

## Negative Lead-Acid Battery Electrodes Doped with Glass Fibres

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Negative lead-acid battery electrodes doped with microscopic glass fibres show similar properties during accelerated partial state of charge cycling as those doped with carbon or titanium dioxide, including a long cycle life of up to 84,000 cycles. The optimum amount of this additive in the negative active mass seems to be between 2 and 3 wt. %.

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**Keywords:** lead-acid battery, glass fibres, negative active mass, PSoC regime

### 1. INTRODUCTION

The issue of improving the parameters of the electric energy accumulators is very actual given the fact that in developed countries are expended significant resources on the development of accumulators and in connection with efforts to increase the number of vehicles powered by batteries, as well as the need to store electricity from solar and wind power plants.

Short high rate charging or discharging pulses are applied to maintenance-free VRLA lead-acid accumulators operated for a long time in PSoC (Partial State of Charge) or HRPSoC (High Rate PSoC) regime. This regime is typically used in HEV (Hybrid Electric Vehicles) or in RAPS (Remote Area Power Supply) systems. Negative active mass of lead-acid accumulator has smaller specific surface area, during PSoC regime charge acceptance is low, current density is high and progressive sulphation of negative plates occurs. This phenomenon is known as PCL3 (Premature Capacity Loss 3).

Additives such as mixture of barium sulphate  $\text{BaSO}_4$  and carbon black and “organic expanders” (for instance lignosulphates) are used to stabilize structure of NAM (Negative Active Mass).

Some years ago we studied and compared the effects of powdered carbon, carbon nanotubes, titanium dioxide, glass fibres, silicon dioxide, and aluminum oxide on the performance of negative lead accumulator electrodes in high-rate, partial-state of charge (PSoC) cycling [1, 2]. Accelerated

PSoC cycling of laboratory VRLA cells in hermetic system revealed that practical and promising doping agents are, besides certain sorts of carbon, also titanium dioxide and glass fibres. The latter material manufactured by Hollingsworth and Vose Comp. from borosilicate glass exclusively for lead-acid battery applications has been shown to improve plate processing including several production operations at lower cost [3]. Moreover, the electrodes made with this additive have been found to have higher surface area and increased active material utilization, which can enhance battery performance [3]. In a further development, expanded graphite and flake graphite mixed with glass fibres (1.5% each) were used by Valenciano *et al.* as additives in negative electrodes [4]. The authors used glass fibres to increase somewhat the surface area of the flake graphite but better results concerning the electrode performance were achieved by using expanded graphite. Since our past work [1] showed that the effect of carbon can be achieved by other substances as well, we thought it worthwhile to investigate glass-doped negative lead electrodes from the point of view of their performance in model batteries.

The use of glass fibres as additives to NAM or PAM is not discussed in the literature with the exception of [3]. Here it is documented that the use of borosilicate glass fibres during the production of active mass has a positive effect on the time and the price of the manufacturing process of the positive and negative electrodes.

Findings from our original experiment where glass fibres were added to electrode active mass indicate ability of glass fibres to support electrolyte and (or) evolved gas distribution from/to inner structure of negative electrode. Active mass utilization is more uniform and degradation mechanisms in the surface area of negative structure during PSoC regime are inhibited.

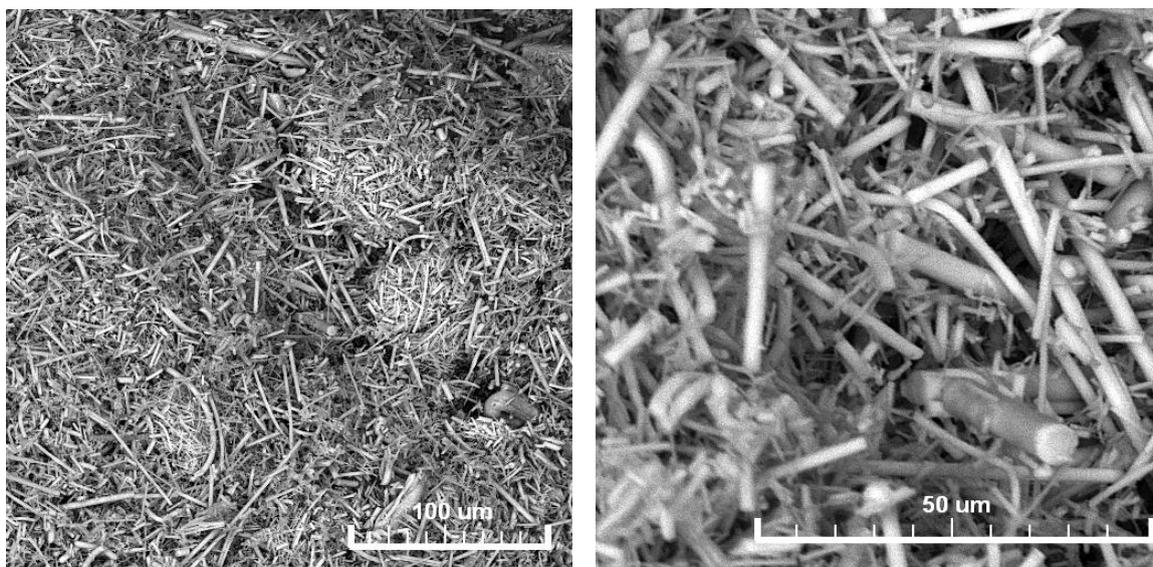
We assume that the capillarity of glass fibres can be important [8] and also fluid transfer properties [9, 10]. These properties depend on electrolyte properties (density and viscosity), and on composition, structure, pores saturation of separators and active mass. Paper presented by Culpin [11] shows that fluid-transfer is regulated by Laplace's equation. For two different-sized capillary tubes (or pores) connected to one another, fluid will move spontaneously from the wider to the narrower capillary due to the larger pressure difference across the interface in the latter capillary. Situation is much more complex in porous environments of active masses, because wide range of average size of pores occurs (average size of positive electrode pores is smaller than 1  $\mu\text{m}$ , or 6  $\mu\text{m}$  in case of negative electrode pores).

## 2. EXPERIMENTAL SECTION

### 2.1. Preparation of cells and formation

The negative electrodes of dimensions  $55 \times 20 \times 7$  mm were equipped with grids consisting of a system of parallel, insulated ribs. They were pasted with an active material without any form of carbon but doped with 0.46, 0.78, 1.4, 2.65, and 5.15 wt.% of glass fibres provided by Hollingworth and Vose Comp. The glass fibres were, on the average, 10 – 35  $\mu\text{m}$  in length and up to nearly 2  $\mu\text{m}$  in

thickness. Their bulk appearance was a white powder. In Fig. 1 are shown their two microphotographs obtained by the environmental scanning electron microscope (ESEM).



