

## **Analysis of Thermal Runaway Aftereffects in Nickel-Cadmium Batteries**

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In this research, there were obtained and analyzed experimental facts contradicting to the classical mechanism of the thermal runaway in nickel-cadmium batteries. It was shown that all the obtained experimental facts are in exact accordance to the new mechanism of thermal runaway consisting in the colligation of the thermal runaway with a powerful exothermic reaction initiation of the atomic hydrogen recombination.

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**Keywords:** thermal runaway, battery, nickel–cadmium

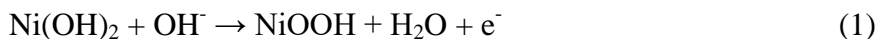
### **1. INTRODUCTION**

The thermal runaway is one of the most unusual and poorly explored phenomena in electrochemical batteries. This phenomenon emerges spontaneously irrespective of qualities of employees maintaining the batteries. For example, the thermal runaways are encountered in nickel-cadmium batteries installed in modern airplanes; however until now yet, this phenomenon nature is understudied. Especially high is a thermal runaway occurrence probability in long-lived batteries [1]. In a case of thermal runaway occurrence, a battery can catch fire and cause a short circuit of a power-supply system, which, in its turn, can lead to failure of a variety of airplane assemblies. In connection with this in aviation always, the thermal runaway causes emergency situations of all kinds of complexity degrees. In spite of the first priority of the thermal runaway problem for a safe work of alkaline batteries, there are desperately few investigations dedicated to this problem. Though, as for the

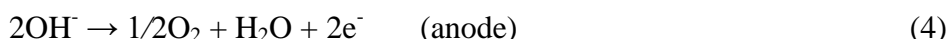
thermal runaway studies in lithium-ion batteries, there are quite a lot of them [2-4]. Far less such researches have been conducted for lead-acid batteries [5,6].

According to the classical explanation of the thermal runaway mechanism, the phenomenon takes place as a result of a long recharge, which can lead to a battery heating up resulted in its internal resistance fall and recharge current growth, which in its turn increases heating up, and so on [7].

So according to the thermal runaway classical mechanism, it occurs because of acceleration of reactions of batteries recharging:



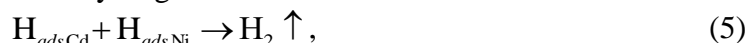
as well as reactions of electrolyte decomposition:



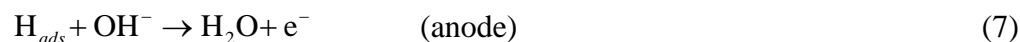
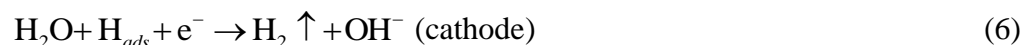
as the thermal runaway takes place at a long recharging of batteries [7].

The acceleration of those electrochemical reactions is connected with batteries resistance decrease as a result of their heating up. But in the papers [8,9], it was shown that as a result of the thermal runaway, from batteries, a lot of gas escapes, 95% of which is the hydrogen. For example, at the thermal runaway of the battery KSX-25, about 268 liters hydrogen and 13 liters oxygen escapes from it [8]. This fact can not be explained with the above electrochemical reactions as at the electrolyte decomposition, the hydrogen/oxygen ratio must make 2:1. Besides, there exist lots of other experimental facts contradicting to the thermal runaway classical mechanism [10-12].

