

THE EFFECT OF THE ADDITIVE IN LEAD-ACIDS ACCUMULATORS FOR USING IN HEV APPLICATIONS

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ABSTRACT

For application lead-acid accumulators in hybrid electric vehicles shows necessity to watch action of storage battery in regime fast cycling PSOC (Partial State Of Charge), when happen to rise new mechanism disfunctions. These are mostly giving to the connection with irreversible sulphation above all negative electrode. 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 , glass fibers. The experimental results have been attributed to hindrance of the crystal growth of lead sulfate deposited in the electrode pores.

1. INTRODUCTION

Starter batteries nor present generation deep-cycle batteries are able to perform the duty required by the new, high-power, automobile systems for an acceptable life. Batteries for these high-power systems will operate from a partial-state-of-charge baseline and will be discharged, and particularly re-charged, at extraordinarily high rates (albeit within a small range of state-of-charge). Within such duty, the life-limiting mechanism appears to involve the progressive accumulation of lead sulfate on the negative plate. This failure mode appears as a result of the very high rates of recharge and persists because the battery is not routinely returned to a full state-of-charge in the required duty.

In order to offer an acceptable life in such applications, conventional designs of VRLA batteries must be revised. The battery must be able to sustain the negative plate charge reaction at very high rates, overcoming diffusion limitations (leading to reduced lead sulfate solubility etc.) which would otherwise lead to the onset of secondary reactions, such as hydrogen evolution, and charge inefficiency.

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 cur-

rent 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 “hardsulfate” [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].

2. ANALYSIS

Test cells were assembled from two positive electrodes of dimensions 55mm×20mm×7mm and a thinner negative test electrode in between of dimensions 55mm×20mm×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 gm⁻², 0.56mm 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).

Three sorts of additives were used in the negative active mass: either powdered graphite of the type CR 2996 (Maziva Týn/Vlt., Czech Republic), TiO₂ (Lachema a.s., Czech Republic) and glass fibers (Hollingsworth & Vose Copany., United States of America).

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 0.5A with voltage limitation to 2.45V, 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 were carried out until the cell voltage after discharge dropped to 1.6V. Samples of the negative electrodes at the end of their cycle life were taken for examination with the optical microscope.

2.1. PROCESS EXPERIMENT

We have measured our self-made electrodes in our experiment. (two types of set-up)

1. experiment

We apply Grafite and TiO₂ as an additive to negative electrode. Fig. 1 show graf of a voltage in different cycles. Scan rate of cycling decrease in subsequent cycles. It can explain degradation of electrode. (Voltage get down under 1.6V). The flooded type of accumulators are independent type and quantity of the additives.

2.experiment

We measured VRLA type of the accumulators. We apply the same type of additives (grafite, TiO₂) than foregoing experiment. (see fig.2).

We suppose a positive electrode effect of the additives on the mechanical character. Dendrite centers decrease crystallization of $PbSO_4$ which negative influence the discharge process in accumulators. The quantity and grain crystals of $PbSO_4$ are more effective decompose in active material.

3.experiment

In the third experiment we tried to find which effect will occur in electrode lifetime when we add glass fibres. Cells with glass fibres come up to less cycles compared to other additives. You can see it in fig.3. Evidently it is caused by not optimal shape of glass fibres added to the active mass.

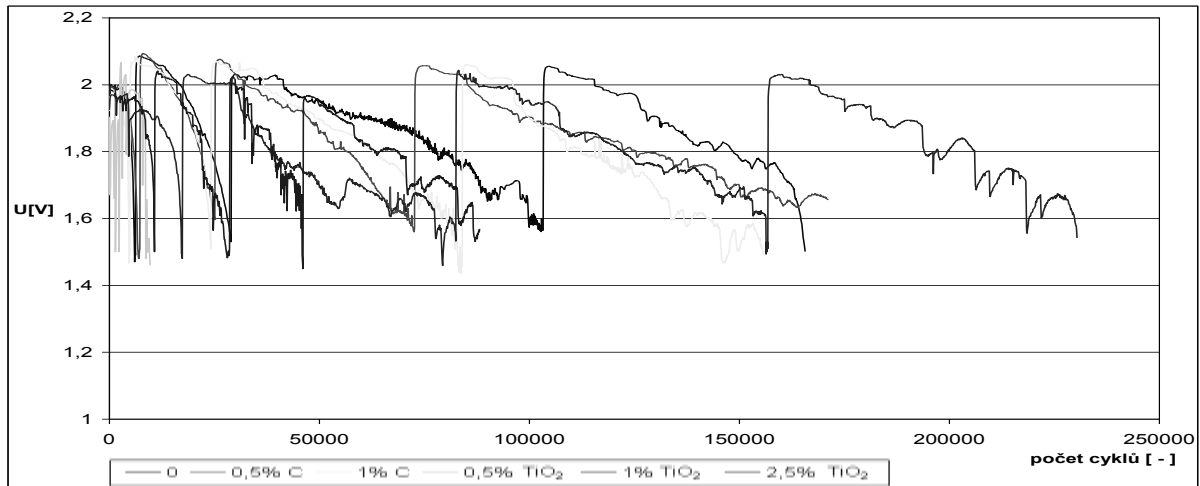


Fig. 1: Voltage on cells versus on cps as measured by at the end battery discharge for experiment flooded type with additive TiO_2 and graphite.

