Probability of thermal runaway in high-capacity nickel-cadmium batteries with pocket electrodes

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Abstract. An experimental investigation was given to the occurrence probability of the thermal runaway in the high-capacity nickel-cadmium batteries with the pocket electrodes. 800 charge-discharge cycles were performed using a hard charge mode at a voltage of 2.2 V and a temperature of 40 ° C. It was shown that in the batteries of this kind, the thermal runaway is either impossible or its probability is much lower than that in the batteries with the sintered electrodes. The explanation was given to this phenomenon based on the previously proposed thermal runaway mechanism based on the exothermic reaction of the thermal runaway.

1. Introduction
Thermal acceleration is very rare. It is found in batteries of various electrochemical systems [1-4]. Typically, a transient thermal acceleration process is observed in accumulator batteries with aqueous electrolyte. Moreover, important conditions for its appearance are recharging of storage batteries or their operation in floating mode [1]. The generally accepted mechanism of thermal acceleration in literary sources occurs as follows. With long-term charging of the storage battery, it is heated, after which its internal resistance decreases. In the future there is an increase in the charging current and a decrease in the resistance of the battery, etc. [1]. The result of this process is heavy heating of the battery, melting of its body, ignition or explosion. However, in works [5-10] it was shown that the conventional mechanism of thermal acceleration is not confirmed by a number of experimental facts obtained.

Firstly, by 96 %, the gas released during the thermal runaway consists of the hydrogen [5]. This experimental fact cannot be explained, for example, by a decomposition of an electrolyte.

Secondly, the generally accepted thermal runaway mechanism assumes that the battery is heated up by the energy of the charger. But our experimental studies have shown that during the thermal runaway, a battery releases 148 times more energy than it receives from the charger. In work [9], results showing that thermal acceleration process is caused by exothermic reaction in which atomic hydrogen accumulated during operation in electrodes of accumulator batteries recombines. Moreover, this reaction has an intensive nature of course and is described by the electrochemical reactions presented below:

\[ \text{H}_2\text{O} + \text{H}_{\text{ads}} + e^- \rightarrow \text{H}_2\uparrow + \text{OH}^- \quad \text{(cathode)} \]
\[ \text{H}_{\text{ads}} + \text{OH}^- \rightarrow \text{H}_2\text{O} + e^- \quad \text{(anode)} \]

and the overall reaction
\[ \text{H}_{\text{ads}} \text{Cd} + \text{H}_{\text{ads}} \text{Ni} \rightarrow \text{H}_2 \uparrow. \]

In the series of works [7-9], it was established that during the operation of accumulators of the nickel-cadmium electrochemical system, hydrogen accumulates in large quantities in their electrodes,
moreover, in the form of hydrides, i.e. in atomic form [1]. Recombination of atomic hydrogen accumulated in electrodes according to reactions (1,2) is electrochemical reaction of thermal acceleration [9]. The heat release in reaction (3) is 436 kJ/mol (hydrogen) [10]. The value of observed heat release is significantly higher than in the reaction of hydrogen combustion in oxygen, which is 285.8 kJ/mol (hydrogen) [11].

It should be noted that so far the thermal runaway is a little-studied phenomenon. Therefore, it can be modeled only with aid of the statistical modeling method [11] or the nonlinear structural modeling method [12] – just as other little-known phenomena in batteries (such as the electrochemical processes underlying the Peukert law [8,9] or the gas generation process during the lithium-ion batteries cycling [13-20].

In work [6] it is shown that when studying the process of thermal acceleration in accumulator batteries of grades SBLE 30, SBM 22, KL-14, KL-28 with pocket electrodes, thermal acceleration is not detected in some cases. However, among the detected cases of thermal acceleration, the probability of its appearance is much lower than in batteries with sintered electrodes. In addition, when cycling storage batteries with sintered electrodes, direct proportionality was found between the capacity of the storage battery and the probability of the thermal acceleration process [9]. This dependence can be explained by the fact that with a large mass of batteries there is a deterioration in the removal of heat from them. In this regard, electrodes inside storage batteries are heated, which in turn increases the probability of thermal acceleration process [7].

The study, which is carried out in this work, is aimed at studying the probability of the appearance of a thermal acceleration process in nickel-cadmium ak-accumulators with a large capacity and pocket electrodes.

In this regard, in this work, cycling of high-capacity nickel-cadmium batteries was performed many times in order to determine the probability of the thermal runaway for them.

2. Experimental
For the experimental studies the following batteries of high capacity with the pocket electrodes were used: KL-55, KL-80, KL-125, KL-150, KL-350 with capacities 55, 80, 125, 150 and 350 Ah respectively.

Thermal acceleration appears in nickel-cadmium storage batteries when charged with constant voltage. The second condition of its appearance is the operation of storage batteries in floating mode. In operation [7] it is established dependence of probability of appearance of process of thermal acceleration on increase of its voltage of charge. In this regard, the following mode was selected for batteries. The battery was charged at a voltage of 2.2 V for 10 hours. The selected voltage in accordance with the operating instructions is significantly higher than the standard charge voltage of 1.67 V. The discharge was performed in accordance with the operating instructions of the battery manufacturer (see Table 1).

| Batteries | KL-350 | KL-150 | KL-125 | KL-80 | KL-55 |
|-----------|--------|--------|--------|-------|-------|
| Charging voltage, V | 2.2    | 2.2    | 2.2    | 2.2   | 2.2   |
| Charging time, h    | 10     | 10     | 10     | 10    | 10    |
| Discharging current, A | 70    | 15     | 12.5   | 8     | 5.5   |
| Final discharging voltage, V | 1      | 1      | 1      | 1     | 1     |

When cycling, such charger was used, which was able to set a number of fixed voltage values: 1.45; 1.67; 1.87; 2.2 V. It allowed to work continuously with currents up to 300 A and – during short times – with currents up to 1000 A.
The charger was connected to a unit consisted of in-parallel-connected batteries joined together with aid of a rigid metal tie – there were used from two to five of them in a set. Parallel connection of the batteries considered in the experiment was carried out using two metal buses. Positive and negative poles of batteries were screwed to the tires. The parallel connection of the batteries made it possible to turn on five pieces at a time. This significantly reduced the time of experiments. Consequently, the parallel connection allowed getting larger statistical data collection within a shorter period of time.

