PULSED CURRENT FORMATION OF LEAD-ACID ACCUMULATORS

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Abstract: This article deals with formation of lead-acid accumulators. There are the results of experiments concerned with pulsed current formation, which were conducted on experimental cells. It was formed by different current pulse. Twelve ampere-hours were delivered to each of them. It's the same value which we use for continuous formation at our laboratory.

Keywords: lead-acid accumulator, formation, pulsed current formation

1. INTRODUCTION

Lead-acid accumulators was invented more than a century ago. So it may seem that it is already fully explored. But it is not true. Due to the development of new applications in this area some of new problems appear. For example hybrid electric vehicles, where battery operates in partial state of charge (PSoC mode). There are different main degradation mechanisms, than automotive batteries have.

2. TEORETICAL

Formation is one of the main steps in the manufacture of lead-acid batteries. It has a great influence not only on the capacity but also on the durability of a lead-acid battery. We can say that after the plates were cured, they contain positive and negative electrode mixture of bivalent lead oxid – tribasic sulfate (3BS), tetrabasic sulfate (4BS), lead oxide (PbO) and pure lead (Pb). During the formation, these compounds make electrochemical active material - lead dioxide (PbO₂) on the positive and spongy lead on the negative electrode [1].

The ratio between 3BS and 4BS depends on the conditions in which the electrode was cured. Tribasic sulfate appears at temperature below 70 $^{\circ}$ C. It is characterized by small crystals with a small surface. Conversely, 4BS is formed at higher temperatures and the crystals are larger, as shown in the following figure [2].

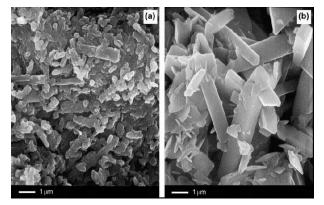


Figure 1: Structure of 3BS (a) and 4BS (b) [1].

The active mass, which was formed by the conversion of 4BS should have longer durability. The disadvantage is a complicated production, because 4BS crystalizes at higher temperatures (over 80° C) and 100 % r. h [3].

3. EXPERIMENTAL

This part presents the results of the experiment, whose aim was to compare different current pulse formation modes. The pulse current formation should have a higher faradaic efficiency for conversion into dioxide than formation with continuous current [4]. For the purposes of the experiment were prepared four cells, which contain one positive and one negative electrode, with discontinuous system of parallel ribs with dimensions of $2 \times 5.5 \times 0.7$ cm. Subsequently, the cells formed by pulses were selected so, that each of the cell had 12 Ah charge after 90 h charging. On the figure 2 and the table 1 are shown parameters of used pulses.

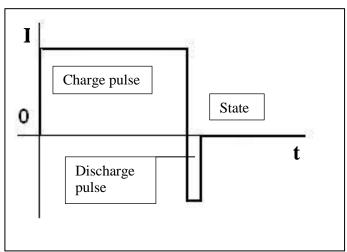


Figure 2: Current profile of pulse mode.

Cell no	Charge pulse [s]	Current of a charge pulse [A]	State [s]
1	4,5	0,22	3
2	12	0,16	3
3	2	0,333	3
4	2	0,333	12

Table 1: The parameters of applied pulses.

Current and time of discharge pulses were 300 mA and 200 ms for each of cells. The conditions were chosen with regarding to the source [5]. It was mentioned there, that the cut-off frequency is approximately 10 Hz for the positive electrode and approximately 100 Hz for the negative electrode in lead-acid batteries.;

After pulse mode ends, all of the cells were applied to conditioning cycles, which allowed measurement of capacity. This is the main parameter of successful formation. The results are shown on figure 3.

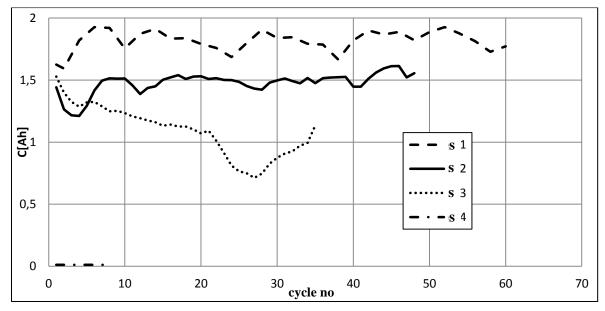


Figure 3: Capacity of the cell due conditioning cycles.

Previous graph shows that the formation was the best at the sample number 1, because its capacity was the biggest. It fluctuates, but no downward trend during cycling is here. For the sample number 2 smaller capacity was measured, but during subsequent cycling here was no fluctuates. The sample number 3 has bigger capacity at the beginning, but then it's going down during conditioning cycles. The following table shows that this decrease was due to the positive electrode failure. The sample number 4 reached a capacity nearly 0. It should be caused by destroying of the separator and subsequent short circuit of positive and negative electrode.

Cell no	Electrode	State at the end of experiment	
1	+	Forming ribs, active mass was ok	
	-	forming, active mass without sulfate	
2	+	Sulfate on surface	
	-	Sulfate on surface, partly in the active mass	
3	+	Sulfate on surface	
	-	Without sulfate	
4	+	Sulfate on surface	
	-	Partly sulfate on surface	

Table 2: State at the end of experiment (checked by optical microscope).

4. CONCLUSIONS

This article deals with pulsed current formation of lead-acid accumulators. There is a description of the experimental formation of 4 samples of lead-acid battery cell. The lead-acid battery cell consists of one positive and one negative electrode with discontinuous system of ribs pasted by active mass with dimensions of $2 \times 5.5 \times 0.7$ cm. The formation of the cells was performed by current pulses and then it was evaluated by capacity conditioning cycles measurement.

The results shown, that pulse formation with depolarization pulses isn't advisable for positive electrode and the standing after depolarization pulse is counterproductive. Pulse formation is suitable for negative plate. The results of this experiment will require further research of influence of depolarization pulse on chemical reactions in positive electrode.

ACKNOWLEDGEMENT

This work was supported by the EU CZ.1.05/2.1.00/01.0014 and by the specific graduate research of the Brno University of Technology No. FEKT–S–11–7.

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