**Figure 1.** Microphotographs of glass fibres

The electrodes were placed in cells with two counter electrodes and with the usual electrolyte of  $1.28 \text{ g cm}^{-3}$  density. The cells were subjected to eighteen formation cycles in the flooded state (4 hours charging at 0.2 A and 2 hours stand, in total 72 h charging and 36 h stand). The course of formation was followed by recording the cell voltage as a function of the time as in our preceding paper [5].

### *2.2. Conditioning cycles – first run*

Prior to the PSoC cycling, the cells were subjected to eight conditioning cycles in the flooded state. The cells were discharged with constant current of 0.7 A to the cut-off voltage of 1.6 V and charged with the same current under voltage limitation to 2.45 V. The whole cycle lasted for 24 h.

### *2.3. Accelerated PSoC cycling – first run*

The excess electrolyte in the cells was sucked off so that the remainder was only in the separators. The cells were then hermetically closed and discharged to 50% of their capacity; the first PSoC run consisted of the following four steps:

Charging for 25 s with a current of 2.5 A; stand for 3 s; discharging for 25 s with a current of 2.495 A; and stand for 3 s. As soon as the cell voltage dropped below 1.5 V, the measurement was finished.

#### 2.4. Conditioning cycles – second run

After finishing the first PSoC run, the tested cells in the hermetized state were subjected to conditioning cycles analogous to those after formation.

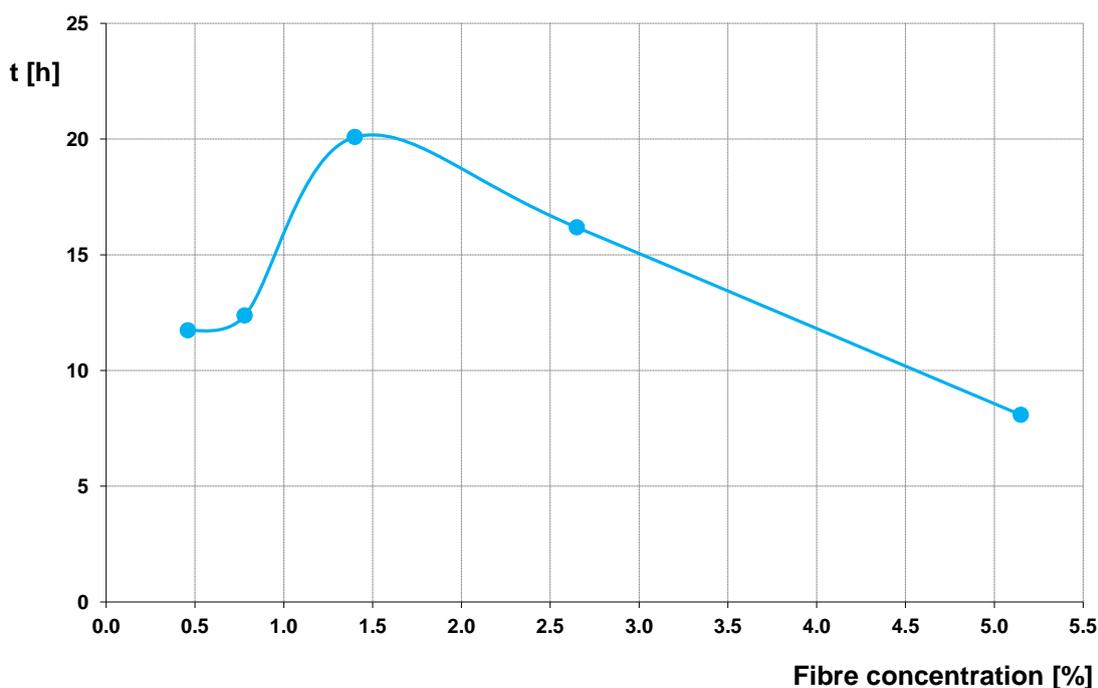
#### 2.5. PSoC cycling – second run

The parameters are analogous to the preceding case. The voltage and potentials of the negative electrodes were measured at the end of the charge or discharge at every hundredth cycle.

### 3. RESULTS AND DISCUSSION

#### 3.1. Formation

The time of formation, defined by the attainment of the voltage of 2.6 V, as a function of the glass fibres concentration is shown in Fig. 2. The time of formation at a doping concentration of 1.5 % reaches a maximum as in the case of graphite (compare Fig. 3 in the cited paper [5]). However, with increasing concentration of glass fibres, the time of formation decreases, in contrast to the case of graphite. In other words, it seems that the glass fibres cause an appreciably less transport hindrance than the graphite particles.



**Figure 2.** Dependence of electrode formation time on the concentration of glass fibres

3.2. Conditioning cycles – first run

The course of the eight conditioning cycles with cell capacities rising to a maximum is shown in Fig. 3. Unlike cited paper [5] and [7], where during the conditioning cycles there was decrease of capacities of carbon doped electrodes. A similar increase in capacity during the conditioning cycles was found at the electrodes containing TiO<sub>2</sub> - see [7].

