



Examination of impact of lignosulfonates added to the negative active mass of a lead–acid battery electrode

Jana Zimáková^{b,*}, Daniel Fryda^a, Sebastian Vaculík^b, Petr Bača^b, Marek Bouška^a

^a Department of Electrical and Electronic Technology, Faculty of Electrical Engineering and Communication, Brno University of Technology, Czech Republic

^b Centre for Research and Utilization of Renewable Energy, Brno University of Technology, FEEC, Czech Republic

ARTICLE INFO

Keywords:

Lead–acid batteries
Expanders
Carbon material
Active mass
Depth of discharge
Partial state of charge regime
Lignosulfonates

ABSTRACT

We employed pasted negative electrodes of dimensions $55 \times 20 \times 7$ mm placed between two pasted positive electrodes of the same dimensions separated with AGM separators of the type BG 260 EB 170 (1.7 mm in thickness). The negative paste was doped with 0.78 wt.% of milled CR2996 carbon (Maziva Týn Company, Czech Republic) and with different amounts of three types of organic lignosulfonates as expanders. The used expanders were commercial products Vanisperse A, Vanillex HW and Vanillex N (Borregaard LignoTech). After formation, the electrode packs were placed in custom cells with the usual H_2SO_4 electrolyte, designed to ensure application of defined pressure to the electrode system. Several conditioning cycles were performed, the excess electrolyte was then aspirated off and the cells were hermetically sealed. The initial capacity of the negative electrodes was around 3 Ah. The cells were then discharged to 50% of their capacity and subjected to partial-state of charge accelerated cycling by using symmetrical 25 s current pulses of 2.5 A followed by 3 s standing. The cells were cycled until their voltage dropped below 1.6 V. In each run, the cell voltage, the electrode potentials against a Cd electrode, and the applied pressure were measured after every 100 cycles. The performance of these electrodes was elevated by applying moderate compression of $4 \text{ N}\cdot\text{cm}^{-2}$. Higher pressures are not recommended.

Cells with higher amount of the added organic expander well tolerate deep cycling, and were able to regenerate better during the conditioning cycles between PSoC runs and its capacities have increased. The low-lignosulfonate-containing cells showed during the PSoC charging good charge acceptance at the beginning of the experiment, but with progression of time (PSoC runs), there was the most significant increase in polarization resistances and gradual degradation of NAM. Medium lignosulfonate cells exhibited the best properties throughout the PSoC runs. During the PSoC charging there is a good charge acceptance, low maximum voltage and stable polarization resistance.

1. Introduction

Concerns about the environment, especially impact of using fossil fuels and its reserves, has increased interest in low-emission transportation, such as electric vehicles, but also in harnessing wind/solar energy [1,2]. These global trends rely on significant amount of battery energy storage. It does not matter whether the battery operates in a hybrid electric vehicle (HEV) or as a backup/storage system. It always has to manage to operate in the partial state of charge (PSoC) and also has to be able to receive a large amount of charge in an extremely short time (e.g. during car braking). Charging and discharging is very short and needs to be quick. These conditions lead to rapid degradation in the lead–acid systems due to surface sulfation of the negative electrodes (NAM) [3].

The lead–acid accumulator is, thanks to its long technological

history (dating back over than 150 years), one of the most used electrochemical power sources [4–6]. By comparing six of the most commonly used secondary sources of electrical energy, we can find that the lead–acid accumulator provides 2–3 times cheaper energy than other types of secondary electricity sources (aggregated data from several studies, especially from [5]). This fact, however, is redeemed by the main disadvantage, which is very small specific energy due to the large atomic mass of the active components, i.e., lead. On the scale of advantages, last but not least it is worth mentioning that up to 95% of the materials used for the production of a commercial lead accumulator can be recycled and in fact, due to incentives at the point of sale or during collection, that percentage is indeed recycled.

The fundamental components of a battery are electrodes and on their design depends the capacity of the battery, value of the discharge current and longevity during a continuous charging operation or

* Corresponding author.

E-mail address: xzimak00@stud.feec.vutbr.cz (J. Zimáková).

cyclical operation around certain somewhat discharged state, usually called PSoC (Partial State of Charge).

The performance parameters depend primarily on the surface of the active material of either electrode – both positive and negative. During discharge/charging, Pb^{2+} ions are produced on the negative electrode, and further react with sulfuric acid to form a thin film of lead sulfate on the surface of the active mass and thus lead to unwanted passivation of the electrodes. From a practical point of view, this phenomenon can be prevented by the use of so-called expanders in the negative active mass (NAM). Primarily, triple combinations of expanders (lignosulfonate + barium sulfate + carbon) are used. Lignosulfonates are in the battery operation chemically bonded to the lead surface and thus the effective active surface of the electrode itself is increased.

Many researchers have studied the effects of lignosulfonates on the lead-acid battery negative plates throughout the years [7–19]. It has been established that lignosulfonates prevent the deposition of the passivating $PbSO_4$ layer on the electrode surface and facilitate the formation of a porous layer built up of individual $PbSO_4$ crystals instead, which results in multifold increase of lead electrode capacity. Recently, Hirai et al. [19] have conducted in situ examinations of the structure of the passivating and of the porous $PbSO_4$ layers.

