Journal of Energy Storage 17 (2018) 336–344

Contents lists available at ScienceDirect

Journal of Energy Storage

journal homepage: www.elsevier.com/locate/est

Benzyl benzoate as an inhibitor of the sulfation of negative electrodes in lead-acid batteries☆

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ARTICLE INFO

Keywords:
Lead-acid batteries
Negative paste additive
Additive to electrolyte
Sulfation
Benzyl benzoate

ABSTRACT

The lead sulfate crystals formed on the surface of the negative electrodes of lead-acid batteries during discharge gradually grow in size as a result of recrystallization processes. The big $PbSO_4$ crystals have low solubility and are involved but very slightly in the charge process, thus causing progressive sulfation of the negative electrodes on cycling. In order to reduce or suppress this sulfation, the processes of $PbSO_4$ recrystallization should be inhibited.

It has been established that, besides lignosulfonates, some organic substances, too, may be used as additives to the negative active material to effectively inhibit the growth of lead sulfate crystals during battery discharge. The research results discussed in the present paper indicate that the aromatic ester compound of carboxylic acid, Benzyl benzoate ($C_6H_5CH_2O_2CC_6H_5$), has such inhibiting properties.

Lead-acid test cells with negative plates containing Benzyl benzoate (BB) have improved cycle life performance, the beneficial effect of the BB additive to NAM being most pronounced at a loading level of 0.3%. Cells with BB added to the electrolyte have also been tested. In this case, the additive exhibits its inhibiting effect on the processes of $PbSO_4$ crystal growth most strongly when added to the electrolyte at concentration levels of 0.3% or 0.5%.

1. Introduction

During discharge of lead-acid batteries, small $PbSO_4$ crystals are formed on the surface of the negative lead electrodes. These crystals are highly soluble and part of the Pb^{2+} ions produced as a result of their dissolution participate in the subsequent charge process. Another part of the Pb^{2+} ions contribute to the growth of big $PbSO_4$ crystals (recrystallization process). The big $PbSO_4$ crystals have low solubility. Hence, they are involved but very slightly in the charge process. Thus, these big $PbSO_4$ crystals cause progressive sulfation of the negative plates. In order to reduce or suppress the sulfation of the negative electrodes the recrystallization of $PbSO_4$ should be inhibited.

The international literature abounds in publications discussing the importance of lignosulfonates as inhibitors of the growth of lead sulfate crystals during discharge of lead-acid batteries [1–3]. A number of technical papers report experimental results that illustrate the beneficial effect of some organic additives to the negative active material that suppress that evolution of hydrogen. Thus, for example, W. Boehnstedt and collaborators [4] have investigated the influence of aromatic aldehydes and wood flour added to the electrolyte of lead-acid batteries and have established that these additives impede the hydrogen evolution reaction on the surface of negative lead electrodes. A similar effect has also been observed with substituted benzaldehydes and their derivatives, as reported in reference [5].

Saakes et al. [6] have performed impedance measurements of a negative electrode containing Induline C and Na-1-naphtol-4-sulfonate. The obtained results indicate that these organic substances exert an influence on the electric double layer and on the diffusion ability of lead sulfate.

It can be generally concluded that, besides lignosulfonates, there are other less studied organic additives to the negative active material that are capable of restricting the growth of lead sulfate crystals during discharge of lead-acid batteries.

We have established that Benzyl benzoate ($C_6H_5CH_2O_2CC_6H_5$) 99% (named BB), an aromatic ester compound of carboxylic acid, has such inhibiting properties.

☆ In memory of Prof. Detchko Pavlov.

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https://doi.org/10.1016/j.est.2018.03.021
Received 29 January 2018; Received in revised form 29 March 2018; Accepted 29 March 2018