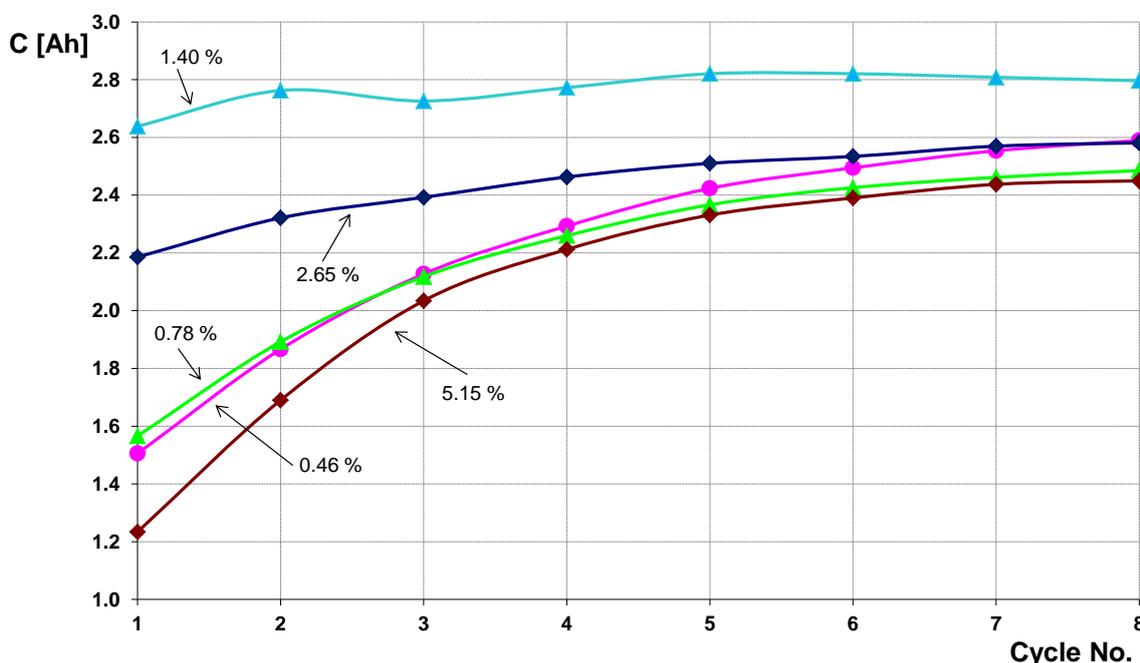
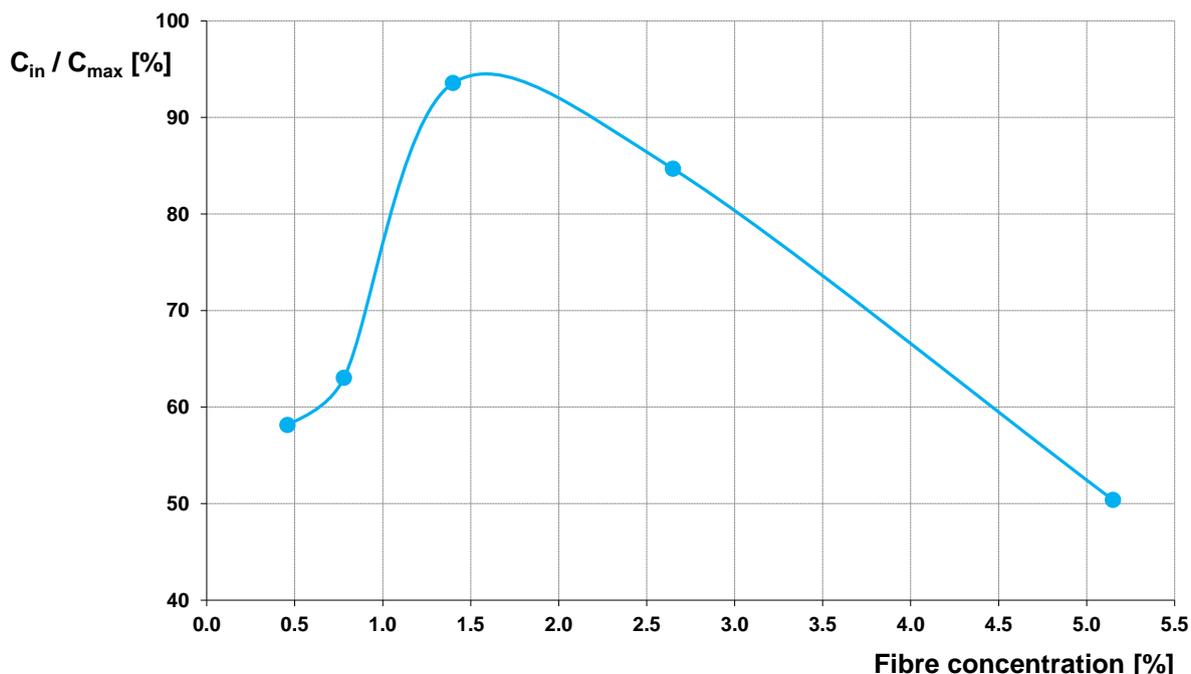


Figure 3. The course of the cell capacities with the cycle number

The electrode with 1.4% of glass fibres attained the highest capacity of 2.8 Ah, while that with 5.15% of glass fibres attained only 2.4 Ah. Two electrodes showed a higher initial capacity, evidence for a better formation. In the cited paper [5] the highest capacity attained electrode containing 0.78% of carbon and smallest capacity attained electrode containing 5.15% of carbon, the same content of additives, as in this work.

In Fig. 4 is shown the ratio of the initial capacity to its maximum value attained (“normalized capacity”, in %) as function of the fibre concentration. The capacity of the electrode with 1.4% of fibres was about 95% of its normalized value, evidence for the best formation. The worst result showed the electrode with 5.15% of fibres (about 50% of the normalized value). There is an interesting similarity between Figs. 2 and 4, *i.e.* between the diagram of the formation time (attainment of 2.6 V) and that of the initial normalized capacity (“quality of the formation process”). In other words, we may say that the quality of the formation process is proportional to the time after which the cell voltage attains 2.6 V. As soon as the voltage exceeds this value, the energy consumed in the formation process is prevalingly dissipated in the electrolysis of water.