In the papers [12-15], it was shown that as a result of a long operation of batteries, in their electrodes, a lot of hydrogen is accumulated. In the papers [16,17], it was proved by experiments that the thermal runaway is connected with a powerful exothermic reaction initiation of the recombination of the atomic hydrogen accumulated in the electrodes



which runs in line with the electrochemical mechanism:



According to the thermal runaway mechanism proposed in the papers [16,17], step-by-step, two accumulation processes bring batteries to the thermal runaway. Firstly, this is the process of the hydrogen accumulation in electrodes of batteries in a course of their operation [12]. Secondly, this is dendrites accumulation on the cadmium electrode. A dendrite grown up through a separator cuts dramatically a distance between electrodes and hence in this spot, a charge current density and an electrode temperature grow in proportion. This leads to a power increase of thermal runaway electrochemical reactions in this spot (6,7) as a limiting stage for these reactions is a decomposition speed of metal-hydrides, which grows up in proportion to the electrode temperature [16]. The reactions (6,7) are powerful exothermic reactions running with exhalation of 436 kJ/mole (hydrogen) [18]. That is why they heat up the electrode even harder in the spot of the thermal runaway and in vicinity. This way, the exothermic reactions of the thermal runaway (6,7) outspread radially from the dendrite location, where the thermal runaway emerged, and burn up through the separator in the form of regular

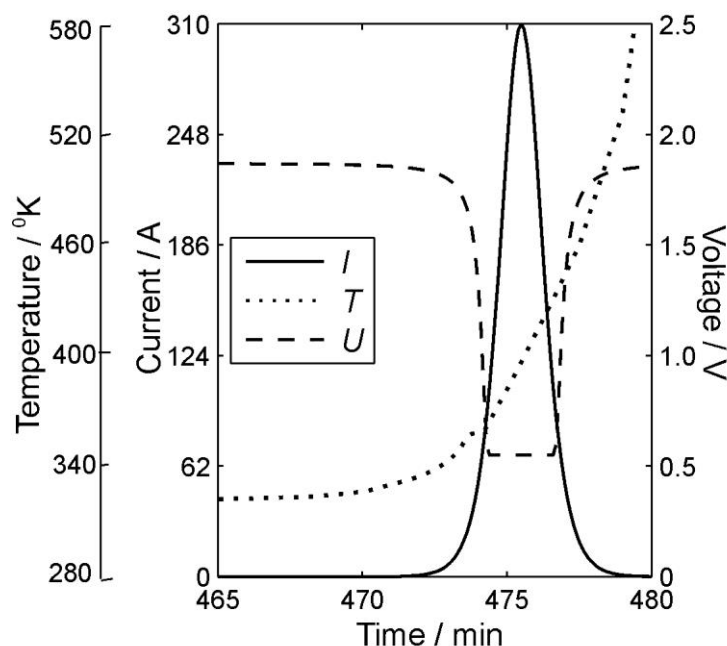
circles [17]. Being generated as a result of the thermal runaway, the hydrogen and the steam form a gas lock between the electrodes; so at a certain moment physically, this gas lock interrupts the electrochemical reactions (6,7).

In this study, we shall conduct an analysis of thermal runaway aftereffects from the point of view of both classical mechanism of the thermal runaway [7] and the mechanism proposed in the papers [16,17].

