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Short Communication

Probability Investigation of Thermal Runaway in Nickel-Cadmium Batteries with Pocket Electrodes

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In this study, there is shown that in nickel-cadmium batteries with pocket electrodes and a long operating life, a lot of hydrogen is contained just like in batteries with sintered electrodes. But a probability of the thermal runaway in the nickel-cadmium batteries with the pocket electrodes is much less than the same in the batteries with the sintered electrodes. This result can be of a great practical importance for new types development of the alkaline batteries with a good thermal runaway resistance.

Keywords: thermal runaway, battery, nickel–cadmium

1. INTRODUCTION

The thermal runaway occurs in nickel-cadmium, lead–acid, lithium-ion, nickel-metal hydride, etc. batteries [1], which is to say that the thermal runaway is a phenomenon inherent in batteries of practically all the electrochemical systems. In outward appearance, the thermal runaway in the batteries of all the above systems runs its course in the same way.

In a case of the thermal runaway initiation, a battery heats up till high temperature values; an electrolyte evaporates instantly; a battery plastic case melts and sometimes it catches fire or explodes depending on the battery case construction and material.

According to the generally accepted thermal runaway mechanism, it emerges in the following way [1]: In a case of a battery long recharging under constant voltage (or at its floating service), heating-up takes place, which results in decreasing of a battery internal resistance and in increase of recharging current, which in its turn magnifies heating up, etc. So the thermal runaway is a result of a positive feedback between the current and the temperature of batteries during their charging under a constant voltage.

In our previous papers [2-9], it was shown that a lot of experimental data exists that contradict to this thermal runaway mechanism.

On the basis of all the available experimental data in the paper [4], there was proved, that the thermal runaway is associated with a powerful exothermic reaction going within the battery. This exothermic reaction in the thermal runaway process in alkaline batteries is the electrochemical reaction of atomic hydrogen recombination

$$H_{ads\mathrm{Cd}} + H_{ads\mathrm{Ni}} \rightarrow H_2\uparrow \qquad (1)$$

($H_2O + H_{ads} + e^- \rightarrow H_2\uparrow + OH^-$ on a cathode and $H_{ads} + OH^- \rightarrow H_2O + e^-$ on an anode). A rate-limiting step for this reaction on both a cathode and an anode is found to be a step of metal-hydrides disintegration. This electrochemical reaction proceeds at voltage 0.5-0.6 V on battery terminals according to experimental data on the thermal runaway. The reaction (1) is a powerful exothermic reaction with heat dissipation in amount of 436 kJ/mole (hydrogen) [10].

In this paper on the base of experiments, a probability is studied of a thermal runaway initiation in nickel-cadmium batteries with pocket electrodes; also here, the obtained experimental results are analyzed from point of view of both the thermal runaway classical mechanism [1] and the proposed above thermal runaway mechanism (1).

2. EXPERIMENTAL

For the experimental studies, there were chosen the batteries with the pocket electrodes (KL-14, KL-28) and the batteries produced by the company SAFT, specifically ones with the pocket electrodes (SBLE 30 and SBM 22).

The cycling was carried out for a group of ten parallel-connected batteries. This allowed us to obtain a large amount of statistical data in a relatively short period of time. Between the batteries were inserted heat-insulating gaskets made of wood 2 centimeters thick. Thus, thermal runaway arising in one battery could not influence the probability of occurrence of thermal runaway in the neighboring batteries due to their additional heating.

According to our previous studies [2], a probability of a thermal runaway increases with growth of the following factors: charge voltage, batteries' operating life and ambient temperature. In connection with this, there were chosen batteries with operating life 7 years. The batteries were charged under the charging voltage 2.2 V during 10 hours and discharged by current down to the voltage 1 V in accordance with operation directives for each of those batteries. A cycling process was conducted in a thermal chamber under temperature 45^0C. For each of the batteries groups there were fulfilled 100 charging-discharging cycles. So 10*100=1000 of the charging-discharging cycles were conducted for each type of the batteries. The investigation results are represented in the Table 1.

Table 1. Results of batteries cycling at environmental temperature 45 ^{O}C

Batteries	KL-14	KL-28	SBLE 30	SBM 22
Charge voltage (V)	2.2	2.2	2.2	2.2
Period of operation (years)	7	7	7	7
Number of charge-discharge cycles	1000	1000	1000	1000
Number of thermal runaways	0	0	0	0

One of processes facilitating a thermal runaway initiation is the process of hydrogen accumulation in electrodes of nickel-cadmium batteries during their operation [5-8]. In the papers [7,8], there was proved that in the battery KSX-25 with the sintered electrodes, a lot of hydrogen accumulates. The pocket electrodes distinguish with conceptually other construction. So in this section, let us experimentally check the hydrogen presence in the electrodes of the batteries KL-14, KL-28, SBLE 30 and SBM 22 with a long operating life as well as a possibility of its release from the electrodes in the thermal way.