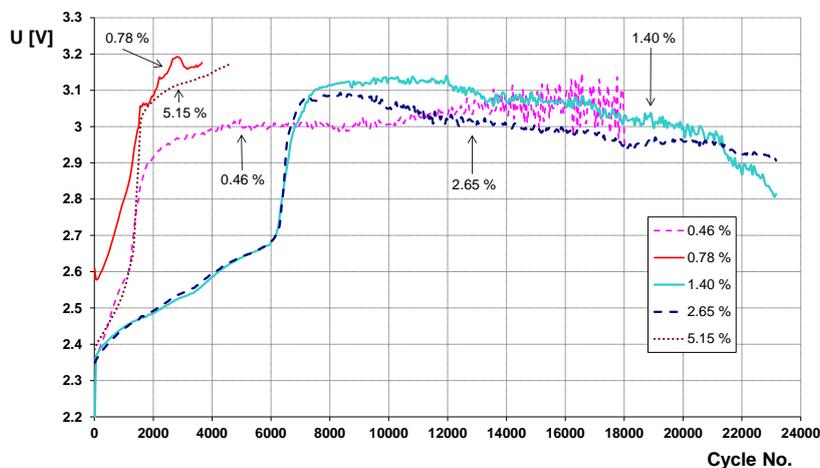


**Figure 4.** Dependence of the normalized capacity on the fibre concentration

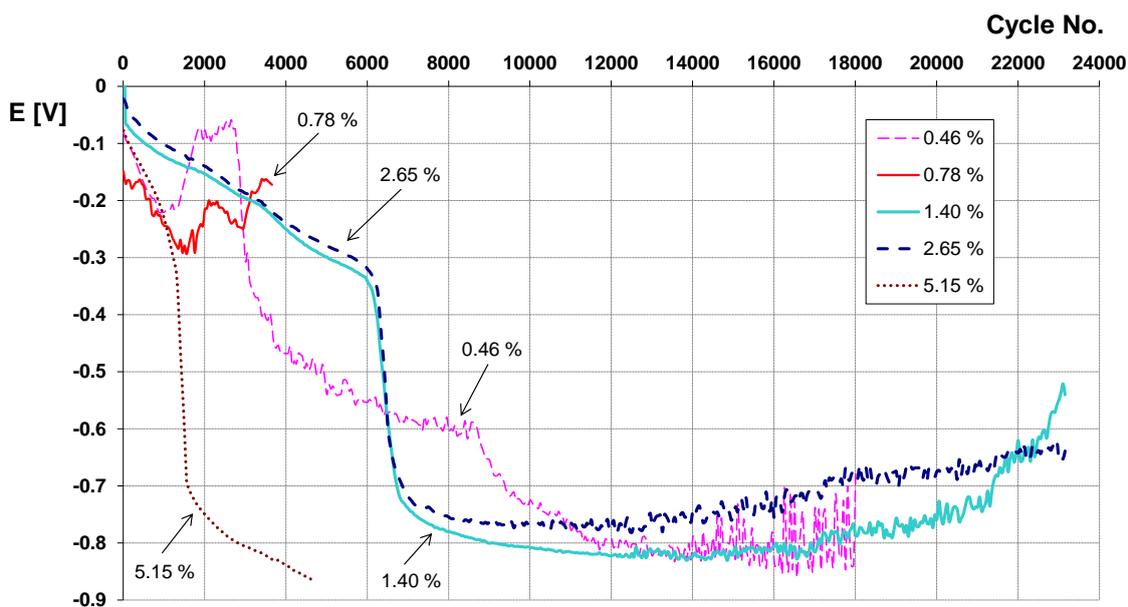
### 3.3. Accelerated PSoC cycling – first run

#### 3.3.1. Charging half-cycles

At the end of every 100th charging PSoC half-cycle, the cell voltage and the negative electrode potentials were recorded. The voltage values for the first PSoC run are shown in Fig. 5 and the potentials in Fig. 6. By comparison, it follows that the course of the cell voltage is given by the course of the negative electrode potential.



**Figure 5.** Dependence of cell voltage on the charging half-cycle number



**Figure 6.** Dependence of negative electrode potential on the charging half-cycle number

The initial cell voltage was between 2.35 – 2.40 V except for the electrode with 0.78% glass fibres. The voltage of the corresponding cell was by about 200 mV higher than normal, while the potential of the negative electrode was by about 100 mV higher without any significant rise during the experiment and the cell voltage increased by 600 mV. Apparently, the internal cell resistance was sensibly elevated. In the cited paper [5] higher initial cell voltage was found at the electrode with 5.15% of carbon.

Electrodes containing 0.46 and 5.15% of fibres show a rather rapid voltage rise during the first 2000 cycles, while the voltage rise of the other electrodes is somewhat delayed (after about 3500 or 6000 cycles). With the electrodes containing 1.4% and 2.65% fibres, there is even a slow voltage decrease after about 10 thousand cycles. This is apparently due to the starting oxygen cycle: the oxygen overpressure makes free pores in the separator thus facilitating the transport of oxygen to the negative electrode and lowering its potential.

### 3.3.2. Discharging half-cycles.

At the end of every 100th discharging PSoC half-cycle, the cell voltage and the negative electrode potentials were recorded. The voltage values for the first PSoC run are shown in Fig. 7 and the potentials in Fig. 8. By comparison, it follows that the course of the cell voltage is given by the course of the negative electrode potential.

