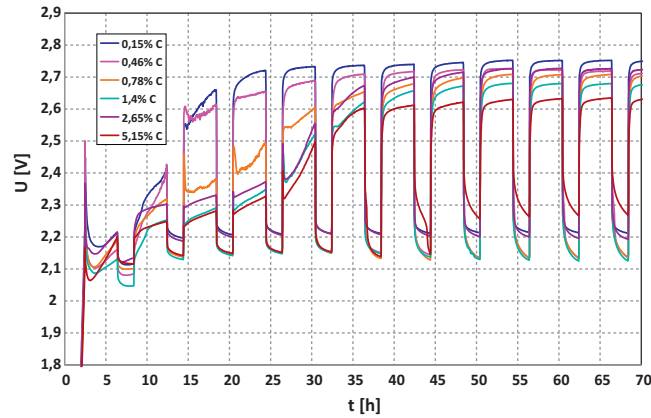


Fig. 1. Course of formation of electrodes with various concentrations of graphite.

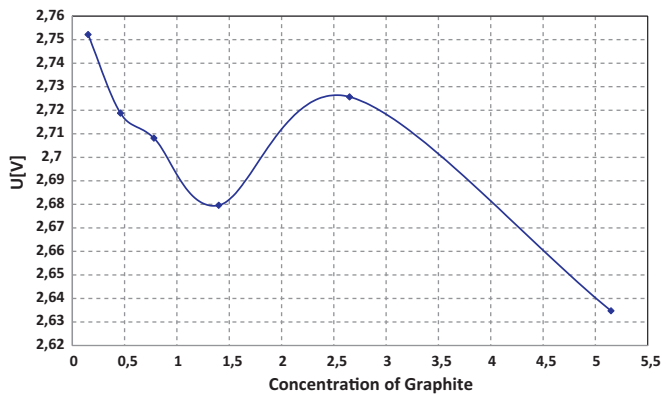


Fig. 2. Dependence of final voltage of the cell charge on the graphite concentration.

The curves in Fig. 1 also show that the rate of formation of the active mass varied. The time after which the cell voltage passed 2.6V reaching the second charging step was deliberately chosen as the end of formation. Accordingly, the active mass with 0.15% graphite reached most rapidly the end of formation (after 16 h). The electrode with 5.15% graphite was the slowest one (ready after 36 h). This situation is illustrated in Fig. 3 where it can be seen that the studied dependence increased most rapidly in the region of 0.5–1.0% graphite content, whereas further increase was slow. This

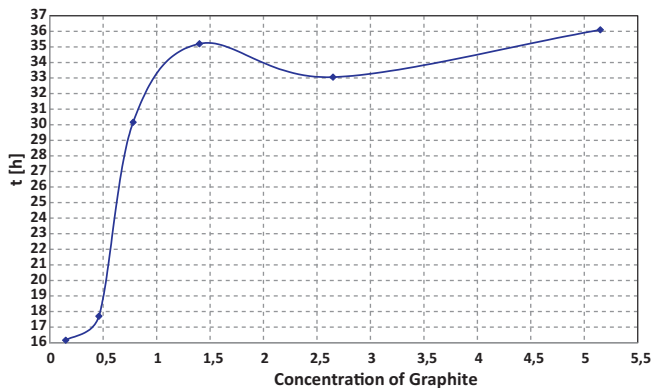


Fig. 3. Dependence of the time needed to end the formation of the negative active mass on the concentration of graphite.

is probably due to stepwise blocking of the pores of the spongy lead by the graphite particles leading to hindrance of the electrolyte transport. On the whole, the rate of formation decreased with the rising carbon content.

2.3. ESEM observations

After finishing the formation process, the negative active mass was examined by the environmental scanning electrode microscope (ESEM). Fig. 4a shows the highly porous spongy structure of the lead electrode without added graphite. It can be seen that the lead sponge shows no lead sulphate crystals. The surface of the electrode with added 0.46% graphite shows a less regular structure with several particles of graphite (Fig. 4b). The irregularities, however, had no influence on the electrode performance.

The surface of the electrode with added 2.65% graphite after formation differed appreciably from the regular spongy structure (Fig. 5). Besides small lead sulphate crystals and graphite particles, many dendritic structures appeared that could not be elucidated. The fibre on the left side originates from the acrylic fabric added to the negative active mass.

