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Combined effect of acrylic fibers and carbon in negative active mass of lead-acid battery

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ABSTRACT

This work deals with the study of influence of additives added to the negative active mass of the lead-acid battery electrode. Specifically, it's studied the influence of acrylic fibers (1,5 wt.%) and different amounts of carbon CR 2996 on the final properties. Carbon was added in an amount of 0.15; 0.46; 0.78; 1.4; 2.65 and 5.15 wt.%. It was performed formation, depth of discharge cycles (DoD) and partial state of charge cycling (PSoC). After 12 DoD cycles it was drained excess of electrolyte from the battery and it was performed another 7 DoD cycles. Thanks to these cycles it was possible to verify the actual capacity of electrodes. The results are shown in relevant graphs.

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1. Introduction

Concerns about the environment, especially about using of fossil fuels and its stocks, increased interest in low-emission transportation, such as electric vehicles, but also about harnessing wind/solar energy [6,7]. It does not matter whether the battery operates in a hybrid electric vehicle (HEV) or as the backup systems. It always has to manage to operate in the partial state of charge (PSoC) and also 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 quick. These conditions leads to rapid degradation due to surface sulfation of lead acid battery negative electrodes (NAM). [1]

In order to use the classic VRLA (valve-regulated lead acid batteries) batteries in HEV, it is necessary to modify their composition. Appropriate additives in NAM improves the properties of the electrodes. Basic components for the manufacturing of active mass are: lead in the form of dust, sulfuric acid with typical density of 1,28 g/cm^3, and demineralised water. To these components are added $BaSO_4$, acrylic fibers, oak flour, Vanisperze A and solution of Indulin AT. These additives are commonly added to VRLA batteries to improve performance and extend the life of the electrode. The active mass of the negative electrode in a lead-acid battery must have sufficient porosity while ensuring a sufficient contact area between the collector/active mass and between the active mass/electrolyte. Among the most important parameters, not only for lead-acid batteries, belongs the greatest capacity and also the smallest internal resistance of the battery. Value of achievable capacity of lead acid battery is determined by the size of the active surface of the electrodes. The higher the porosity of the electrodes, thus active area of the electrodes, ensures the larger capacity of the battery. The internal resistance of the battery is the sum of the individual resistances of components of the battery, while the key parameters include the contact between the collector and the active mass, providing electron conductivity, and contact between the active mass and electrolyte, providing ionic conductivity. Without any added additives, porosity, during cycling, declines very rapidly.

In this experiment it were used these additives: carbon CR 2996 (manufacturer Graphite AG), the size of the active surface is 13 m^2/g, a grain size of 4 μm in combination with the acrylic fibers. Acrylic staple fiber is a synthetic fiber with the properties of the binder of negative active mass. Acrylic staple operates as a mechanical component reinforcing the negative active mass. Its functioning can be thought of similar to "reinforcing steel" in the concrete bed. This leads to better utilization of active mass and to suppress of degradation mechanisms [2,3]. The main task of the carbon is to improve the electrical conductivity of the negative active mass at the end of discharging when the amount of $PbSO_4$ crystals in the negative active mass increases rapidly. It was also

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reported that the carbon increases the electrochemically active surface of the negative active mass, improves the ability of the battery to deliver higher currents and it is also discussed its electrocatalytic effect [4,5,8–11].

2. Experiment

Experimental measurements were carried out in the laboratory of lead battery at the institute of electrotechnology. Container with electrodes was placed in the fume hood in a room that may be well ventilated (to avoid contamination with acid). Measurements were carried out through automated data logger that is designed to measure voltage, current, potencial and temperature. The measurement is controlled by specialized software serving for setting the required charging and discharging values.

It was made a serie of experimental electrodes with active mass – composition according to manufacturer, shown in Table 1. These values are calculated for the total weight of 50 g of active mass /per electrode. Dimensions of electrode active surface is ($50 \times 20 \times 7$ mm). Example of manufactured electrode is shown in Fig. 1.

After the curing process, it assembled experimental cells. Each cell was placed in a container allowing hermetic sealing. Each cell consisted of one of the above-described experimental negative electrode and two positive, already formed, industrially manufactured counter-electrodes. The used electrolyte was sulfuric acid with a density of 1.24 gcm^{-3}. Potentials were measured by using cadmium reference electrode.