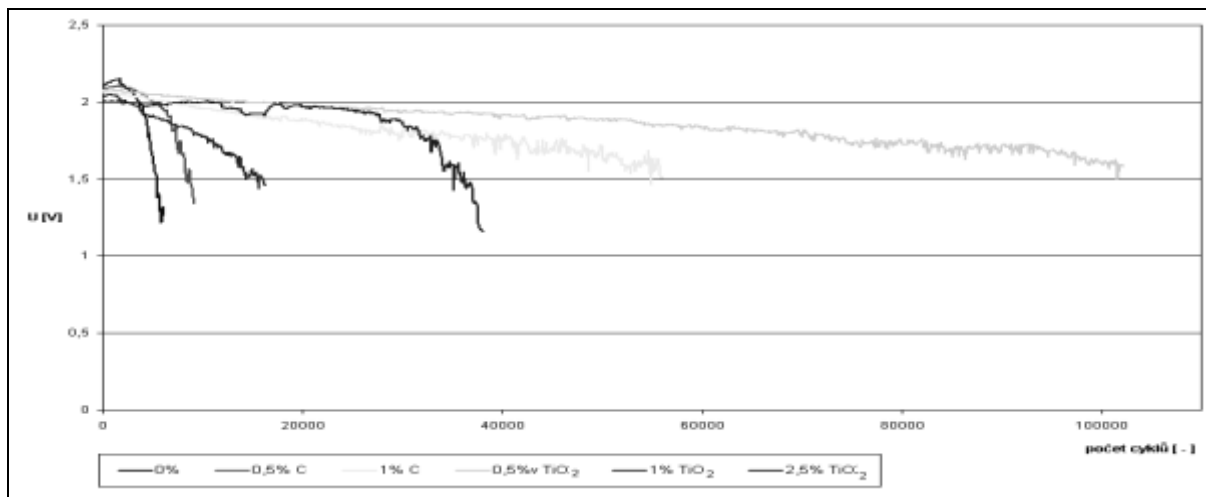


Fig. 2: Voltage on cells versus on cps as measured by at the end battery discharge for experiment VRLA type with additive TiO_2 and graphite.

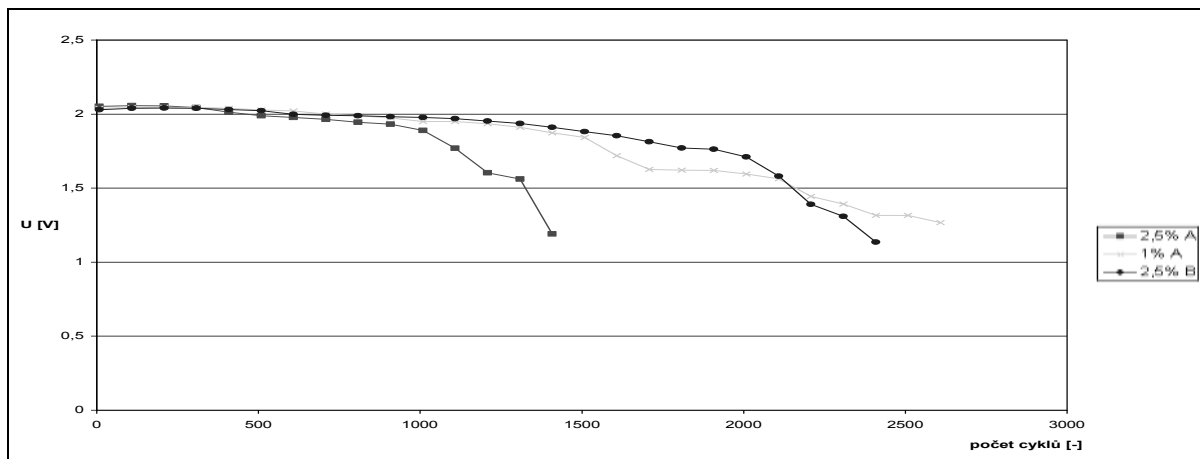


Fig. 3: Voltage on cells versus on cps as measured by at the end battery discharge for experiment flooded type with additive glass fibres.

3. CONCLUSIONS

We did not recognize any fundamental difference between negative electrode doped by graphite or by TiO₂ in flooded type. We have proved positive influence of additives (graphite and TiO₂) in VRLA cells in negative active mass. Cells with glass fibres achieve markedly less number of cycles compared to other additives. At first during cycling the number of cycles grows and then when accumulator reaches end of its life the number of cycles declines. Here interfere two diametric mechanisms - at the beginning of life of negative electrode surface of active mass increases but when the accumulator is near its end of life mechanical consistency and electric characteristics of active mass get worse.

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