2.4. Conditioning cycles

Three conditioning cycles consisted from constant current discharge at 0.7 A to 1.6 V cut-off voltage and constant current charge at 0.7 A with 2.45 V voltage limitation for 20 h. The cell capacity was limited by the negative electrode. The cell capacities showed a decreasing trend as given in Table 1. The negative electrode with added 0.78% of graphite showed the highest capacity, whereas that with the highest concentration of added graphite showed the lowest capacity. The drop in the capacity at the highest graphite content may be due to the drop in the relative content of lead in the electrode. (The thickness of the electrodes was always 7 mm.)

Table 1
Capacities of cells in the conditioning cycles. Capacity in Ah.

Graphite added	0.15%	0.46%	0.78%	1.40%	2.65%	5.15%
Cycle no.1	1.54	2.03	2.36	2.10	2.01	1.73
Cycle no.2	1.51	1.78	2.16	1.95	1.79	1.41
Cycle no. 3	1.53	1.71	2.00	1.83	1.67	1.27

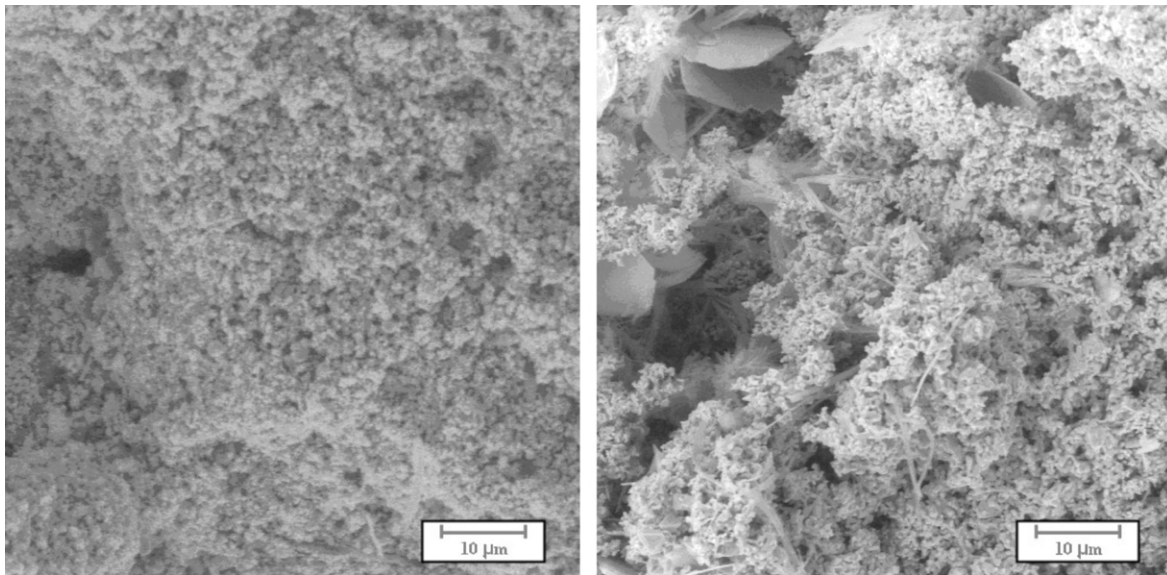


Fig. 4. (a) The spongy structure of the NAM without added graphite; (b) as (a) but with 0.46% of added graphite. Photographs taken by ESEM.

2.5. Accelerated PSoC cycling

After the conditioning cycles, the free electrolyte from the cells was sucked off and the cells were hermetically closed. The cell capacity was then determined by one conditioning cycle, the cells were discharged to 50% capacity and cycled as follows:

Charging with 2 A constant current for 25 s, 3 s stand, discharging with 2 A constant current for 25 s, and 3 s stand. The last PSoC run was finished at a voltage drop below 1.5 V. After 4–6 conditioning cycles and discharge to 50% capacity another PSoC run started. In total, three PSoC runs were carried out. These were similar in character to one another so we shall deal with the last run only.

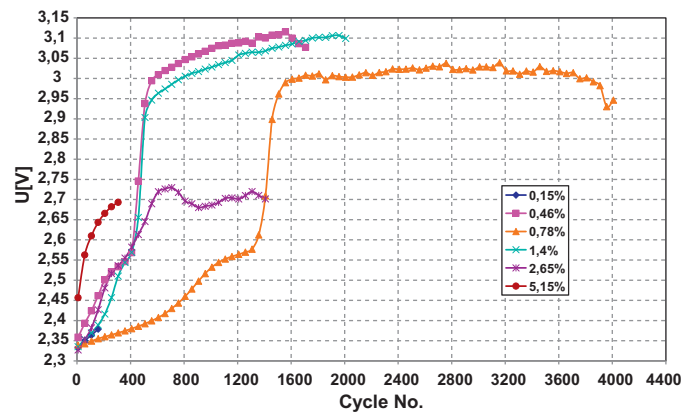


Fig. 6. Courses of voltage during charge PSoC cycles in the third run.