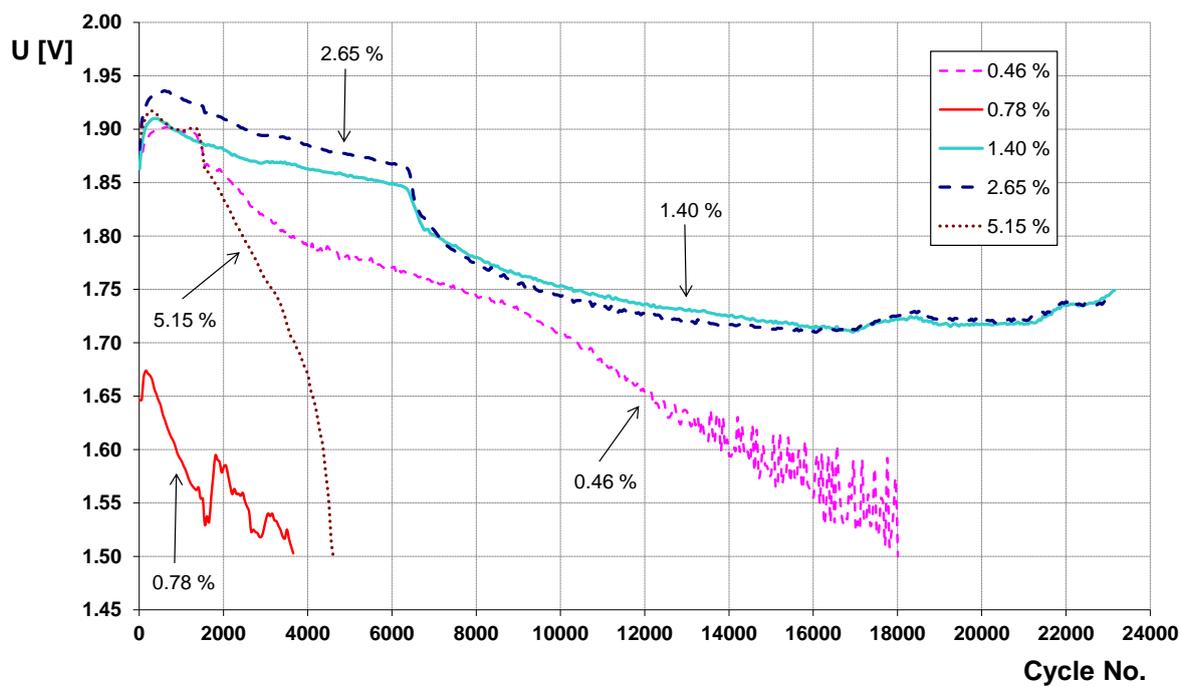


Figure 7. Dependence of cell voltage on the discharging half-cycle number

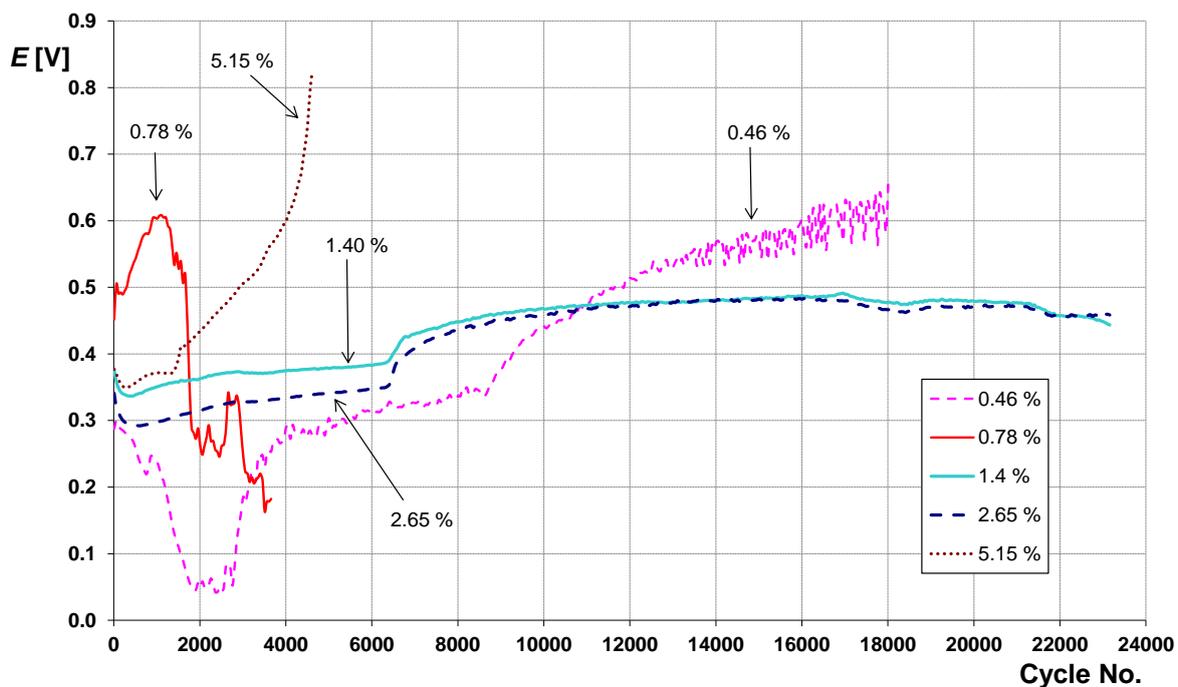
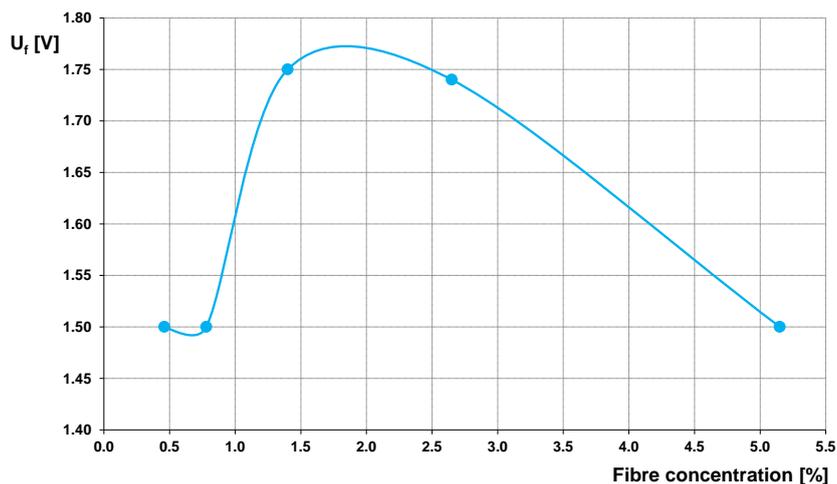


Figure 8. Dependence of negative electrode potential on the discharging half-cycle number

The voltage drop during discharge seems roughly to correspond with the steep rise to 3 V during charge (see Fig. 5). Both these phenomena (taking place nearly simultaneously) are probably related with hydrogen evolution at the negative electrode during charging half-cycles.

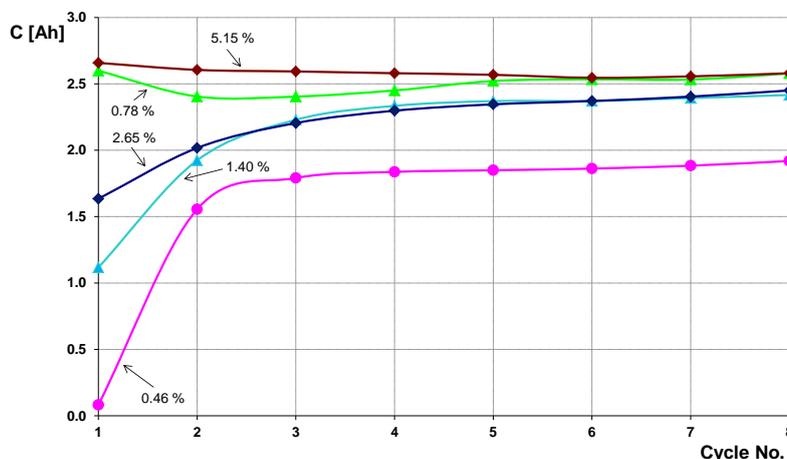
The electrode containing 5.15% fibres attains only 4000 cycles before the voltage drops. Such high concentrations of doping agents were found noxious also in our preceding work – see paper [5]. A comparison of the cycle life of electrodes in the first run of PSoC cycling with various concentrations of glass fibres is shown in Fig. 9. Hence, the most favorable concentrations seem to be in the interval 1.5 – 2.5%. In the cited paper [5] the most favorable concentration was at the electrode with 0.78% of carbon, which reached the highest cycle life from all measured electrodes.



