The Mechanism of Thermal Runaway in Alkaline Batteries

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It was shown on the basis of charge current, terminal voltage, and change in battery temperature that during thermal runaway, the observed changes cannot be explained by the self-acceleration of known reactions (due to overheating), battery charging and electrolyte decomposition. The observed changes can only be explained if we assume, that the thermal runaway is associated with a powerful electrochemical reaction going within the battery with a terminal voltage approximately 0.55 V. It is shown that the recombination reaction of atomic hydrogen accumulated in the electrodes is exothermic thermal runaway reaction in alkaline batteries. New mechanism of thermal runaway in Ni-Cd batteries, which explains all the experimental data known currently is proposed.

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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, thermal runaway is quite a rare phenomenon. Technicians servicing batteries for decades might never witness the phenomenon or encounter it very rarely in their life. However, 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 an earlier communication2 we have studied the phenomenon of thermal runaway in KSX-25 nickel-cadmium batteries, and analyzed the gases evolved during its occurrence. It was demonstrated, that in the process of the thermal runaway from a battery KSX-25, the steam-gas mixture releases in amount about 350 liters, including 280 liters of hydrogen and 70 liters of steam. 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\(^{-3}\) (Refs. 3 and 4). The thermal runaway phenomenon was investigated also in works5–8 etc. In this manuscript we shall analyze the change in some of the key battery parameters during the process of thermal runaway in perspective of the commonly accepted mechanism for it.1

Experimental

Analysis of the change in parameters in Ni-Cd batteries during thermal runaway.— In the experiments, there were used vented Ni-Cd batteries KSX-25 with sintered plates by capacity 25 Ah. In our previous report6 it was shown, that the probability for thermal runaway increases with the service life of the battery and increase in charging voltage. Hence, batteries with a service life of over 6 years were used for this study. Charging was performed under a voltage of 1.87 V for 10 hours. Discharge was performed according to the operation manual of KSX-25 battery under a current of 10 A to a voltage of 1 V. Charging and discharging was performed for a pack of ten batteries connected in parallel. This increased the number of experiments during the same time period and therefore the possibility of thermal runaway also increased.

Wooden thermal insulating pads two centimeters thick and clamped in a metal brace were inserted between the batteries to exclude the possibility of thermal runaway initiating in one battery to influence or initiate the thermal runaway in neighboring batteries due to additional overheating.

The voltage was measured separately on terminals of each battery. Charge current was measured with a shunts resistance of 0.001 Ohm and maximum current of 500 A. Shunts were included in a circuit separately for each battery between a negative terminal and a common bus. The temperature was measured with aid of thermocouples connected to positive terminals of each battery. Via analog-to-digital converter, all data were delivered to computer. The steam and gas evolved as a result of the thermal runaway got out freely into flexible reservoir 1060 l in volume. Figures 1 and 2 shows the parameters for two batteries during the process of thermal runaway.

Visual consequences of the thermal runaway.— Let’s consider some visual consequences of the thermal runaway. On the Figures 3 and 4 the electrodes are shown of two accumulators exposed to the process of the thermal runaway. From the visual analysis of the Figures 3 and 4, the following conclusions can be made. Firstly, as because of the thermal runaway a separator is burnt through only in certain places but not on the whole electrode surface,

![Figure 1](link)

**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.

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the conclusion can be made that the thermal runaway is a local phenomenon.

Secondly, as the circles of burning-through of the separator on the electrodes are located in absolutely various places at different accumulators exposed to the thermal runaway, the conclusion can be made that the process of the initiation of the thermal runaway lacks any regular pattern and occurs at random and in absolutely incidental places.

Thirdly, due to the fact that the places of burning-through of the separator possess a shape of regular circles and also absolutely different radius, one can suppose that the thermal runaway initiates from a point of a surface and then (like a combustion process) expands radially in a uniform manner from this point.

Fourthly, as the circles of burning-through of the separator do not spread on the entire electrode surface and besides all of them have a different random radius, a conclusion can be made that in the course of the thermal runaway some processes exist, which prevent its propagation on the whole electrode and assist to an extinction of the thermal runaway.