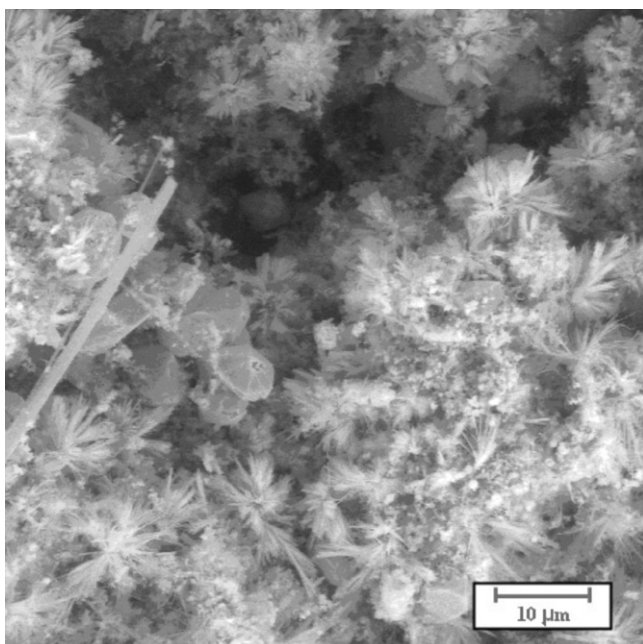


Fig. 5. ESEM photograph of NAM with 2.65% of added graphite.

3. Results

3.1. The charge course

In Fig. 6 are shown the characteristics of the individual electrodes recorded during charge periods. The initial voltage was in all cases similar except for the electrode doped with 5.15 graphite; its potential was by 100 mV more negative, evidence for a higher internal resistance. This was checked by measurements of both the contact and active mass resistances as described in Section 3.3. The attained voltage shows some trend toward lower values with increasing concentration of the added graphite in accord with the assumed catalytic effect of carbons on the cathodic reduction of lead sulphate [3]. The voltage course is in accord with the course of the negative electrode potential.

3.2. The discharge course

The characteristics of the individual electrodes recorded during discharge periods are shown in Fig. 7. The initial voltage values were in the range 1.91–2.02 V; the lowest value corresponded again to the cell with the highest graphite concentration. The cell with the 0.78% graphite content attained the longest cycle life (nearly 4000

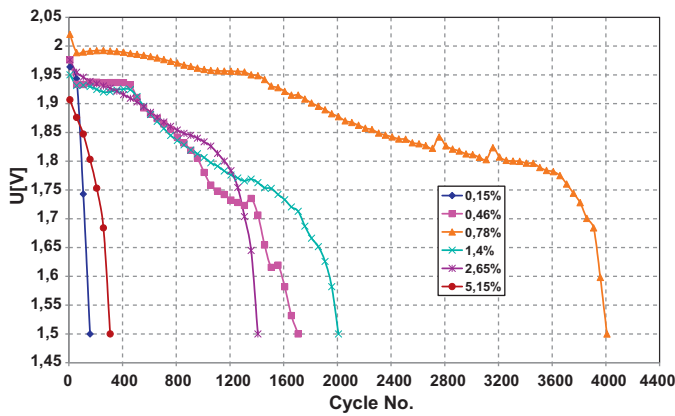


Fig. 7. Courses of voltage during discharge PSoC cycles in the third run.

cycles); its voltage was permanently higher than that of the other cells. The graphite concentrations in the cells with the shortest cycle life corresponded to 0.15 and 5.15%.

3.3. Contact resistance and active mass resistance

In the course of the PSoC run, the cycling was interrupted at intervals (for about 10 min) and both the active mass resistance, R_m , and the collector/active mass contact resistance, R_k , were measured. The method, which is based on a discontinuous system of parallel ribs, has been described in detail in our previous work [10,11].

It follows from Fig. 8 that the initial value of R_k (measured at the 50% charge state before the start of cycling) with electrodes containing a low carbon concentration is about 2 mΩ. This value is by an order of magnitude higher with electrodes doped with 5% graphite. (Owing to a very short cycle life of electrodes with 0.15 and 5.15% graphite, only one value of R_k and R_m could be measured.) With the electrode containing 0.46% graphite, the both resistance values were measured up to the end of cycle life to observe their conspicuous increase. The active mass resistances were nearly twice as large (Fig. 9). The electrode containing 0.46% graphite shows a steep rise of R_m toward the end of cycle life.

