

Short communication

Significance of carbon additive in negative lead-acid battery electrodes

M. Calábek^a, K. Micka^{b,*}, P. Křivák^a, P. Bača^a

^a Department of Electrotechnology, Technical University, 602 00 Brno, Czech Republic

^b J. Heyrovský Institute of Physical Chemistry, 182 23 Prague 8, Czech Republic

Available online 20 December 2005

Abstract

Improvement of the cycle life of negative lead-acid battery electrodes in the partial state of charge regime can be achieved not only by the addition of graphite to the active mass but also by the addition of titanium dioxide. The experimental results have been attributed to hindrance of the crystal growth of lead sulfate deposited in the electrode pores.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Negative lead battery electrode; Cycle life; Graphite additive; Titanium dioxide additive

1. 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 sulfate formed during discharge, whereby its originally fine crystals become larger. VRLA batteries are especially apt to loose capacity by this process since part of the charging current is consumed in the “oxygen cycle”, i.e. oxygen evolved at the positive electrodes is reduced to water at the negative electrodes [1,2].

The solution of this problem was attempted by many authors; apparently the easiest way would be the application of charging pulses which should minimize the formation of the “hard sulfate” [3,4]. In recent years, however, more attention is paid to the discovery of Japanese authors [5,6] who investigated the influence of small additions of certain (not specified) sorts of carbon into the negative paste and found a favourable effect on the hindrance of sulfation. This idea was further elaborated by a research team sponsored by ALABC [7]. They found that additions of up to 2% of carbon black or – still better – powdered graphite into the negative paste indeed hinder sulfation of negative electrodes.

In spite of many experiments, the mechanism of this effect is still not clear. Nakamura et al. [5] performed thorough laboratory tests of standard VRLA cells and found, after 400 simulation cycles, 20% of sulfate in positive plates and about 40% in the negatives. While the former *could be recharged*, the latter showed 20% of sulfate after charging. On increasing the carbon content in the negative paste ten times, the cells withstood 1100 simulation cycles; the final sulfate content in the negatives was 30%, and after charging only 10%. (Probably, they used carbon black whose standard content in the negative paste is 0.2% [8].) The authors [5,6] attributed the beneficial affect of carbon to the formation of conducting bridges of carbon particles surrounding the sulfate crystals, as documented by SEM microphotographs. This concept would imply that the sulfate crystals are too large for the dissolution mechanism to proceed at a sufficient rate, so more conducting paths must be created to bring the electrons closer to the crystal surface. However, a question arises why a similar problem was not observed with the positive electrodes, which contain no carbon.

Some authors [7] 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 sulfated. We investigated extensively the resistance of the negative electrode active mass both in the charged and discharged states at various mechanical pressures and at increasing numbers of charge–discharge cycles [9]. The resistance of the active mass between two neighbouring ribs

* Corresponding author. Tel.: +420 266 053 287; fax: +420 286 582 307.
E-mail address: micka@jh-inst.cas.cz (K. Micka).

ranged from 0.2 to 0.5 m Ω , the differences between the values in the charged and discharged states being within experimental errors. (For comparison, the values for the positive electrodes were 7–8 m Ω in the charged state and 20–50 m Ω in the discharged state.) In view of these facts, any attempts to improve the conductivity of the negative active mass by the addition of graphite (a far less conductor than lead) would obviously have no sense.

Electrode processes in lead-acid batteries have traditionally been discussed in terms of the dissolution–precipitation mechanism [10–12]. This is well possible in the case of discharge, where a supersaturated sulfate solution is formed, followed by nucleation and crystallization. However, the charging process would require a sulfate solubility of the order of 10⁻⁵ molar [10], whereas in the accumulator electrolyte, this value is an order of magnitude lower. Hence, it appears that diffusion transport is of minor importance in this case and that the reaction site is the contact between lead sulfate and the electron conductor [12] as in analogous cases of the battery electrode reactions. Naturally, the efficiency of this process is low when the sulfate 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 [13,14], and so the sulfate crystals are limited in their growth [13]. With negative electrodes, the pores are sensibly larger as follows from the fact that their specific BET surface area, 0.5–0.8 m² g⁻¹ [15], is an order of magnitude lower than with the positives, 6.4 m² g⁻¹ [13]. This means that the lead sulfate crystals have more space available for their growth by recrystallization when the battery stands without current load or in the PSoC regime.

By adding finely powdered graphite to the negative electrode, the larger pores will more or less be occupied by the graphite particles, whereby the lead sulfate crystal 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 nonconducting substances can be used instead. Experiments to support this conclusion form the subject of the present work.