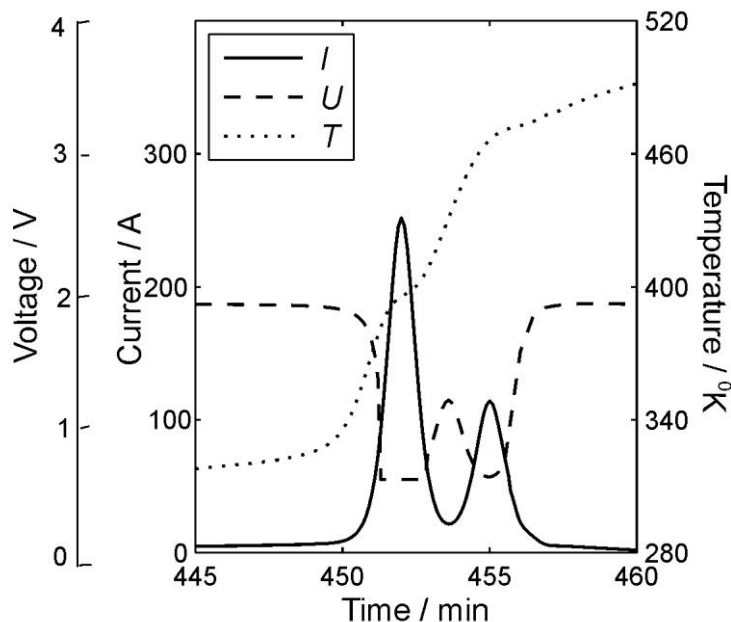
## 2. EXPERIMENTAL

In the experiments, the nickel-cadmium batteries KSX-25 were used with sintered electrodes by capacity 25 Ah. In the paper [1], it was proved by experiments that a thermal runaway probability grows with higher values of an ambient temperature, a charge voltage and operating life of the batteries. That is why in the experiment, the battery was used with the operating life 7 years. Battery cycling was fulfilled in a thermal chamber at the temperature 45°C. The battery charging was performed under a voltage of 1.87 V for 10 hours. The discharge was performed according to the operation manual of KSX-25 battery under a current of 10 A to a voltage of 1 V.

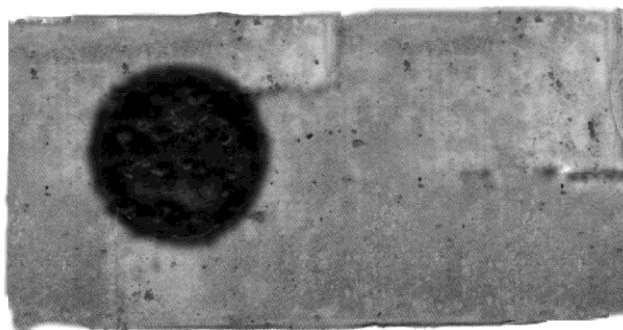
In order to obtain more statistical data for a less time interval, the group was cycled consisted of ten paralleled batteries. With a consideration in mind that a thermal runaway emerged in one battery would not make an impact on a thermal runaway occurrence probability in neighboring batteries (due to an additional heating up), between the batteries, there were inserted heat-insulating blocking lumbers two centimeters thick.



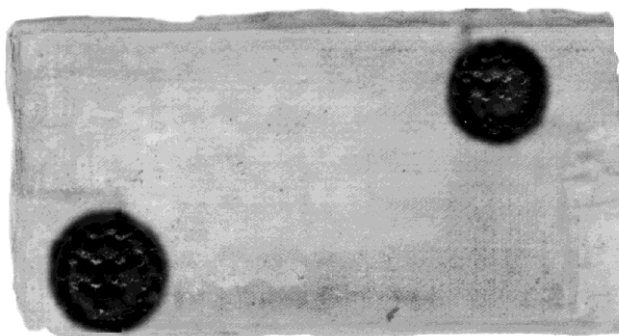
**Figure 1.** Change in parameters of the KSX-25 battery (No. 1) during thermal runaway:  $I$  is the charging current of the battery,  $U$  is the voltage of the battery terminals,  $T$  is the temperature of the battery positive terminal.



**Figure 2.** Change in parameters of the KSX-25 battery (No. 2) during thermal runaway:  $I$  is the charging current of the battery,  $U$  is the voltage of the battery terminals,  $T$  is the temperature of the battery positive terminal.



**Figure 3.** Oxide–nickel electrode of KSX-25 battery (No. 1) after thermal runaway.



**Figure 4.** Cadmium electrode of KSX-25 battery (No. 2) after thermal runaway.

In the process of the thermal runaway, the voltage was measured on the terminals of the batteries. The charge current was measured with a shunts resistance of 0.001 Ohm and maximum

current of 500 A. Shunts were included in the circuit separately for each battery between a negative terminal and a common bus (in the condition of the batteries joining-up in parallel). The temperature was measured on the positive terminals of the batteries. For the batteries group, 80 charge-discharge cycles were performed. So in total for those batteries,  $80 \times 10 = 800$  charge-discharge cycles were performed. During the cycling, the thermal runaway was observed twice. Batteries parameters changes during the thermal runaway are represented in the Figures 1,2. The electrodes after the thermal runaway are shown in the Figures 3,4. The gas released as a result of the thermal runaway was collected into an elastic container by 1000 liters in volume.