Nakamura et al. and Shiomi et al. [20,21] have found that introduction of increased amounts of carbon black to the negative paste retards substantially the sulfation of the negative plates on HRPSoC (High Rate Partial State of Charge) cycling and the number of completed micro-cycles increases to about 5000. The authors explain the observed effect of carbon black by the formation of a conductive network of carbon around the $PbSO_4$ crystals, which is evidenced by scanning electron microscopy of the negative active mass (NAM). Hollenkamp et al. [22] have established, within a project of the Advanced Lead-Acid Battery Consortium (ALABC) program, that addition of graphite or carbon black to the negative paste improves notably its conductivity and lowers the charge voltage of the cells. Calabek et al. [23] have proved that the presence of carbon in NAM reduces its pore radii and thus impedes the continuous growth of $PbSO_4$ crystals, sustaining formation of small crystallites of high solubility and hence efficient charge process.

It is generally assumed that carbon black is introduced in the negative paste mainly to improve the electric conductivity of the negative active mass at the end-of-discharge, when the content of $PbSO_4$ crystals in NAM increases substantially [23–28].

In this paper, ten mixtures that combine carbon material and three different type of lignosulfonates were prepared in order to study the influence of NAM in lead acid cell performance. The electrical characterizations were made and different mixtures were compared depending on their performance on capacity, charge acceptance and cycle life at PSoC test.

2. Experiment

2.1. Lignosulfonates used in negative active mass

The organic additive Vanisperse has been produced for lead accumulators. The main advantages of this additive include increasing of the number of charging/discharging cycles, improving cold start performance and improving capacity. It also prevents an increase and formation of a new non-permeable layer of sulfate crystals on the NAM surface. Lead accumulators have been found not to work optimally without the use of Vanisperse.

2.1.1. Vanisperse A

Highly modified lignin, which is based on organic ingredients. This type of additive finds its use especially for VRLA accumulators. Table 1 lists the chemical composition of Vanisperse A. The manufacturer is Borregaard LignoTech Company.

2.1.2. Vanillex

These are the newest types of lignins that have excellent temperature resistance. Table 2 lists typical values for the two samples used – Vanillex HW and Vanillex N. The samples are supplied by the Japanese manufacturer Sorfin Yoshimura.

In this experiment was also always used a carbon additive, a commercial product CR 2996 (manufacturer Graphite AG). The active surface of this preparation is $13\text{ m}^2/\text{g}$, the grain size $4\text{ }\mu\text{m}$.

2.2. Preparation of experimental electrodes

Experimental measurements were carried out in the Laboratory of the Lead Battery at the Institute of Electrotechnology. The cells were placed in a fume hood at room temperature. Measurements were carried out through an automated multichannel data logger that is designed to measure voltage, current, potential and temperature. The measurement is controlled by specialized software serving for setting the required charging and discharging values.

Ten experimental cells were assembled. As the positive electrode a classical, already formed, industrially produced electrode was used. The negative electrode was an experimental electrode with parallel ribs filled with a negative active mass. The physical dimensions of the electrode was $50 \times 20 \times 7\text{ mm}$. The active surface area is 980 mm^2 . The composition of this mass is shown in Table 3. These values were calculated for the total weight of 50 g of the active mass/per electrode. Electrodes, together with the separator, were placed in a container allowing hermetic sealing. Sulfuric acid with density of 1.24 g cm^{-3} was used as the electrolyte. The reference cadmium electrode was selected for the measurement of the potential. Measurements were made at a constant ambient temperature of $25\text{ }^\circ\text{C}$. Constant temperature was maintained by automatic air conditioning system.

An example of a prepared electrode is shown in Fig. 1.

2.3. Formation

The first charging process of the cell is the formation. During this slow charging is the lead sulfate contained in the negative active mass reduced to sponge lead. The formation is performed with slow charging cycles with a constant current of 0.2 A for 4 h and standing in the free-flowing state for 2 h. We observe two parameters during the electrodes forming. The first is the time at which the electrodes reach a voltage of 2.6 V. When this limit voltage is reached, we consider the electrodes to be formed. The longer time of reaching the limit voltage means that the greater amount of the electrode mass is converted into an active charged form of the mass, and the better the formation of sponge lead in the active mass of the cell electrode. The second parameter is the final cell voltage at the end of the formation cycle.

The cells were in the vented state allowed to stand for an hour and then subjected to formation. The cells were formatted for 18 cycles (charging/discharging). Formation thus took 108 h. The voltage during formation is plotted in the graph in Fig. 2.

2.4. Conditioning cycles

Conditioning cycling (Depth of Discharge cycling, DoD) is the next step in preparation of the electrodes for the PSoC cycling. The purpose of this cycling is to stabilize the conductive bridges between the particles in the volume of the active mass, and to remove the residual active mass, which did not convert into a charged form during the formation process. Processes during DoD cycling result in maximizing of the active area of the lead cells, thereby maximizing the charge acceptance of the cell and uniformity of current density in the volume of the active mass. The DoD cycle was also applied after every PSoC cycling. Here the DoD cycle is also referred to as a conditioning cycle.

The whole process was controlled by charging and discharging in the voltage range from 1.6 V to 2.45 V. The discharging is done by

Download English Version:

<https://daneshyari.com/en/article/7539784>

Download Persian Version:

<https://daneshyari.com/article/7539784>

[Daneshyari.com](https://daneshyari.com)