

SIGNIFICANCE OF CARBON ADDITIVE IN NEGATIVE LEAD-ACID BATTERY ELECTRODES

P. Bača¹, P. Křivák¹, M. Calábek¹, K. Míčka²

¹ *Institute of Electrotechnology, Technical University of Brno, 602 00 Brno*

² *J. Heyrovský Institute of Physical Chemistry, 182 23 Prague 8, Czech Republic*

Introduction

Lead-acid batteries suffer from sulfation of negative electrodes when allowed to stand in the partial state of charge (PSoC) for a longer time, which occurs mainly in hybrid electric vehicles (HEV). This phenomenon is commonly attributed to recrystallization of the lead sulphate formed during discharge, whereby its originally fine crystals become larger. A solution of this problem was proposed by Japanese authors [1, 2] who investigated the influence of small additions of some sorts of carbon into the negative paste. In spite of many experiments, the mechanism of this effect is still not clear. The authors [1, 2] attributed the beneficial affect of carbon to the formation of conducting bridges of carbon particles surrounding the sulphate crystals, as documented by SEM microphotographs. However, a question arises why a similar problem was not observed with the positive electrodes, which contain no carbon.

Some authors [3] observed that the addition of graphite to the negative active mass in the unformed state improved sensibly its conductivity, and they supposed that a similar effect might take place even in the active mass after formation, especially if the electrode is strongly sulphated. We investigated the resistance of the negative active mass both in the charged and discharged states at various mechanical pressures and at increasing numbers of charge-discharge cycles [4]. The resistance of the active mass between two neighbouring ribs was below 1 mΩ, the differences between the values in the charged and discharged states being within experimental errors. In view of these facts, any attempts to improve the conductivity of the negative active mass by the addition of graphite would obviously have no sense.

Since the solubility of lead sulphate in the electrolyte used is very low (about 10^{-6} molar), its dissolution cannot play any significant role. The cathodic reaction site is apparently the contact between lead sulphate and the electron conductor [5] as in analogous battery electrode reactions. Naturally, the efficiency of this process is low when the sulphate crystals are larger than a few micrometers. With positive electrodes, this presents almost no problem since their pores (in the charged state) are very small, most of them being in the range from 0.05 to 2 μm [6, 7], and so the sulphate crystals are limited in their growth [6]. But with negative electrodes, the pores are sensibly larger as follows from the fact that their specific BET surface area is only 0.5 - 0.8 m²/g [8], in contrast to that of the positives, 6.4 m²/g [6]. By adding finely powdered graphite to the negative active mass, the pores will more or less be occupied by the graphite particles, whereby the lead sulphate crystal

Corresponding author: Petr Bača

E-mail: baca@feec.vutbr.cz

Phone: +420 541 146 188, Fax: +420 541 146 147

growth will be disturbed. Thus, the crystals will remain small even during standing. If this reasoning is correct then the effect of graphite has nothing to do with electric conductivity, and non-conducting substances can be used instead.

Experimental

Test cells were assembled from two positive electrodes of dimensions 55×20×7 mm and a thinner negative test electrode in between of dimensions 55×20×2 mm. The active mass of commercial provenience was pasted on lead grids of composition Pb Ca 0.2 Sn 0.5. Two sorts of additives were used in the negative active mass: either powdered graphite of about 4 µm nominal particle size, or pure titanium dioxide of particle size 1 – 3 µm according to SEM microphotograph. The initial capacity of the test electrodes after formation was about 1.5 Ah.

The test cells were subjected to accelerated cycling in PSoC (to 50%) regime. During the experiment, the current for discharging as well as for charging was 1 A. The time of discharge was 10 s followed by 2 s standing, then the cells received the same charge as in the preceding discharge. After 2 s standing they were again discharged and so on until the cell voltage after discharge dropped to 1.6 V. Samples of the negative electrodes at the end of their cycle life were taken for examination with the environmental scanning electron microscope (ESEM). To prevent oxidation with the air, there were kept wetted with the electrolyte.

Results and Discussion

The course of the cell voltage during cycling is shown in Fig. 1. for cells containing negative electrodes with different additives. The highest cycle life was attained by the cell with negative electrode containing 2.5% TiO₂, namely 205,000 cycles, and by that with 2.5% graphite, namely 197,000 cycles. The content of 5% TiO₂ is less favourable probably owing to blocking of some pores with the excess additive. Lesser amounts of the additives (e.g. 0.5 or 1 % C) are apparently not sufficient to occupy the larger pores in the negative electrode, so the lead sulphate crystals can, in the course of the experiment, grow to larger sizes causing a drop in the electrode performance. At any rate, it would be desirable to continue this research since the curves in Fig. 1 show some anomalies. At this stage, it seems that the graphite additive can be replaced by titanium dioxide with equally good results, hence that the effect of graphite is not due to electric conductivity.