### 3. RESULTS AND DISCUSSION

First of all, we shall analyze those new experimental facts, which do not correspond to the classical mechanism of the thermal runaway [7].

As a result of the thermal runaway (Fig. 1) from the battery, 486 liters of the steam-gas mixture released. After the mixture cooldown, it turned out to be 297 liters gas and 152ml water in the measuring container, which corresponds approximately to 189 liters steam. The analysis of the released gas conducted with aid of the gas analyzer VOG-2M showed that it consisted of 95.6% hydrogen and 4.4% oxygen. The absolute error in the concentration percentage was 0.3-0.5. Thus from the batteries, 284 liters hydrogen and 13 liters oxygen released. Hence, during the total time of the batteries charging process plus the thermal runaway (Fig. 1), according to the reactions (3,4), in the battery, about 20.1 ml electrolyte was decomposed. The rest electrolyte released from the battery in the form of the steam. In average, the battery KSX-25 contains about 180 ml electrolyte. After the thermal runaway completion, in electrodes pores, some amount of electrolyte stays in spite of very high temperature of battery electrodes (Fig. 1), Also it is characteristic that the batteries plastic body was melt in the spots of the thermal runaway (Fig. 3). Besides, it is worthwhile to say that the amount of the released hydrogen (284 liters ( $H_2$ )) was much more than it is contained in the whole electrolyte, if to decompose it onto hydrogen and oxygen (about 224 liters ( $H_2$ )). Thus, this fact can not be explained based on the acceleration of the electrochemical reactions (1-4). This analysis shows clearly that the thermal runaway is connected with a new electrochemical process, an active participant of which is hydrogen, which corresponds in full to the thermal runaway new mechanism [16,17].

Hydrogen is accumulated in abundance in electrodes of nickel-cadmium batteries in a course of their operation [12-14].

Depending on KSX-25 batteries use and maintenance, their manual overcharge exceeds their nominal capacity by 1.6 times. The overcharge is required for a complete charging of batteries. Consequently, one cycle of charging of a KSX-25 battery produces 6 liters of hydrogen and 3 liters of oxygen. The hydrogen is characterized by very high diffusion permeability. The diffusion coefficient of hydrogen atoms is many times higher than the same of all other atoms, including oxygen atoms. For example, at the temperature 20°C, a diffusivity of hydrogen in nickel is approximately  $10^{10}$  times higher than a diffusivity of nitrogen or oxygen [19]. That is why oxygen escapes from a battery, while hydrogen escapes from a battery partially and another part of it is accumulated in electrodes. In our

earlier study [12], 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 [8,12]. The capacity of an oxide-nickel electrode as a hydrogen absorber was quantified as 13.4 wt% and 400 kg m<sup>-3</sup> [13,14]. This amount of hydrogen is much greater than it is contained in the entire electrolyte (about 224 liters (H<sub>2</sub>)) if it is decomposed into hydrogen and oxygen. In course of a battery KSX-25 operation, electrolyte is added when required as this is an ordinary vented battery. That is why, in principle, the found amount of the hydrogen can be accumulated by a battery for 800/6=134 charge-discharge cycles. To operation life end, such batteries would have passed through ten times more charge-discharge cycles. Hence, indeed, they are able to accumulate the mentioned above hydrogen volume.