2. Experimental

Test cells were assembled from two positive electrodes of dimensions 55 mm \times 20 mm \times 7 mm and a thinner negative test electrode in between of dimensions 55 mm \times 20 mm \times 2 mm. The active mass of commercial provenience (AKUMA, Mladá Boleslav, Czech Republic) was pasted on lead grids of composition Pb Ca0.2 Sn0.5 (mass%). The initial capacity of the test electrodes was about 1.5 Ah. The electrodes were separated by a HOVOSORB BG089GB056 type glass mat separator (square density 89 g m⁻², 0.56 mm thick). The assembled electrodes were immersed in standard accumulator cases with an excess of sulfuric acid of 1.28 g cm⁻³ density (without mechanical pressure).

Two sorts of additives were used in the negative active mass: either powdered graphite of the type CR 2996 (Maziva Týn/Vlt., Czech Republic) of about 4 μm nominal particle size

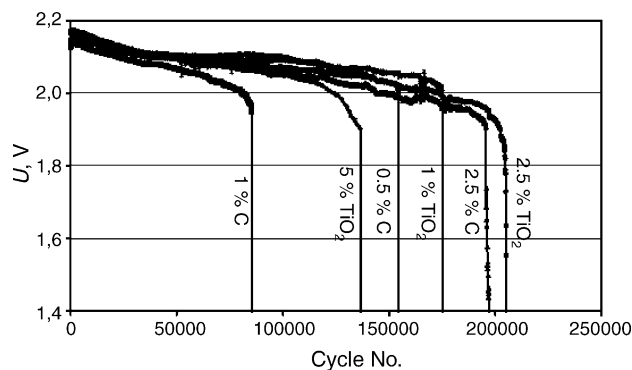


Fig. 1. Dependences of the cell voltage, U , on the number of accelerated cycles in the PSoC regime for six negative test electrodes with different additives.

and 13 m² g⁻¹ specific surface area, or pure titanium dioxide (Lach-Ner s.r.o., Czech Republic) of particle size 1–3 μm according to SEM microphotograph.

The cells were left for an hour on open circuit and afterwards subjected to formation by 4 h charging with a current of 0.2 A, 2 h standing on open circuit, in total 72 h charging and 36 h standing. Afterwards ten formation cycles were carried out as follows: discharge at 0.5 A, charge at 0.5 A with voltage limitation to 2.45 V, i.e. two cycles daily.

Accelerated cycling in PSoC regime: Prior to the experiment, the cells were discharged to 50% of their capacity. 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, the cells were charged to 100% (i.e. they received the same charge as in the preceding discharge), after 2 s standing they were again discharged and so on. In this way, up to 205,000 cycles were carried out 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, they were kept wetted with the electrolyte.

3. 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 sulfate crystals can, in the course of the experiment, grow to larger sizes causing a drop in the electrode performance. Measurement of the electrode resistance in situ with our method [16] would cause periodic interruptions of the experiment. 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

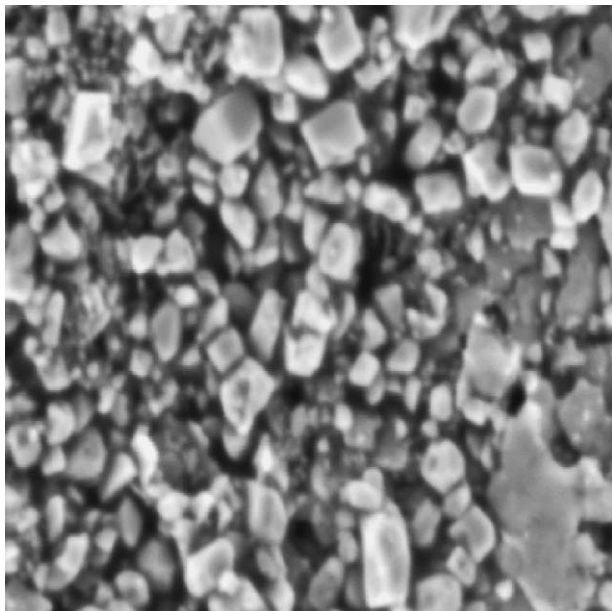


Fig. 2. Microphotograph of the negative electrode without additive at the end of its cycle life. The base of the square corresponds to 75 μm .

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 in accord with the idea outlined in Section 1.