3. Results
The batteries were cycled in the heat chamber Binder MK240 (BINDER GmbH, Germany). It was done at the temperature of 40°C and charging voltage 2.2 V, which also increases the likelihood of the thermal runaway occurrence [7]. The results of the batteries cycling are shown in Table 2.

Table 2. Results of cycling of nickel-cadmium batteries with pocket electrodes at temperature of 40°C and charging voltage 2.2 V

| Batteries | KL-350 | KL-150 | KL-125 | KL-80 | KL-55 |
|-----------|--------|--------|--------|-------|-------|
| Number of used batteries | 10     | 10     | 10     | 10    | 10    |
| Charge-discharge cycles   | 800    | 800    | 800    | 800   | 800   |
| Thermal runaways          | 0      | 0      | 0      | 0     | 0     |
| Warranty lifetime, years  | 1      | 5      | 3      | 3     | 3     |
|                          | (cycles) | (1000) | (1000) | (1000) | (1000) |
| Used batteries’ real lifetime, years | >10 | >10 | >10 | >10 | >10 |

As a thermal runaway probability increases with batteries’ service life prolongation [7], purposely in our experiments, the batteries were used with at least twice longer lifetime as compared to their warranty period. This should contribute to the occurrence of the thermal runaways.

4. Discussion
Table 2 shows that in the case of nickel-cadmium batteries with pocket electrodes, the thermal acceleration process never occurred, despite the fact that 800 charge-discharge cycles were performed for each type of battery and a hard charge mode was chosen (at a voltage of 2.2 V, which was significantly higher than 1.67 V, which is the usual charge voltage). In addition, these batteries had a long service life and were charged at a temperature of 40°C. According to the results of [7-9], all these factors had to increase the probability of thermal acceleration. Unlike accumulator batteries with pocket electrodes, in a similar series of experiments with nickel-cadmium accumulator batteries including sintered electrodes, the latter revealed the fact of thermal acceleration process [7-10]. Therefore, referring to the above-described series of experiments, it can be stated that the probability of a thermal acceleration process in accumulators of a nickel-cadmium electrochemical system with pocket electrodes is significantly lower than in accumulators of the same electrochemical system with sintered electrodes. The above facts are also confirmed by statistical studies on the operation of nickel-cadmium batteries with pocket electrodes conducted by us at real facilities over a period of more than 30 years. We have established the fact that there are no cases of observing the thermal acceleration process in the batteries of this electrochemical system.

Based on the studies conducted in [7-10], it follows that two irreversible accumulation processes gradually lead nickel-cadmium batteries to thermal acceleration. First, it is the process of accumulating hydrogen in the electrodes of the battery during its service life.

Secondly, this is the process of growth of dendrites on the cadmium electrodes of nickel-cadmium batteries.
In our opinion, the appearance of the thermal acceleration process in the battery is caused by the germination of dendrites through the separator. The physical dimensions of the dendrites significantly reduce the distance between the electrodes. Because of this, local highly heated areas will appear on the electrodes in places where dendrites are deployed. Their appearance will be due to the fact that the resistance in these places will be less, and the average current density will accordingly be much higher than in the sections of electrodes adjacent to dendrites. The totality of the above facts leads to the appearance of the process of thermal acceleration in accordance with the mechanisms presented in works [1,2] or proposed by us in works [7-10].

According to the conventional view [1], the thermal acceleration process in the batteries proceeds as follows. If the batteries are charged for a long time at a constant voltage (or when operating in buffer mode), they are heated, which leads to a decrease in the internal resistance of the batteries and an increase in the charging current, which, in turn, increases the heating, etc. Thus, it is generally believed that thermal acceleration is the result of a positive feedback between the current and temperature in the battery during its charging at a constant voltage. Besides, it is believed that in sealed batteries, the exothermic reactions of the oxygen cycle make a significant initial contribution to the battery’s heating up. And yet the thermal runaway occurs in non-sealed batteries, too [7-9]; notably, in the latter batteries, it runs in much more intensive manner.

From the point of view of the generally accepted thermal runaway mechanism [1], the observed dependence of the thermal runaway probability on a type of electrodes in nickel-cadmium batteries is inexplicable. Indeed, following the [1] logic, when a battery is warmed up, its internal resistance should decrease (and therefore the charge current will increase, etc.) regardless of the type of the electrodes. However, experimental studies show that in batteries with pocket electrodes, thermal acceleration never occurs, unlike batteries with sintered electrodes.

Consider the case for nickel-cadmium batteries with pocket electrodes. If during the operation of the battery, the dendrite grows between its electrodes, then it will simply close the circuit to the metal lamella of the opposite electrode. therefore, it will simply burn without causing a local high-temperature heating site due to the high conductivity of the lamella metal. But according to the results [7-9], it is exactly the electrodes’ strong local heating-up that triggers the exothermic reactions of the thermal runaway (1,2).

5. Conclusions

Based on the data obtained from experimental studies, it can be argued that in batteries having pocket electrodes, the appearance of a thermal acceleration process is impossible. However, this statement still needs to be rechecked with additional experiments and theoretical considerations. The result can be used in practice in the development of new types of accumulators of a nickel-cadmium electrochemical system resistant to the appearance of a thermal acceleration process.

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