Now, let us evaluate the energy balance of the thermal runaway phenomenon (Fig. 1). An energy received by a battery from a recharger during a thermal runaway can be evaluated by the formula

$$Q_r = \int_{t_1}^{t_2} U(t) \cdot I(t) dt, \quad (8)$$

where  $Q_r$  – energy received by a battery from a recharger during a thermal runaway;  $U(t)$  – voltage change on battery terminals during a thermal runaway;  $I(t)$  – charging rate change during a thermal runaway;  $t_1$  and  $t_2$  – time of start and end of a thermal runaway, respectively. For the value  $Q_r$  calculation, let us make use of the experimental data (Fig. 1). Let us consider the experimental functions  $U(t)$  and  $I(t)$ , approximate them by splines and integrate them by the formula (8). We'll obtain:

$$Q_r = 32.6 \text{ kJ}. \quad (9)$$

On other hand, let us evaluate the energy produced in the battery as a result of the thermal runaway and do it judging on external thermal effects. According to the experimental data (see earlier), during the thermal runaway from the battery, 152 ml electrolyte was evaporated. The energy needed for it is equal to:

$$Q_e = r \cdot m = 343.5 \text{ kJ}, \quad (10)$$

Besides, an energy is also needed for the electrolyte heating up from 30°C (battery's working temperature at charging session) up to 100°C

$$Q_h = c \cdot m \cdot (T_2 - T_1) = 52.8 \text{ kJ}, \quad (11)$$

The resulted from the thermal runaway steam released from the battery at the temperature at least not lower than 300°C (Fig. 1). For its heating up, the energy is needed as follows:

$$Q_s = c \cdot m \cdot (T_3 - T_2) = 55.3 \text{ kJ}, \quad (12)$$

In the considered experiment, the electrodes and other metal parts of the battery were heated up to the temperature not lower than 300°C (Fig. 1). Taking into account the masses of the electrodes and other metal parts equal to 0.8 kg, an energy needed for it must be not lower than

$$Q_m = 77.2 \text{ kJ}. \quad (13)$$

So the total amount of the produced heat is

$$Q = Q_e + Q_h + Q_s + Q_m = 528.8 \text{ kJ} \quad (14)$$

It will be observed that the evaluation (14) is minimal as it takes into consideration neither the heat dispersed to the atmosphere in the course of the thermal runaway, nor the energy spent on the electrolyte decomposition onto hydrogen and oxygen, nor the heat spent on the melting-through of the battery plastic body. Thus as a matter of fact, the real heat production is much greater.

Of course, one can suppose that as a result of a thermal runaway, also the electrochemical energy is produced, which is accumulated inside of a battery during its charging session. This is approximately 25 Ah or 108 kJ. But even in this case, the generated energy will be much greater than the energy obtained by the battery from its recharger plus the electrochemical energy accumulated in it. Besides, the battery used by us in the experiment had the operating life 7 years and upon a standard charging process, it delivered 14-15 Ah. In other words at its best, the energy possessed by it was 65 kJ.

After the thermal runaway and the battery cooling down, we placed it into electrolyte. Then after its electrodes saturation during a day&night, we discharged the battery. Upon that, the battery delivered 6.4 Ah. Hence during the thermal runaway, not more than 39 kJ of the accumulated electrochemical energy could be disposed.

Besides, this assumption was verified by experiments, too. A fast release of any accumulated electrochemical energy is possible only via a process of a kind of a sudden short circuit of battery electrodes. This condition was met by an instantaneous puncture of a battery with a solid metal nail. The experiments showed that the temperature of both electrolyte and electrodes in the case of their internal short circuit grows up to 70-80°C being accompanied with an insignificant vaporization. This corresponds to production of a heat not more than 30-40 kJ.

According to the classical mechanism [7], the energy generated as a result of a thermal runaway comes to a battery from a recharger. Indeed, in this mechanism, a presence is not supposed of any other electrochemical processes during a thermal runaway except of the electrochemical reactions (1-4). Nevertheless, even an approximate estimation of the thermal runaway energy balance shows that as a result of a thermal runaway, a battery generates much more energy than at the same time it obtains from a recharger. The electrochemical reactions (1-4) are not exothermic. Hence, a thermal runaway must be accompanied by a new exothermic reaction, which corresponds to the new mechanism of the thermal runaway proposed in the papers [16,17].