Of the ESEM microphotographs taken, in Fig. 2 is shown a microphotograph of the discharged negative electrode without additive. Crystals or agglomerates of lead sulphate of dimensions up to 20 µm can be seen (more agglomerates were found at a lower magnification).

A similar figure 3 shows an electrode with 2.5% TiO₂. Here, the size of the sulphate crystals is only up to 5 µm. Finally, a discharged electrode with 2.5% graphite is shown in Fig. 4 where the size of the sulphate crystals is up to 10 µm.

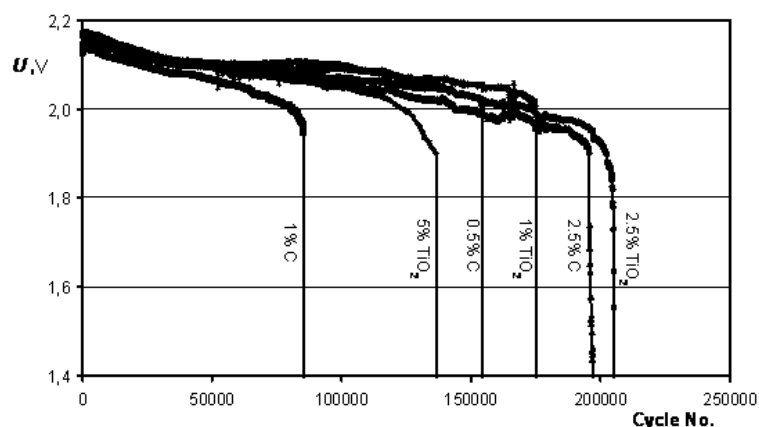


Fig. 1 Dependences of the cell voltage, U , on the number of accelerated cycles in the PSoC regime for six negative test electrodes with different additives.

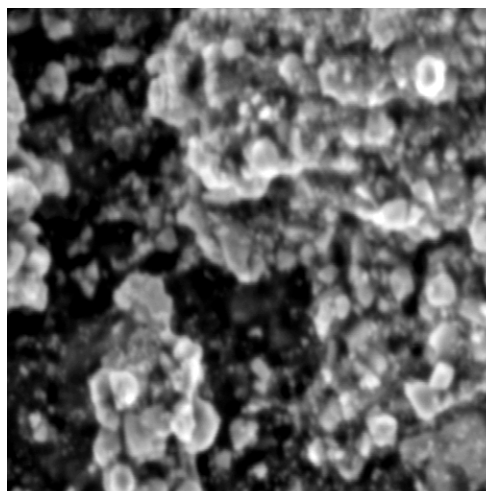
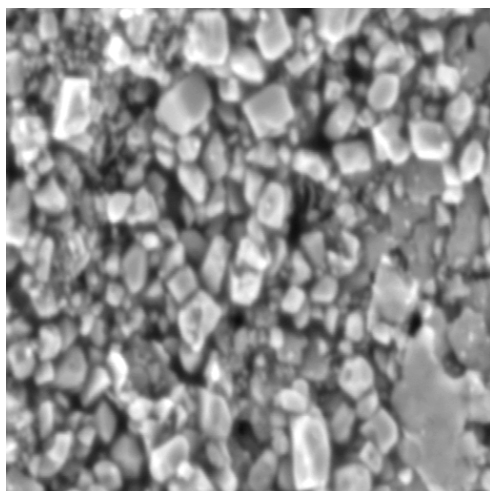


Fig. 2 (left) Microphotograph of the negative electrode without additive at the end of its cycle life. The base of the square corresponds to 75 μm .

Fig. 3 (right) As Fig. 2 but with 2.5% of titanium dioxide as additive.

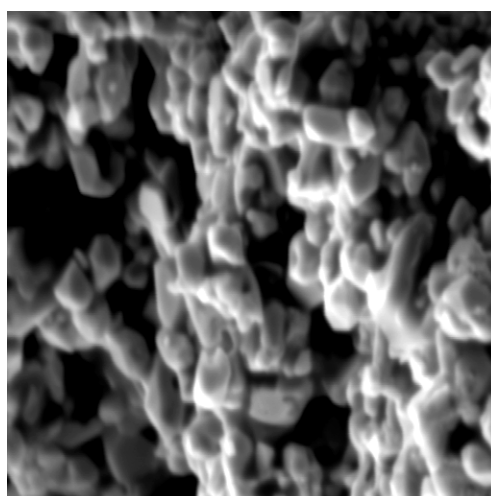


Fig. 4 As Fig. 2 but with 2.5% graphite as additive.

Although the quality of these pictures (owing to the presence of the electrolyte) is not so good as with the classical SEM method, it can be seen that some limitation of the crystal size due to the additives indeed exists. This observation may elucidate the improvement of the cycle life by the additives used. Further experiments in this direction are in progress.

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