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

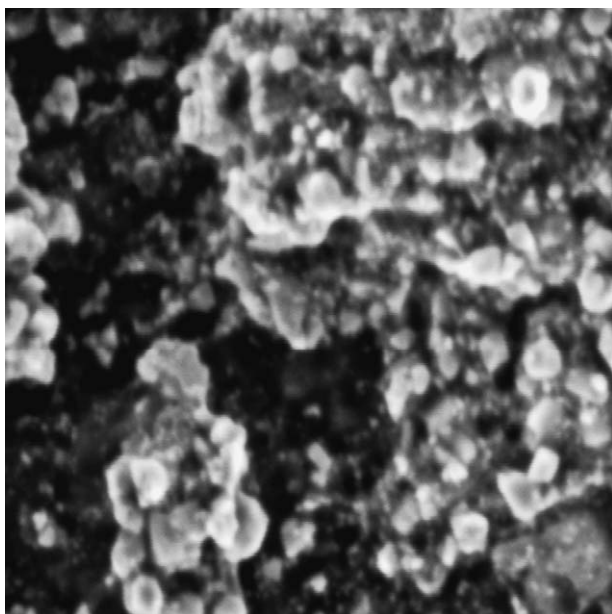


Fig. 3. Microphotograph of the negative electrode with 2.5% of titanium dioxide as additive at the end of its cycle life. The base of the square corresponds to 75 μm .

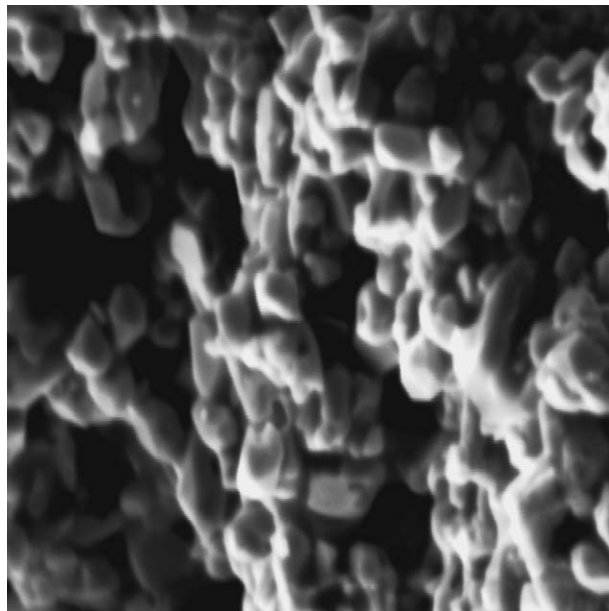


Fig. 4. Microphotograph of the negative electrode with 2.5% of graphite as additive at the end of its cycle life. The base of the square corresponds to 75 μm .

A similar Fig. 3 shows an electrode with 2.5% TiO_2 but here, the size of the sulfate 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 sulfate crystals is up to 10 μm .

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.

References

- [1] B. Culpin, D.A.J. Rand, *J. Power Sources* 36 (1991) 415.
- [2] A. Cooper, P.T. Moseley, *J. Power Sources* 113 (2003) 200.
- [3] L.T. Lam, C.G. Phyland, D.A.J. Rand, A.J. Urban, ALABC Project No. C 2.0, Progress Report, August 2001–January 2002.
- [4] L.T. Lam, N.P. Haigh, C.G. Phyland, Presented on the 9ELBC, Berlin, September 2004.
- [5] K. Nakamura, M. Shiomi, K. Takahashi, M. Tsubota, *J. Power Sources* 59 (1996) 153.
- [6] M. Shiomi, T. Funato, K. Nakamura, K. Takahashi, M. Tsubota, *J. Power Sources* 64 (1997) 147.
- [7] A.F. Hollenkamp, W.G.A. Balasing, O.V. Lim, R.H. Newnham, D.A.J. Rand, J.M. Rosalie, D.G. Vella, L.H. Vu, ALABC Project No. N 1.2, Annual Report, July 2000–June 2001.
- [8] F. Saez, B. Martinez, D. Marin, P. Spinelli, F. Trinidad, *J. Power Sources* 95 (2001) 174.
- [9] M. Calábek, K. Micka, P. Bača, P. Křivák, L. Šácha, ALABC Project No. AMC-10, Final Report, October 1995–September 1997.
- [10] K.J. Vetter, *Chem. Ing. Techn.* 45 (1973) 213.
- [11] N.A. Hampson, J.B. Lakeman, *J. Power Sources* 6 (1981) 101.
- [12] Z. Takehara, *J. Power Sources* 85 (2000) 29.

- [13] P. Ekdunge, D. Simonsson, in: K.R. Bullock, D. Pavlov (Eds.), *Proceedings of Advances in Lead-Acid Batteries*, The Electrochem. Soc., Inc., Pennington, NJ, 1984, p. 252.
- [14] A. Tokunaga, M. Tsubota, K. Yonezu, K. Ando, in: K.R. Bullock, D. Pavlov (Eds.), *Proceedings of Advances in Lead-Acid Batteries*, The Electrochem. Soc., Inc., Pennington, NJ, 1984, p. 314.
- [15] K. Míčka, I. Roušar, *Electrochim. Acta* 21 (1976) 599.
- [16] M. Calábek, K. Míčka, P. Bača, P. Křivák, V. Šmarda, *J. Power Sources* 62 (1966) 161.