It can be seen that a higher content of graphite in the active mass causes an increase of the both resistance values. This is conceivable since the ohmic resistance of graphite is by 1–2 orders of magnitude higher than that of lead. Nevertheless, according to our experience based on our previous work [10,11,14], the observed resistance values are too small to cause breakdown of the negative electrodes. However, as pointed out in Section 2.2, it seems that

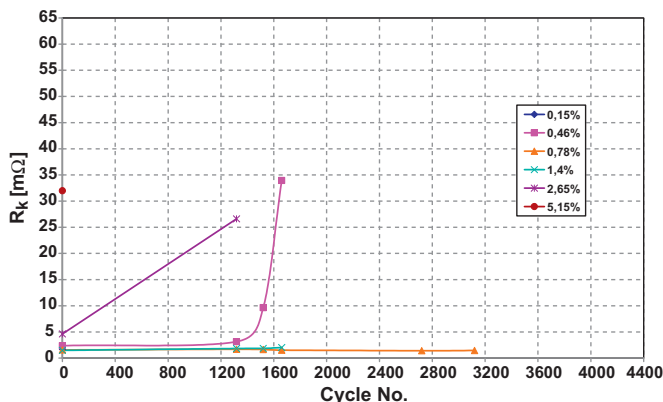


Fig. 8. Contact resistance (R_k) during the third PSoC cycling run.

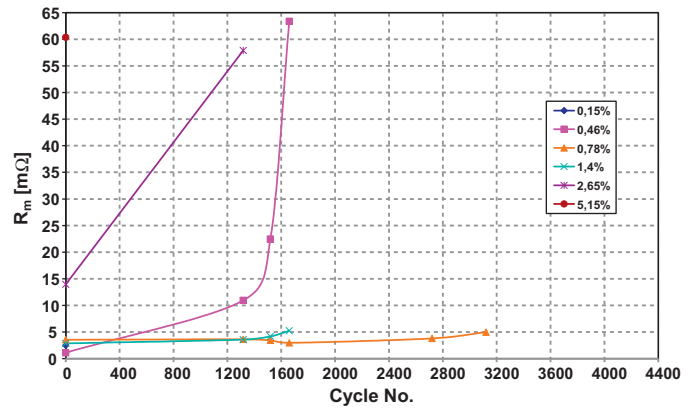


Fig. 9. Active mass resistance (R_m) during the third PSoC cycling run.

the adverse effect of too much carbon consists in transport restriction in the electrode pores. An additional transport restriction is probably related with the lead sulphate that is slowly and gradually accumulated close to the surface of the negative electrodes. This phenomenon, observed by many authors, may be bound to a relatively thin surface layer that hinders both the electrolyte and charge transport (cf. our theoretical work [12]).

Thus, we assume that the electrodes are gradually sulphated in the course of PSoC cycling, the sulphation beginning at the visible surface and involving a relatively thin layer that causes ohmic passivation. This process is the slowest with electrodes containing 0.78 and 1.4% graphite where the active mass resistance increases only in the last phase of the electrode cycle life.

3.4. Application of external pressure

With the electrodes containing 0.78, 1.4, and 5.15% graphite, an additional pressure was applied starting from the beginning of the third run by using additional spacers in the hermetic laboratory cells. The dependences of the cell voltage on the cycle number in the second (2) and third (3) run are compared in Fig. 10.

It can be seen that the initial voltage in the third run is higher by about 50–70 mV than in the second, evidence that the compression causes a decrease of the cell internal resistance. The cycle life of the tested electrodes under compression in the third run is significantly higher than in the preceding run without compression. We assume that the reason for this phenomenon is the same as in the case of lead accumulator plates with AGM separators in the classical regime [13,14] where compression prevented loss of cohesion

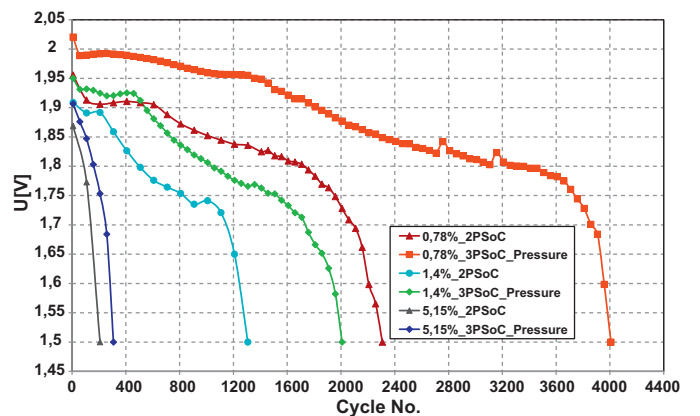


Fig. 10. Comparison of the influence of pressure on the cycle life of electrodes during the second and third run (2PSoC and 3PSoC).