Experimental installation for hydrogen extraction of the electrodes of nickel-cadmium battery is a sealed thermal chamber in the form of a pipe 1.8 m length and 2 cm in diameter [5]. One end of the pipe was sealed. At the other end of the pipe was inserted a rubber stopper with a tube for discharging the gas. The investigated electrode was placed in the cartridge that then was inserted into the thermal chamber. The sealed end of the thermal chamber was placed in a muffle furnace. Three oxide–nickel and three cadmium electrodes were taken from each battery to perform experiments.

Table 2 demonstrates the average values calculated for three experiments for the amount of hydrogen inside of an electrode for each type of electrodes. The electrodes' decomposition was fulfilled at the temperature 700°C as at this temperature level, an intensive hydrogen emission takes place both from oxide-nickel and cadmium electrodes. Each cadmium or oxide–nickel electrode was decomposed over an average period of 7 days, during 11 hours per day. As a rule the decomposition process was stopped when the hydrogen emission became less than 100 mL per day. The results of this experiment are shown in the Table 2.

Table 2. Hydrogen content in oxide-nickel and cadmium electrodes of batteries[a]

Batteries	KL-14		KL-28		SBLE 30		SBM 22	
Period of operation (years)	7		7		7		7	
Type of electrode	Ni	Cd	Ni	Cd	Ni	Cd	Ni	Cd
Amount of gas released (l)	37	26	69	39	71	40	41	23

[a] The relative error in the data in Table 2 is 5–7%.

Analysis of gas released as a result of thermal decomposition of the electrodes was performed using a gas analyzer VOG-2M. This analysis showed that the gas consists only of hydrogen.

So in the nickel-cadmium batteries with pocket electrodes and a long operating life, a lot of hydrogen is contained, just like in the batteries with the sintered electrodes [5,6].

3. RESULTS AND DISCUSSION

Therefore despite of the long operating life of those batteries and conducting of 1000 charging-discharging cycles for each type of batteries (in tough conditions), a thermal runaway never had place, even in one of them. But in the similar experiments set conducted with the nickel-cadmium batteries with the sintered electrodes, (for example, for the batteries KSX-25), the thermal runaway occurred with a very high probability [2].

Consequently, at least, this experiments set shows that the probability of a thermal runaway in nickel-cadmium batteries with pocket electrodes is much less than the same in nickel-cadmium batteries with sintered electrodes.

In favor of this affirmation, one can give other arguments, too. We never have managed achieving a thermal runaway in the nickel-cadmium batteries with the pocket electrodes (during more than thirty years of this phenomenon investigation), while in the nickel-cadmium batteries with the sintered electrodes, the thermal runaway has been watched and studied by us repeatedly [2-6]. Technicians maintaining nickel-cadmium batteries with the pocket electrodes univocally assert that there is no such thing as the thermal runaway in batteries of this kind. We also have found no information on a thermal runaway possibility in the nickel-cadmium batteries with the pocket electrodes in the scientific literature.

From the point of view of the classical mechanism of thermal runaway [1], the obtained experimental result is inexplicable as this mechanism does not take into considerable neither batteries construction nor a type of their electrodes. Therefore, a thermal runaway should occur with the same probability for any nickel-cadmium batteries with any type of electrodes. Although the experimental results show that it's not like that (Table 1 and (Ref. 2)).

From the point of view of the thermal runaway mechanism outlined in the papers [3,4] this experimental result is both natural and obvious.

The batteries with the pocket electrodes are of two kinds: with free electrodes location (in this case as separators, there are used ebonite sticks, rubber cords, plastic grills; it concerns the batteries KL-28, SBLE 30, SBM 22, etc.) and with closed-packed arrangement of electrodes and micro-porous separators (battery KL-14).

In the first case between the electrodes, there are large distances, through which dendrites practically can not intergrow. Also dendrites intergrowth in these batteries is not facilitating neither by a free electrolyte convection between the electrodes nor by an absence of a mechanical support for dendrites in a form of separator material. This way in these batteries, a formation is impossible of stable dendrites able to a strong local electrodes heating up and to an exothermic reaction launching (1); and hence there can not be any thermal runaway.

In the case of the batteries with a closed-packed arrangement of electrodes and thin separators, an electrodes strong local heating up is impossible, too; and hence also a launching is impossible of an exothermic reaction (1). Indeed, even if a dendrite intergrows between the electrodes of this construction, it will close the chain onto the metallic pocket of the opposite electrode and simply burn down not causing any essential local heating up by virtue of a high conductivity of the pockets metal.

4. CONCLUSION

So in the batteries with the pocket electrodes, it is impossible that there would occur a powerful local electrodes heating up connected with dendrites intergrowth, while namely this phenomenon is the reason of the thermal runaway initiation [3,4]. That is why to all probability in these batteries, the thermal runaway is impossible at all. But this statement requires further both experimental and theoretical investigations. Nevertheless, the conducted experimental studies univocally show that the probability of the thermal runaway in the nickel-cadmium batteries with the pocket electrodes is many times less than the thermal runaway probability in the batteries with the sintered electrodes. This result can be of a great practical importance for new types development of the nickel-cadmium batteries with a good thermal runaway resistance.

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