

Short Communication

Probability Investigation of Thermal Runaway in Nickel-Cadmium Batteries with Sintered, Pasted and Pressed Electrodes

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In this study, it was experimentally proved that a probability of a thermal runaway in nickel-cadmium batteries with sintered oxide–nickel electrodes is higher than in batteries with pressed or pasted oxide–nickel electrodes. Besides, it is shown that a probability of the thermal runaway falls with decrease of a batteries capacity.

Keywords: thermal runaway, battery, nickel–cadmium

1. INTRODUCTION

Thermal runaway is encountered in batteries of almost every electrochemical type. During battery recharging under constant voltage or its operation in float mode, it may suddenly strongly overheat, melt, burn, smoke or burst, depending upon its design, electrochemical system, body material, etc [1]. However, the thermal runaway is quite rare phenomenon. As for technicians maintaining batteries during decades, for example, in airports, they do not encounter this phenomenon often or encounter it as a rule not more than once or twice for their entire life. Nevertheless, at the present time, the batteries, in which the thermal runaway is watched, are installed in many equipment units of both household and special purpose: airplanes, standby power supplies of communications networks, etc. The thermal runaway in those equipment units and systems will inevitably result either

in systems failures or problems with their operation. So the thermal runaway is a great obstacle in work of lots of modern equipment and systems.

The main goal of this paper is studying a probability of a thermal runaway initiation in nickel-cadmium batteries with different types of electrodes and various constructive features. In connection with this, there were studied batteries with sintered, pressed and pasted oxide–nickel electrodes. In this paper, the investigations started in the papers [2-7] were continued.

2. EXPERIMENTAL

For the experimental studies, the batteries were used with oxide–nickel electrodes of the following kinds: sintered (KSX-25, KSL-15, KSX-6, KSM-3.5), pasted (KM-3.5), and pressed ones (KL-24, KL-20, KL-10).

For batteries cycling process, a recharger was used, which allowed installing of one of a number of fixed charge voltages: 1.45; 1.67; 1.87; 2.2 V. The recharger allowed working on constant basis with currents up to 300 A and on short-duration basis with currents up to 1000 A.

In order to obtain more voluminous statistics for less period of time, the recharger was connected to a group of ten paralleled batteries in a hard metal clamp band. This batteries' joining up in parallel was made with a help of two heavy duty metal runs, to which separately batteries' positive and negative terminals were screwed on. To the end that a thermal runaway developed in one battery had no influence on a probability of a thermal runaway development in neighboring batteries (which could happen because of their additional heat-up), between the batteries in the metal clamp band, the heat-insulating wood block fillers two centimeters thick were inserted.

The batteries were charged in succession under constant voltage values: 1.45; 1.67; 1.87; 2.2 V. The charging process lasted ten hours. Discharge was conducted according to the operation manual for a specific battery.

Since in our previous studies [4] there was shown that a probability of a thermal runaway grows with an increase of operating life duration, in these new experiments, batteries were used with the operating life, at least, twice larger than their guaranteed service life, which supposedly would facilitate the thermal runaway process initiation. In a group of ten paralleled batteries, those batteries were installed that distinguished with the same operating life. Each batteries group was cycled 80 times. This way for each batteries type and for each charge voltage value (1.45; 1.67; 1.87; 2.2 V), there were conducted $10 \cdot 80 = 800$ charge-discharge cycles.

3. RESULTS AND DISCUSSION

The results of the batteries' cycling are represented in the Tables 1 and 2. In the Tables 1 and 2, only charge voltages are given, under which a thermal runaway took place; for those batteries, the operating life is specified.

Table 1. Results of batteries cycling with sintered electrodes

Batteries	KSX-25	KSL-15	KSX-6	KSM-3.5
Charge voltage (V)	1.87; 2.2	2.2	-	-
Period of operation (years)	6.5; 7	6.6	> 6.5	> 6.5
Number of charge-discharge cycles	800	800	800	800
Number of thermal runaways	2	1	0	0

Table 2. Results of batteries cycling with pressed and pasted electrodes

Batteries	KL-24	KL-20	KL-10	KM-3.5
Charge voltage (V)	-	-	-	-
Period of operation (years)	> 6.5	>6.5	> 6.5	> 6.5
Number of charge-discharge cycles	800	800	800	800
Number of thermal runaways	0	0	0	0

Thus from 800 conducted charge-discharge cycles for each type of batteries in tough conditions of charging, i.e. under high charging voltage values, the thermal runaway was watched only in two cases with the batteries KSX-25 and in one case with the battery KSL-15. Therefore, it is fair to say that the thermal runaway is a quite rare phenomenon.

In all the cases of the thermal runaway, the batteries in question distinguished with operating lives more than six years in spite of their three-year guaranteed service period. I.e. these experimental results confirm directly the conclusions of the paper [4] that the probability of the thermal runaway initiation grows along with an increase of their operating life.

In all the observation cases of the thermal runaway, the batteries charge was conducted under the voltage values 1.87 and 2.2 V, which significantly exceeds a voltage being an average one for such batteries operation in field conditions in float mode (1.35-1.5 B). So it may be deduced that the probability of the thermal runaway grows with a batteries charge voltage increase.

No one of batteries with pressed and pasted oxide–nickel electrodes (KL-24, KL-20, KL-10, KM-3.5) did not develop a thermal runaway (Table 2). This can be connected with types of both electrodes and used separators.

