

Short Communication

Thermal Runaway in Sealed Alkaline Batteries

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The experiments proved that during a thermal runaway, hydrogen is evolved from sealed nickel–cadmium batteries in amount approximately ten times less than from unsealed batteries of the same capacity equipped with electrodes of the same type. Besides, the electrodes of the sealed nickel–cadmium batteries with a long operating life contain an amount of hydrogen 10-12 times less than the similar unsealed batteries.

Keywords: thermal runaway; alkaline batteries; hydrogen accumulation.

1. INTRODUCTION

In our earlier study it was shown that in a case of operation of batteries KSX-25 in floating mode or during their charging under a constant voltage, an initiation of thermal runaway is possible [1]. When this occurs, a charging rate in the batteries starts steep rising; electrolyte boils up instantaneously and turns into steam. The following events are also possible: melting and a rupture of an battery housing, destruction of jams under action of the steam, an abundant smoke formation and even an inflammation. The thermal decomposition of electrodes demonstrated that hydrogen accumulates in the electrodes of nickel–cadmium batteries in the process of their operation. So KSX-25 battery with the service period of over five years contains approximately 800 liters of hydrogen. The capacity of an oxide-nickel electrode as a hydrogen absorber was quantified as 13.4 wt% and 400 kg · m⁻³ [2]. The obtained result exceeds the earlier obtained results for nickel hydride (obtained using traditional methods) by 10 times [3], and for any reversible metal hydrides, including magnesium hydride or complex hydrides by 2 times [4,5].

The batteries in which thermal runaway is observed are used today in many domestic appliances and industrial applications such as mobile phones, computers, aircraft, uninterruptible power supplies (UPS) of communication networks, etc. Thermal runaway in all such devices and systems shall inevitably expose them to failure or fault. Hence, thermal runaway is a serious obstacle in the operation of numerous modern devices and systems. In spite of all the importance of the above problem, studies (except of the lithium batteries [6-9]) are desperately scant in the world literature dedicated to investigation of this dangerous and interesting phenomenon, and especially this concerns the alkaline batteries [1,10,12]. Meanwhile the alkaline accumulators are an integral part of electric systems of airplanes, electric vehicles, railway transportation, etc.

In this work, a possibility was investigated of the thermal runaway in the sealed nickel–cadmium batteries.

2. EXPERIMENTAL

2.1. Thermal Runaway

For our experimental investigations, the following sealed nickel–cadmium batteries were chosen: KCSM-3, KCSH-8, KCSL-11, KCSM-30, KCSL-90. These batteries are equipped with sintered electrodes.

The batteries were charged at constant voltage. Before a charge voltage change – in order to exclude a mutual influence of investigated charge-discharge cycles (via various residual phenomena, memory effect, etc.) – some checking cycles were conducted in amount from one to three. An obtained battery capacity after each checking cycle was compared with an initial capacity. If the obtained capacity showed difference more than by 10%, some additional checking cycles were conducted. This way the same initial conditions were guaranteed for all the investigated charge-discharge cycles. Discharge and checking cycles were performed according to an operation manual of the batteries.

In the sealed batteries before cycling in each battery top, a hole was made, in which a rubber plug with a tube was inserted with purpose of a gas withdrawal into elastic reservoir 1060 l in volume.

On the base of the preliminary investigations, there was established that in a case of thermal runaway, gas and steam get out from the batteries with temperature more than 300⁰C. Accordingly, for a damage protection of the reservoir, the entire gas was cooled by passage through the standard coil.

The recharger allowed setting of one of the following fixed voltage values: 1.45; 1.67; 1.87; 2.2 V. It also allowed working on constant basis with currents up to 150 A and on short-term basis with currents up to 500 A.

The results of the cycling of those batteries are shown in the table 1. In the experiments, eight batteries of each type were used. Under each value of the charge voltage (1.45; 1.67; 1.87; 2.2 V), 640 charge-discharge cycles were done. The charging was conducted under pointed above voltage values during 10 hours.

Table 1. Results of cycling of sealed nickel–cadmium accumulators

Batteries	KCSL-90	KCSM-30	KCSL-11	KCSH-8	KCSM-3
Number of thermal runaways	1	1	0	0	0
Period of operation (years)	8	9	-	-	-
Charge voltage (V)	2.20	2.20	-	-	-

Thus, from the 640 conducted charge-discharge cycles for each type of batteries under various values of voltage, the thermal runaway was observed only in two cases for the batteries KCSL-90 and KCSM-30. Hence, the thermal runaway is quite rare phenomenon in the sealed nickel–cadmium batteries.