3. Formation

The cells were in vented state allowed to stand for an hour and then subjected to formation. The cells were formatted for 20 cycles when each of them consisted of 4 h of charging by constant current 0.04 A/g (0.2 A) and two hours of standing. Formation thus took 120 h. The voltage during formation is plotted in the graph in Fig. 2.

From the data obtained during the formation of cells, shown in Fig. 2, is evident that with increasing amounts of added carbon, decreases the maximum reached voltage and time of transition to the second charging stage is rising. These values are shown in Table 2. The table also lists the values of charge needed to achieve the second charging stage, and the total charge delivered at the end of the formation.

Achieved results are in agreement with our previous experiments [5]. Carbon operates on formation process positively. With the increasing amount of carbon is more energy consuming for formation of electrodes (creating active mass) and less to undesirable decomposition of the electrolyte.

4. Conditioning cycles (DoD – depth of discharge)

After formation there were running 100% depth of discharge cycles. These are used to finish formation, to stabilization of conductive bridges between the particles of the active mass and to maximize the active surface of the electrodes. The whole process is controlled by charging and discharging in the voltage range from

Table 1
The composition of the active mass of the experimental negative electrode.

Ingredients	m [g] exp. electrode	Volume of components [%]	CR 2996 wt.%						
			0%	0.150%	0.460%	0.780%	1.400%	2.650%	5.150%
Pb dust	41.915	83.829	41.328	41.266	41.138	41.005	40.740	40.232	39.190
Dem. water	4.569	9.137	4.505	4.498	4.484	4.469	4.441	4.385	4.273
H_2SO_4	2.515	5.030	2.479	2.476	2.468	2.460	2.445	2.414	2.352
borosilicate	0.105	0.210	0.103	0.103	0.103	0.102	0.102	0.100	0.098
vanisperze	0.042	0.084	0.041	0.041	0.041	0.041	0.040	0.040	0.039
expander	0.855	1.710	0.843	0.841	0.839	0.836	0.831	0.820	0.799
Acryl fibers	–	–	0.700	0.698	0.696	0.694	0.690	0.681	0.663
CR 2996	–	–	–	0.075	0.230	0.390	0.700	1.325	2.575

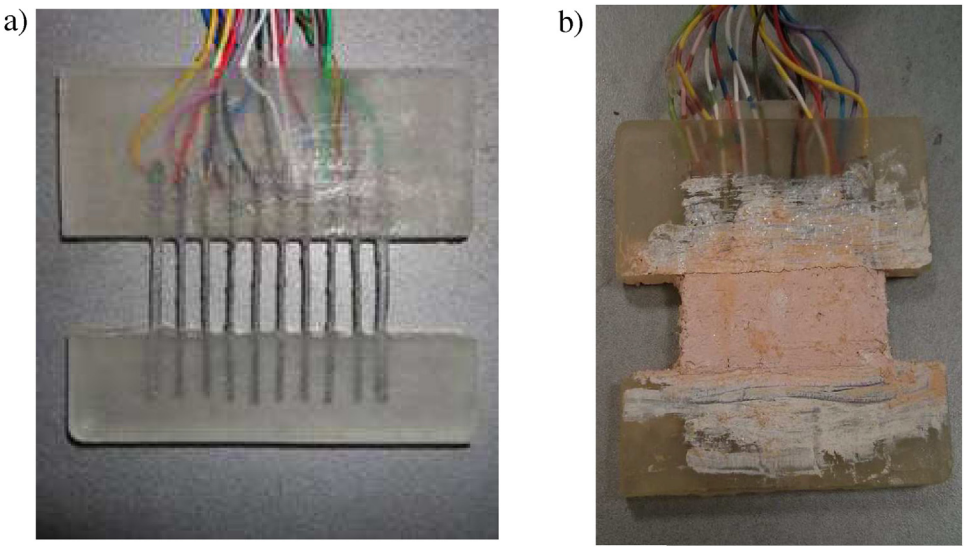

Fig. 1. a) experimental electrode with parallel ribs; b) electrode with NAM after curing process.

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