In the paper [4,5], it was proved that a thermal runaway initiation is connected with dendrites intergrowth through a separator. The dendrites cut distance between electrodes drastically; and consequently in dendrites locations, electrodes will locally heat up to a large extent due to the fact that a resistance in such spots would be much less, while an average charge density would be essentially higher than in other places in vicinity of those spots on the electrodes. This is exactly what can be a reason of a thermal runaway launching as judged by any thermal runaway mechanism; both the one described in the literature [1] or the one proposed in the papers [4,5].

In the batteries with the pressed electrodes, the separators are used based on thick fabrics (battery KL-10). In the batteries KL-24, KL-20, the positive electrode plate is wrapped by an alkali-proof paper and placed into a housing made from a capron fabric.

As the process of intergrowth of cadmium dendrites depends strongly on a separator thickness, a structure and a pores diameter, so with the separator's thickness growth and pores diameter decrease, the process slows down considerably [8]. Even if a dendrite inter-grows in the batteries with thick separators, due to a large length, it will not be able to sustain the high charge density needed for an electrodes' significant local heating up.

Nevertheless, univocal asserting based on the conducted experimental studies, that in the batteries with the pressed electrodes a thermal runaway is impossible, is undoubtedly premature as studying of the four battery types does not provide with a sufficient statistical material. However the analysis of the literature data on the thermal runaway as well as of these batteries' operation on various enterprises counts in favor of this presumption. In particular, an analysis of mining batteries operation over the period of more than 40 years showed that a main reason of batteries 3KL-10 failures is an exfoliation of an active mass from an internal current-collecting net on an oxide-nickel electrode. The exfoliation occurs because of long-run batteries' overcharging. A gas released in a case of the overcharging (primarily on the current-collecting net because of its high conductivity) pulls away the active mass step by step. A long-run overcharging can occur, for example, in a case that a coalminer did not come to work in his shift; in this case the battery stays connected to a charging stand not 16 hours as it is prescribed by an instruction but instead three times longer. So the long-run overcharging of these batteries leads primarily not to an immediate thermal runaway but instead to the exfoliation of the electrodes active mass. In the batteries with the sintered electrodes, there can not be such phenomena. So it is possible that the active mass exfoliation in the batteries with the pasted and pressed electrodes (which occurs with them with probability being higher than the same of the thermal runaway) does not let thermal runaway process to be developed and in so doing it decreases the probability of the thermal runaway in these batteries.

In any case, these experimental studies univocally show that the thermal runaway in the batteries with the pressed electrodes either impossible or its probability is much lower than in the batteries with the sintered electrodes.

Also on the base of the conducted experimental studies, one may not univocally assert that a reason of a thermal runaway absence in these batteries is the separator thickness inasmuch as it is necessary to investigate thoroughly the mechanism of cadmium dendrites intergrowth through separators' various materials and also to study an impact of a structure and pores diameter of a separator on processes of the dendrites formation. Such investigations would allow deducing a dependence of dendrites growth speed on separator thickness and pores diameter. After that, it would be possible to determine, which separators should be considered as thin and which ones thick enough from the point of view of the prognosis of a thermal runaway initiation. Such studies are beyond the scope of this paper.

In our experiments, also the batteries of the low capacity did not develop the thermal runaway, no matter what kind of electrodes there were installed on them: sintered electrodes (KSX-6, KSM-3.5) or pasted ones (KM-3.5) or pressed ones (KL-10). In all probability for a thermal runaway initiation,

the important factors are the battery' overall mass and the total charging rate. In a case of a greater battery mass, its internal electrodes will be heated up to a larger extent because of a worse heat-removal. A higher total charging rate will lead to a situation that in a case of a short-circuit due to a dendrite, a high local current will be concentrated in this spot and therefore this electrode part will be heated up to a larger extent than in batteries of a small capacity. Undoubtedly, both these factors facilitate a thermal runaway initiation.

Nevertheless, certainly on the base of the conducted experimental studies, it is undue to assert univocally that in batteries of a small capacity the thermal runaway is impossible. However an analysis of both literature data on the thermal runaway and those batteries' operation data on various enterprises counts in favor of this presumption. In particular, the batteries KSX-6 have the same electrodes (but of less size) than batteries KSX -25; and nevertheless no one case of a thermal runaway in these batteries was encountered by us neither in our experiments nor on real objects.

Thus, these experimental studies show univocally that a probability of a thermal runaway lowers with a decrease of a battery capacity.

4. CONCLUSION

The fact that the thermal runaway probability lowers with a decrease of a battery capacity is in entire congruence with the classical mechanism of the thermal runaway [1]. But from point of view of the thermal runaway classical mechanism [1], the dependence of the thermal runaway initiation probability on types of electrodes and separators is completely incomprehensible because this mechanism takes into account neither battery construction nor types of its electrodes and separators. Hence, according to the classical mechanism [1], the thermal runaway can occur with the same probability for any nickel-cadmium batteries with any types of electrodes and separators. But the experimental results demonstrate that it is not so (Tables 1, 2). From point of view of the thermal runaway mechanism earlier proposed by us [4], for the obtained experimental results (Tables 1, 2), the quite natural explanation exists (see above). However, certainly, the proposed mechanism of the thermal runaway [4] requires further confirmations of both experimental and theoretical nature.

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