**Figure 9.** Dependence of the final voltage on the concentration of glass fibres

### 3.4. Conditioning cycles – second run

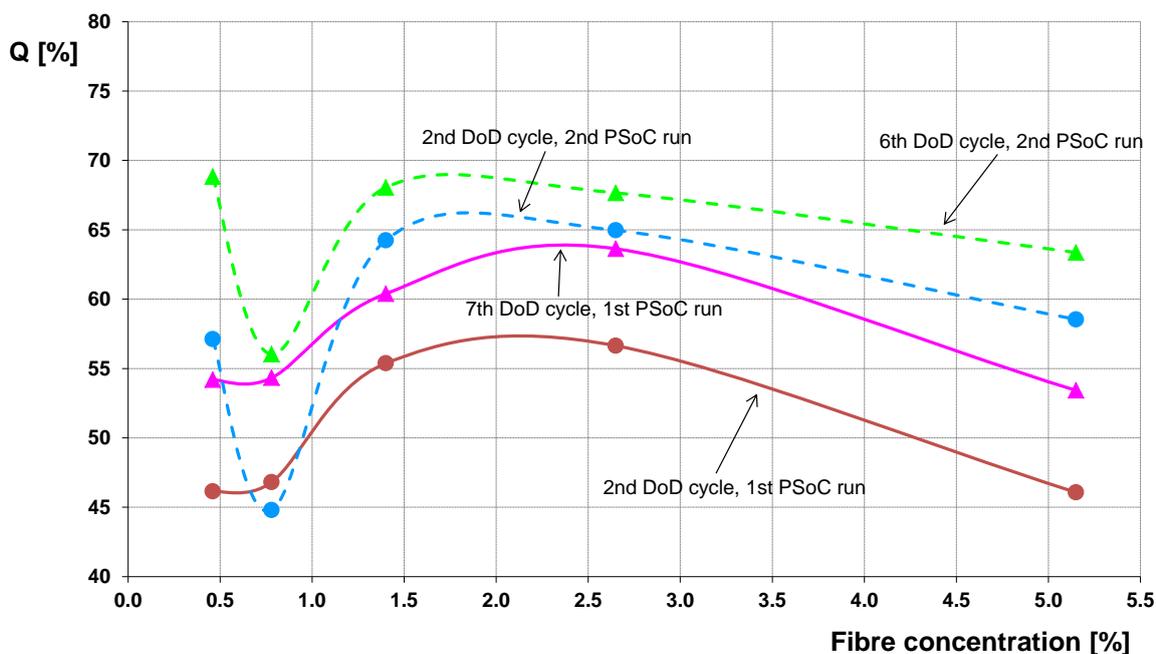
The courses of the capacities of the individual cells are shown in Fig. 10.



**Figure 10.** The course of the cell capacities with the cycle number

The cells with 0.78% and 5.15% additive were at the maximum capacity since their cycle life was ended at the first PSoC run (their voltage dropped below 1.5 V), so they were automatically charged by the electronic system used. The other cells showed a capacity increase that was especially conspicuous during the first two cycles.

To compare the second run of the conditioning cycling with the first one, all the results are shown graphically in Fig. 11. It can be seen that the charge acceptance in the second run was much better, possibly owing to an improvement of the internal structure of the electrodes. The poor results attained by the electrode with 0.78% of glass fibres are due to the anomalous internal cell resistance mentioned above. In the cited paper [7] it was measured the charge acceptance at the electrodes containing 1% of carbon and at the electrodes containing 1% of TiO<sub>2</sub>. At the electrodes with carbon addition the charge acceptance was about 80% and at the electrodes containing TiO<sub>2</sub> it was about 65%, as in this work at the electrodes containing 1.4% and 2.65% of glass fibres.



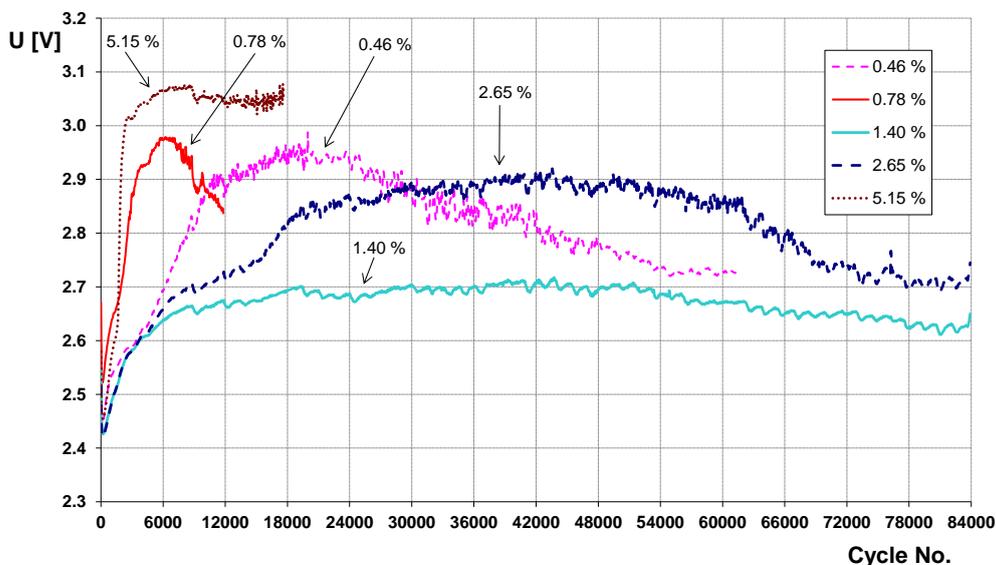
**Figure 11.** Charge accepted for both runs of the conditioning cycling