Now, let us consider visual aftereffects of a thermal runaway. After a thermal runaway completion, on electrodes, a separator turns out to be burned-through in the form of regular circles (Fig. 3,4). In the spot of the separator burning-out, on the electrodes, traces are seen of a powerful thermal action. For evaluating the electrode temperature in the spot of separator burning-out, we heated electrode fragments up to various temperatures and kept each of these electrode temperatures during 4 minutes, which was in accordance with a thermal runaway duration (Fig. 1). Then the obtained thermal burns were compared by us with the electrodes obtained after the thermal runaway (Fig. 3). These experiments showed that in the place of the thermal runaway the electrode temperature was more than 900°C.

According to the thermal runaway classical mechanism [7], at a battery self-heating up, an internal resistance decreases of the entire battery. That is why the thermal runaway effect on electrodes should be uniform. But our experiments show that a thermal runaway is a local process (Fig. 3.4). It is

possible to suppose that because of an irregularity of dendrites distribution on a cadmium electrode, the current density is also distributed in a non-uniform manner on an electrode surface (in a course of a thermal runaway) and subsequently an action on electrode is irregular, too. But why always (because of a thermal runaway) a separator is burned through in the form of the regular circles, it is impossible to explain with aid of the thermal runaway classical mechanism. According to the thermal runaway mechanism proposed in the papers [16,17], a thermal runaway exothermic reaction starts in a spot of a dendrite upspring through a separator. Then the reaction expands radially from this point burning the separator out in the form of the regular circles, which is observed in experiments every time (Fig. 3,4).

During a thermal runaway, a lot of hydrogen and steam escapes, which forms gas locks between electrodes (in the place of the thermal runaway) and this physically interrupts electrochemical reactions of the thermal runaway (6,7). As this process depends on many coincidental factors, the circles of separator burning-out will have a different radius, which was observed indeed in the experiments (Fig. 3,4). Besides, dendrites are formed on a cadmium electrode in occasional places. This fact explains the occurrence of the separator burning-out circles in different places of electrodes in different experiments (dedicated to the thermal runaway phenomenon) (Fig. 3,4).

Absolutely impossible is explaining of the results of the experiment (Fig. 2,4) in the frame of the thermal runaway classical mechanism [7]. Usually at a thermal runaway, one or two current bumps are observed (Fig. 1,2). Much more rare, from three up to five current bumps are observed. According to the thermal runaway classical mechanism, such current bumps must be connected with changes of battery temperature and internal resistance during a thermal runaway. However, such changes of battery temperature and internal resistance are impossible to be explained by any physical or electrochemical processes.

Meanwhile, according to the thermal runaway mechanism proposed in the papers [16,17], occurrence and dying out are possible of several foci of the thermal runaway in different places of electrodes (Fig. 3,4) and in different instants of time. Indeed, in a case of a thermal runaway occurrence in vicinity of some dendrite and its development, in this spot at the same time, a gas lock is formed, which can interrupt the thermal runaway electrochemical reactions (6,7). In this case, a current density will grow up in other places of the electrodes or inside of other electrodes group, where there is no gas lock and electrolyte is more abundant yet. This can lead to an initiation of other focus of the thermal runaway in another place (Fig. 4). This process can be continued until the entire electrolyte evaporation in the battery would take place. In this case, the thermal runaway electrochemical reactions (6,7) would be stopped completely. From a comparison of Fig. 2 and Fig. 4, one can see that to the two current bumps, two loci of the thermal runaway correspond on the electrodes, which is in line with the new thermal runaway mechanism [16,17].

There exist also other experimental facts contradicting to the thermal runaway classical mechanism highlighted by us in the earlier papers [1,17]

#### 4. CONCLUSION

The analysis conducted showed that the proposed in the papers [16,17] thermal runaway mechanism corresponds to all the known experimental facts. Meanwhile in the frame of the thermal



runaway classical mechanism [7], those experimental facts are impossible to be explained. However such unusual and unique phenomenon as the thermal runaway in nickel-cadmium batteries requires further both theoretical and experimental studies.

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