In all the cases that the thermal runaway took place, the batteries had their operating lives approximately twice longer than their warranty periods, i.e. these experimental data confirm assumption that the probability of the thermal runaway initiation grows with an increase of the battery operating life period [1].

As for all the used charge voltage values (1.45; 1.67; 1.87; 2.2 V), the thermal runaway was observed only at the charge voltage 2.2 V. From this fact, the conclusion can be made that the probability of the thermal runaway grows with an increase of the charge voltage.

The thermal runaway was observed only in case of the batteries KCSL-90 and KCSM-30 (table 1). However from our operation experience of the batteries KCSL-11 and KCSH-8, it is known that the thermal runaway is possible also in case of these batteries. The fact that in our experiments the thermal runaway in these batteries was not observed can be explained only by a notice that the thermal runaway is rather rare phenomenon in common. Along with it, it is a random phenomenon in nature: there are no guaranties that in repeated series of the same experiments with the batteries of the same types KCSL-90 and KCSM-30, which developed the thermal runaway, it will happen again. Our experience of those batteries cycling shows that in some consignments of batteries, the thermal runaway is not observed even in really great number of such charge-discharge cycles (several thousands). Though in other consignments of batteries of the same type with the same operating life, the thermal runaway initiates quite easy if to apply to them really tough charging rates (that is if to conduct the charging at very large values of charge voltage). In all probability, the thermal runaway initiation as a random phenomenon depends very much on features of every individual battery and on all the history of its operation.

In our experiments, no thermal runaway was initiated in the battery KCSM-3 of a small capacity. We never have succeeded in getting the thermal runaway emergence in batteries with capacity less than 8 ampere-hours. In all probability, this is a common phenomenon for all nickel–cadmium batteries of a small capacity. Obviously, for initiation of the thermal runaway, two factors are significant, namely these two are a total mass of an battery and a total charging rate.

In a case of a big mass of an battery, its internal electrodes will warm up to a considerable extent because of their bad heat-dissipation.

In a case of a short circuit via dendrite, a high total charging rate will allow to focus a high local current in this place and, hence, to warm up this electrode fragment locally more intensively. Undoubtedly, both these factors are promotive of the thermal runaway initiation.

In any case, these experimental investigations show that the probability of the thermal runaway falls with a decrease of a capacity of an battery.

2.2 Composition Analysis of Gas Evolved During Thermal Runaway

The composition of the gas mixture evolved as a result of the thermal runaway is represented in the table 2.

Table 2. Composition of steam/gas mixture evolved from sealed nickel–cadmium accumulators as result of thermal runaway ^a

Batteries	KCSL-90	KCSM-30
Steam/gas mixture (l)	126	54
Steam (l)	31	17
Gas (l)	95	37

^a The relative error of volume measurements is 5 %.

A total amount of the steam/gas mixture was determined according to an initial volume of a gas catching reservoir. Then the steam/gas mixture catching reservoir was cooled up to the ambient temperature and the steam was condensed. Afterwards the repeated finding out took place of the volume of the gas catching reservoir. The difference of those volumes was considered as the volume of the steam evolved.

The composition analysis of the gas evolved from the sealed nickel–cadmium batteries in course of the thermal runaway was fulfilled with aid of the voluminous-optical gas analyzer VOGA-2M.

The analysis results of the gas mixtures obtained from the diverse batteries after the thermal runaway are shown in the table 3.

Table 3. Composition of gas mixture evolved from sealed nickel–cadmium batteries as result of thermal runaway ^a

Batteries	KCSL-90	KCSM-30
Gas concentration (%)		
H ₂	97	96.5
O ₂	2.6	3.0
Other gases	0.4	0.5

^a The absolute error in the percentage concentrations is 0.3–0.5.

2.3 Investigation of Hydrogen Accumulation in Electrodes of Sealed Nickel–Cadmium Batteries

In this part, an assumption will be verified on a hydrogen presence in the electrodes of the nickel–cadmium batteries even before a thermal runaway initiation and a possibility will be examined of its extraction from the electrodes in thermal way as it takes place in the unsealed batteries [1].

The experimental installation for the process investigation of the gas extraction from the battery electrodes when heated is described in detail in the work [1]. It consists of a metal thermal chamber in shape of a tube 1.8 m long and 2 cm in diameter; a sealed end of this tube is placed into a muffle furnace and as for the opposite end, a rubber plug is inserted into it with a tube for the gas withdrawal.