### 3.5. PSoC cycling – second run

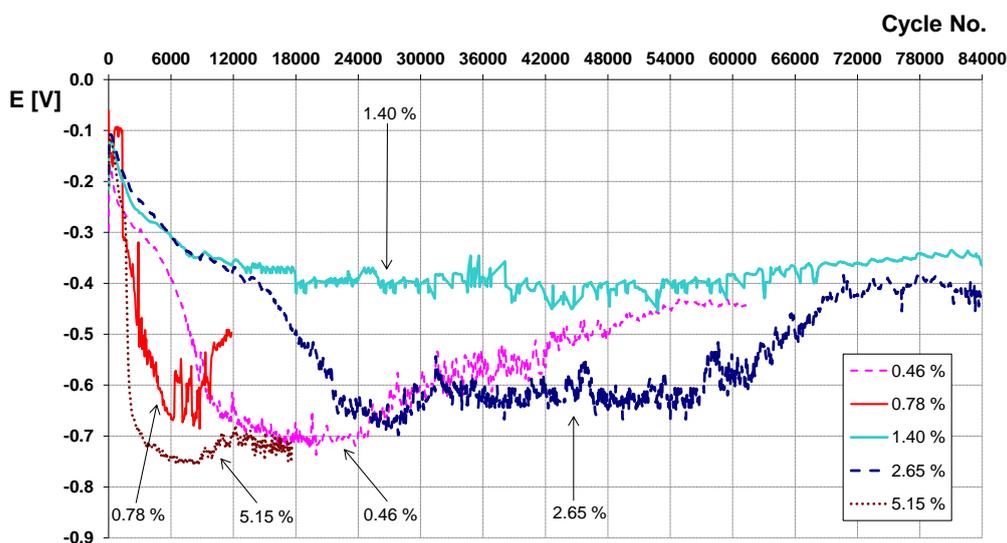
#### 3.5.1. Charging PSoC half-cycles.

The curves of the voltage and potential measured during the charging half-cycles are shown in Figs 12 and 13, respectively. It can be seen that the potential curves correspond to the curves of the voltage. For the electrodes containing 0.78 and 5.15% of glass fibres, the voltage increases abruptly during the first 2000 cycles up to 3 V. The electrode with 1.4% glass fibres performs best keeping the voltage of 2.6 – 2.7 V. Similar results were obtained in the cited paper [7] at the electrodes containing 1% of carbon and at the electrodes containing 1% of TiO<sub>2</sub>, where the similar voltage was achieved by

pressure from 2 to 6 N/cm<sup>2</sup> applied on the negative active mass. This is probably due to a better charge acceptance (Fig. 11) as well as to a more intense oxygen cycle that lowers the potential of the negative electrode (causing a lower cell voltage).



**Figure 12.** Dependence of the cell voltage on the charging half-cycle number



**Figure 13.** Dependence of negative electrode potential on the charging half-cycle number

### 3.5.2. Discharging PSoC half-cycles.

The second run of PSoC cycling lasted for more than three times as long as the first one. The cycle life of the cells was again given by the 1.5 V cut-off voltage. The discharge characteristics are shown in Figs 14 and 15.