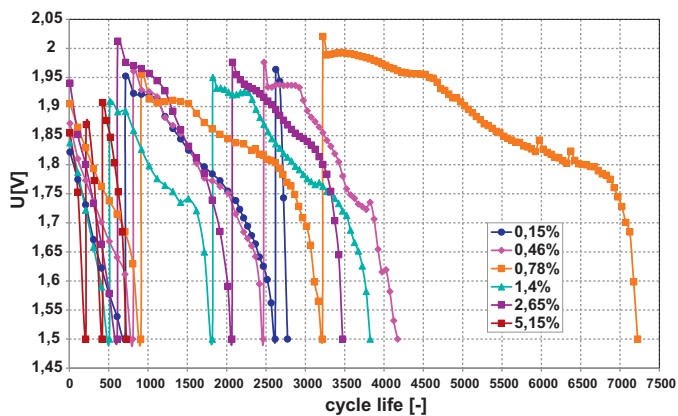


Fig. 11. Voltage courses during the discharge PSoC cycles in the cumulative runs.

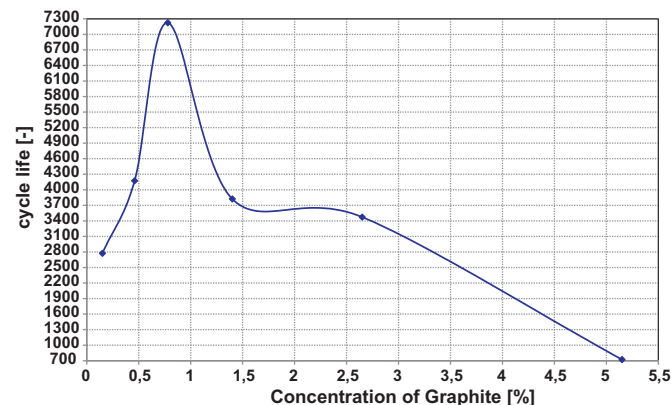


Fig. 12. Dependence of the cycle life of the negative electrodes on the concentration of graphite in cumulative PSoC runs.

of the active mass. As a result, a decrease of the plate resistance caused by compression was observed together with a considerable increase of the cycle life. A detailed investigation of the influence of compression on the performance of carbon-doped electrodes in the PSoC regime will be the subject of a further work.

3.5. Comparison of the PSoC runs

The cumulative results obtained from all PSoC runs are shown in Fig. 11. These characteristics are based on the total number of cycles that were realized by the tested electrodes. It can be seen that the electrode containing 0.78% graphite attained the longest cycle life. The second best was the electrode with 0.46% graphite; and that with the highest graphite content was the worst one.

The interpolated dependence of the cumulative cycle life on the concentration of graphite is illustrated in Fig. 12. There is a conspicuous maximum of the cycle life at low graphite concentrations between 0.6 and 1.1%. Pavlov et al. who used a much smaller

concentration interval of carbon (up to 2%) have found an analogous maximum of the cycle life of negative electrodes doped with three sorts of commercially available carbons [3]. This phenomenon brings some evidence for our earlier publication [7] where we have presented the probable mechanism of the action of carbon, namely, that the carbon particles modify somewhat the porous structure of the negative electrode to make the pores smaller, thus preventing the formation of larger lead sulphate crystals. Any more profound modification would, naturally, be undesirable since too many carbon particles may clog the pores causing transport problems; moreover, they may interrupt the bonds between lead particles causing softening of the active mass. This reasoning is also supported by our present results obtained with elevated carbon concentrations; hence it does not seem to us fruitful to study negative electrodes containing up to 25% of high surface area carbon as proposed by Moseley to make use of its property as supercapacitor [2].

4. Conclusions

Comparison of the effect of different concentrations of powdered graphite on the properties of negative lead accumulator electrodes revealed that the longest cumulative cycle life in accelerated PSoC tests can be attained at low graphite concentrations, apparently not exceeding 1%. It was also found that the rate of formation of the lead electrodes decreases with rising additions of graphite. The cycle life of the laboratory cells can be further increased by the application of external mechanical pressure.

Acknowledgements

This work was supported by the Grant MŠMT ČR No. MSM 0021630516 and by the specific graduate research of the Brno University of Technology No. FEKT-5-10-14.

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