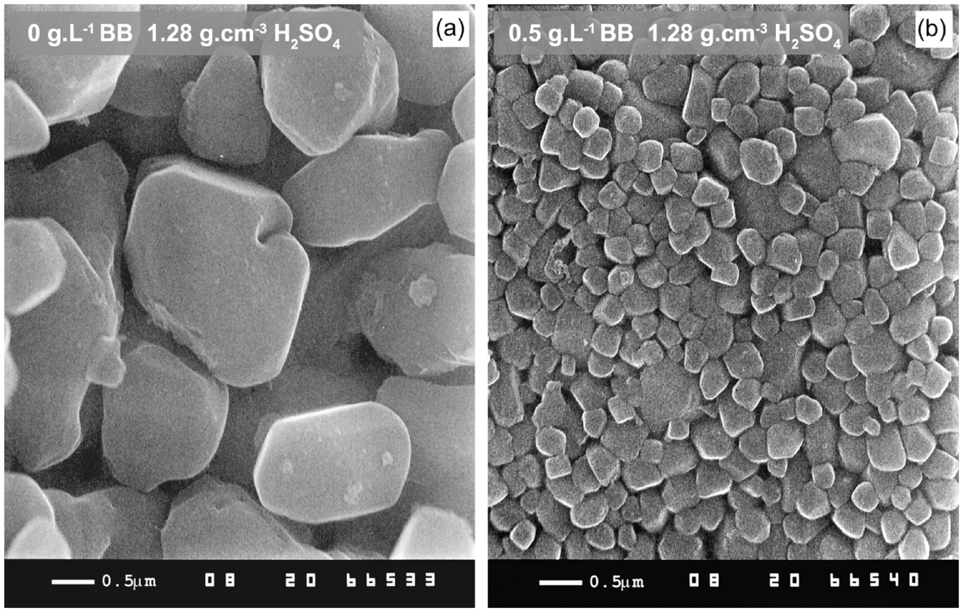

Fig. 1. SEM images of $PbSO_4$ crystals obtained after cycling of Pb electrodes in H_2SO_4 solution, (a) without or (b) with BB additive.

The main objectives of the present research were:

- To evaluate the effect of the BB additive on the processes that occur during the technological processes of negative plate manufacture, i.e. paste preparation, plate curing and formation.
- To determine the optimum concentration of the BB additive in NAM or in electrolyte that guarantees maximum inhibition of the sulfation of the negative plates during battery operation, and hence, most beneficial effect on battery performance.
- To verify whether this beneficial effect of BB is preserved under the operating conditions of different battery duties.

2. Experimental

First, the effect of the BB additive on the processes that occur during the technological processes of negative plate manufacture was evaluated through characterization of paste samples with BB added in different concentrations: 0.1%, 0.3%, 0.5%, 0.8%, 1.2% as well as of plates with the above formed negative active masses.

Test cells (4.6 Ah) were assembled with negative plates containing the above loading levels of BB additive to NAM: 0.1%, 0.3%, 0.5%, 0.8%, 1.2% BB. For comparison, reference (control) cells with no BB additive were also manufactured.

Two types of test cells (5.0 Ah and 42 Ah cells) were tested in order to evaluate the effect of BB added to the electrolyte on the electrical parameters and the cycling performance of the cells in the High-Rate Partial-State-of-Charge (HRPSoC) duty.

The effect of BB added to the electrolyte on the self-discharge processes in test cells left on open circuit for 42 days was evaluated by determining the residual capacity of the cells after the open-circuit stay (OC stay).

The small 5 Ah test cells were produced employing the cell design and technology routinely used in our research work. The cells comprised 3 negative and 2 positive plates per cell separated by 2.4 mm thick AGM separator. The cells were of the flooded type and BB was added to the electrolyte (at four different concentration levels), after which the cells were subjected to formation in our laboratory employing a standard formation algorithm.

The larger 42 Ah cells were produced using commercial non-formed SLI positive and negative plates, supplied by the Bulgarian battery plant MONBAT. These plates were assembled in test cells comprising 4 positive and 5 negative plates per cell. The active blocks of the thus assembled cells were pressed tightly (to 20% compression) and the cells were filled with H_2SO_4 solution (1.23 sp.gr.) with addition of BB at 4 concentration levels: 0.1%, 0.3%, 0.5% and 0.8%. Reference (control) cells with no BB added to the electrolyte were also assembled. All cells were left to soak for 2 h to allow the electrolyte to saturate the AGM separator and were then subjected to formation employing a standard formation algorithm.

All types of test cells were subjected to the following electrochemical tests to determine their electrical parameters and cycling performance:

- Initial capacity tests at 20-h discharge rate;
- Float charge test;
- HRPSoC cycling tests with a current $I = C_{20}/2$ A (i.e. at 10-h discharge rate);
- Residual capacity tests.

The formed active masses of the cells under test were characterized, immediately after formation and after cycling, by different analytical methods, incl. scanning electron microscopy, X-ray diffraction and chemical analysis to evaluate the effect of BB on the processes at the two types of plates.

3. Results and discussion

3.1. Morphology of $PbSO_4$ crystals formed on flat Pb electrodes after LSV cycling between −0.70 V and −1.30 V

Linear sweep voltammetry (LSV) measurements were performed with flat Pb electrodes immersed in H_2SO_4 solutions, with or without addition of BB, and polarized between −0.70 V and −1.30 V at a scan rate of $5\,mV\,s^{-1}$ for 660 cycles. Then, the electrodes were washed, dried in nitrogen atmosphere and examined by scanning electron microscopy (SEM). The obtained SEM images are presented in Fig. 1.

SEM examinations of the electrode surface after LSV cycling evidence big $PbSO_4$ crystals formed in pure H_2SO_4 solutions and small ones formed in the solution containing BB additive. These results indicate that BB has inhibited the $PbSO_4$ re-crystallization process and has suppressed the rate of $PbSO_4$ crystal growth.