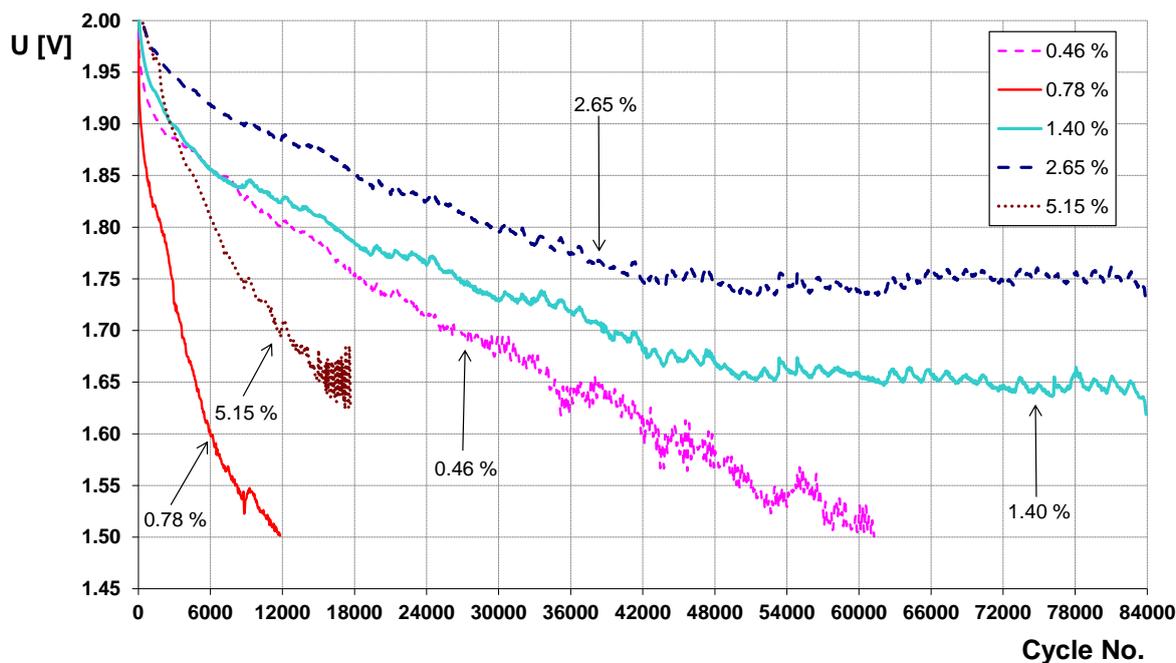


Figure 14. Dependence of cell voltage on the discharging PSoC half-cycle number

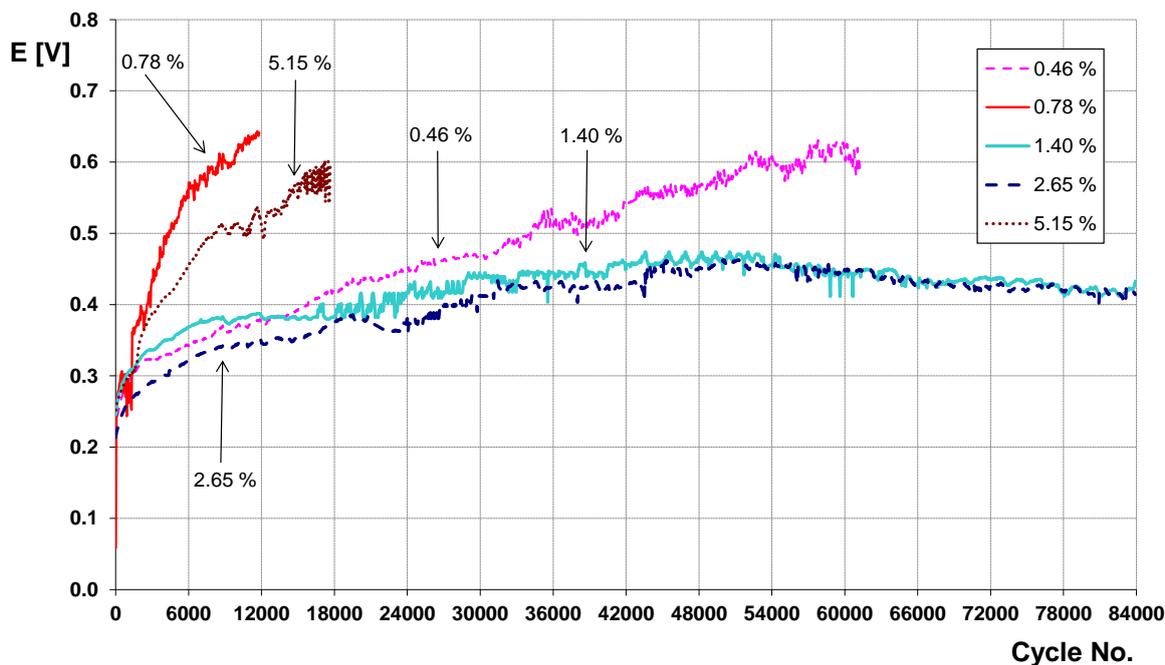
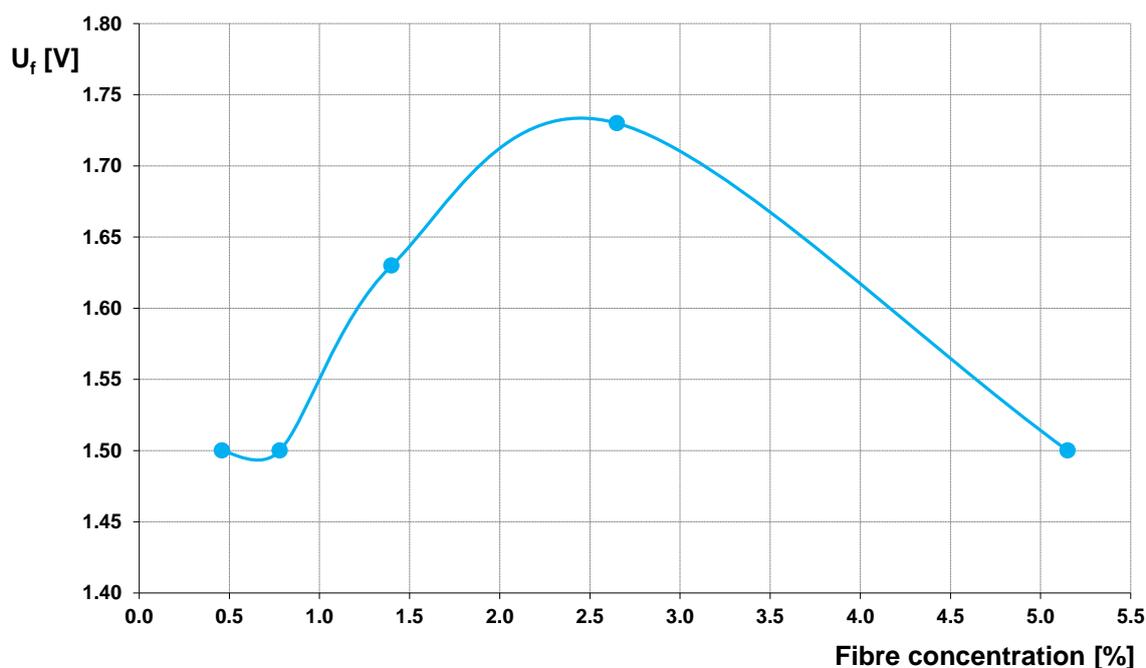


Figure 15. Dependence of negative electrode potential on the discharging half-cycle number

The shortest cycle life, due to the cells with 0.78 and 5.15% glass fibres (resembling the first run) was now equal to 12 and 18 thousand cycles, respectively, evidence for a lower internal cell resistance. The highest concentration of the additive, of course, causes a hindrance of the transport

processes. It is remarkable that the electrodes with 1.4, and 2.65% additive were still in good condition even after 84,000 accelerated PSoC cycles. Their positive properties were observed during formation, conditioning cycling, as well as during accelerated PSoC cycling. In the cited paper [5] the most favorable concentration in the second PSoC run was at the electrode with 0.78% of carbon and its cycle life increased, when compared to the first PSoC run, as in this paper. The worst cycle life in the cited paper [5] was at the electrode with 5.15% of carbon.

In Fig. 16 is shown the dependence of the voltage at the end of the second run on the glass fibre concentration. The course of the curve resembles that of Fig. 9, evidence that the basic properties of the electrodes doped with glass fibres (including the mentioned three best ones) were in both runs similar although their cycle life was much longer in the second run.



**Figure 16.** Dependence of the final voltage on glass fibre concentration in the second run

The favorable properties of the electrodes with 1.4, and 2.65% glass fibres are manifested during the formation, conditioning cycling, as well as during the accelerated PSoC cycling.

### 3.5.3 Measurement of contact resistance and active mass resistance.

During the second PSoC run, we measured the contact resistance and active mass resistance of the negative active electrode using our original method [6]. The two electrodes attaining the best performance (with 1.4, and 2.65% of glass fibres) showed practically constant contact resistance (1 m $\Omega$ ) and active mass resistance (0.5 m $\Omega$ ) in the course of 78 thousand cycles. Both the two resistances of the electrodes with poor performance (with 0.46, 0.78, and 5.15% of glass fibres), on the other hand, showed an early steep increase in the course of several thousand cycles and thus indicating the end of

cycle life. In our preceding work with electrodes containing powdered carbon under mechanical pressure [7], the cycle life exceeded 100 thousand cycles, without essential increase of contact resistance and active mass resistance.

#### 4. CONCLUSIONS

Microscopic glass fibres as doping agent in negative lead acid electrodes cause nearly the same effect as carbon or titanium dioxide in prolonging the cycle life during partial state of charge in hermetic regime. Results indicate more uniform active mass utilization and reduction of degradation mechanisms in the surface area of negative active mass structure during PSoC regime. This is reflected in increase of cycle life of negative electrodes cycled in high-rate, partial-state of charge cycling. The optimum amount of glass fibres in the negative active mass seems to be between 2 and 3 wt. %.

#### ACKNOWLEDGEMENTS

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