Due to the fact that by the action of a high temperature as a rule, any tested electrode melts partially and sticks to thermal chamber walls, then with a purpose of their convenient extraction from the chamber after the experiment conducting, every electrode was placed in a ‘cartridge’.

With a purpose of a heat exchange decrease, into the thermal chamber above the cartridge, a round porous ceramic plug 20 cm long was inserted.

Each electrode was decomposed at 800 °C. This particular temperature was chosen from the following considerations. In our preliminary experiments there was established that visible release of gas starts for a cadmium electrode from 340°C and for oxide-nickel electrode from 660°C. A significant gas release starts both for oxide-nickel and cadmium electrodes under temperatures more than 740°C. The rate of gas release increases with increasing temperature but after 800°C this increase is rather negligible. Thus the temperature 800°C was chosen as an optimal one for a thermal decomposition of both cadmium and oxide-nickel electrodes.

Every electrode decomposition took place until a day when a daily gas release still exceeded 4 ml g⁻¹ (milliliters of gas per one gram of an electrode weight). Under these conditions decomposing took place in average for a cadmium electrode during 5 days and for oxide-nickel electrode during 9 days; the process took place during 11 hours daily.

In the experiments, one or two electrodes – which depended on a cartridge capacity – were subject to the thermal decomposing. Then data were re-calculated to all the electrodes of this battery. Such cumulative data are given in the table 4.

Table 4. Hydrogen content in oxide-nickel and cadmium electrodes of sealed nickel–cadmium batteries

Batteries	KCSL-90		KCSM-30		KCSH-8		KCSM-3	
Period of operation (years)	8.0		7.8		8.3		6.8	
Type of electrode	Ni	Cd	Ni	Cd	Ni	Cd	Ni	Cd
^a Amount of gas released (l)	127	73	44	26	127	73	44	26

^a The relative error of the data is not more than 5 %.

The analysis of the gas evolved was conducted in the end of each experiment with aid of gas analyzer VOGA-2M. This analysis showed that the gas evolved consists of hydrogen not less than by 99%.

3. RESULTS AND DISCUSSION

According to the experiment results (table 4) in electrodes of nickel–cadmium sealed batteries even before a thermal runaway, there is a lot of hydrogen. A hydrogen volume in the electrodes of the sealed batteries is 10-12 times less than in the electrodes of the same type of the unsealed batteries of the same capacity [1].

This experimental fact logically follows from the hermetic nature of the considered batteries. In the work [1] there was shown that the hydrogen is collected in the electrodes of the nickel–cadmium batteries in the process of their operation due to the electrolyte decomposing process on hydrogen and oxygen. But in the sealed batteries an electrolyte amount is limited because the sealed batteries are not subject to a procedure of electrolyte addition in course of the battery technological preventive maintenance unlike the unsealed ones. That is why the hydrogen amount in the electrodes of the sealed batteries can be collected not more than its content in the electrolyte of the battery.

Let's give consideration for example to the battery KCSM-30. The electrolyte amount in the sealed batteries is 2 to 4 cm³ Ah⁻¹ [11], that is for this battery the electrolyte mass makes 60 to 120 ml. According to our records this battery contains 90-100 ml of the electrolyte. Hence, by decomposing of the entire electrolyte one can get no more than 150 liters of hydrogen. As the electrolyte was present in the batteries examined by us and they could work, hence, not the entire electrolyte had been decomposed on hydrogen and oxygen. That is why in the electrodes of the battery KCSM-30 the hydrogen could only be collected much less than 150 liters, which in fact was observed in the experiments.

As for the sealed batteries into the cadmium electrode, an active mass (in capacity) is put in much more than into the oxide-nickel electrode. That is why on the oxide-nickel electrode the oxygen starts its release earlier and this process is going on according to the oxygen cycle [12], so the oxygen will be re-built on the cadmium electrode. Thus, in the new sealed nickel–cadmium batteries in all probability, the hydrogen would not release at all. Nevertheless, as it is shown by the experiments described above, while operating life of the sealed batteries grows, the hydrogen yet releases and collects in the electrodes.

4. CONCLUSIONS

Thus, for sealed nickel-cadmium batteries the probability of thermal runaway increases with increase the charger voltage and battery life and decreases with decreasing their capacity. In addition, the amount of hydrogen accumulated in sealed batteries and released as a result of thermal runaway is approximately ten times less than in unsealed batteries of the same capacity.

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