Fifthly, in the experiment there were two current bumps (Fig. 2) and exactly two areas of burning-through of the separator on the electrodes correspond to them (Fig. 4). Hence, during one charging a thermal runaway can be initiated and die out repeatedly. That is why the following mechanism can be proposed for initiation and extinction of the thermal runaway. The initiation and the extinction of the thermal runaway in any place of an electrode causes first a fast growth of a charge current and then an equally fast current downfall because of an electrolytic solution evaporation in this place and of vapor locking in the burnt hole of the separator. In its turn this would result in enlargement of an average current density in other areas of the electrodes, which can launch the thermal runaway in another place, probably between the other couple of the electrodes, etc.

**Calorimetric analysis of thermal runaway.**— In our earlier study, on the base of analysis of an energetic balance of a thermal runaway for a KSX-25 battery, it was shown that in the process of the thermal runaway, the battery emits energy at least 6 times larger than it obtains from the recharger. Moreover, in this work was estimated only the lower limit of the energy emitted. In fact, the energy released during the thermal runaway is much more. In the quoted assessment, only the energy was taken into account that was spent on the accumulator heating up and electrolytic solution evaporation but not the energy dissipated by the accumulator during the thermal runaway and not the energy spent on meltdown of the accumulator plastic housing, and so on.

In this work we performed calorimetric analysis of thermal runaway Figure 1. Experimental research showed, that in the result of thermal runaway the energy equal to 5012 kJ (relative error 7%) released from the accumulator. Meanwhile the accumulator receives from charging device the energy equal to 33.7 kJ (Ref. 2) (during the process thermal runaway). Besides 270 liters of hydrogen evolves in the process of thermal runaway. Usually during such a thermal runaway all electrolyte evaporates and the plastic body of the battery melts down.

### Results and Discussion

Let’s consider the standard mechanism of the thermal runaway initiation from point of view of our experimental data received in this work and earlier in the works. According to the standard point of view, the thermal runaway in accumulators has the following scenario. In a case of an accumulator long recharging under constant voltage (or at its floating service), heating-up takes place, which results in decreasing of an accumulator 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 accumulators during their charging under a constant voltage. Besides as for hermetic accumulators there is a belief that an essential initial contribution to accumulators heating-up is made by exothermic reactions of an oxygen cycle.

The investigated by us accumulators KSX-25 are not hermetic. They are the typical vented accumulators with a closed-packed arrangement of the electrodes. This is why the oxygen cycle at these accumulators is absent.

In our previous report it was shown, that the probability for thermal runaway increases with increase in temperature of battery and increase in charging voltage. This results correspond to the standard mechanism of the thermal runaway completely. Indeed, both the increase of the constant charge voltage leading to the increase of the recharging current and the environmental temperature growth must considerably increase an initial temperature of the accumulators and...
hence both these factors must increase the probability of the thermal runaway. But the other results do not correspond to this mechanism of the thermal runaway.

Firstly, according to the standard mechanism of the thermal runaway, at the same conditions the thermal runaway must be initiated with an equal probability both in the new accumulators and in the accumulators with the long operation lives. This follows from the fact that in the standard mechanism of the thermal runaway, the processes of ageing of the accumulators are ignored completely. But the direct experimental data just show that the thermal runaway probability depends on the accumulator life, a great deal! This correlation is thoroughly confirmed (in private conversations) by technicians servicing alkaline accumulators in airports. At least for thirty years of our studies of the thermal runaway phenomenon in alkaline accumulators we had no chance to observe aftereffects of the thermal runaway in new accumulators KSX-25 under actual operating conditions. Meanwhile the aftereffects of the thermal runaways of the accumulators of the type with the long operation lives working on real objects were studied and described by us many times. So the established by us correlation between the thermal runaway probability and the accumulator operation life obviously indicates that the ageing processes must be considered as integral part of thermal runaway mechanism.

Secondly, according to the standard mechanism of the thermal runaway, along with heating-up, an internal resistance of the whole system of an accumulator decreases. Hence, if some thermal runaway aftereffects are possible, then they must be regularly spread on all the surface of the electrodes. But a visual analysis of the thermal runaway aftereffects (Figs. 3 and 4) shows that the thermal runaway takes place only in small areas having the regular shape of circles and in no way it affects the rest part of the electrodes. Even the visual analysis of the burnt-through areas of the separators on the electrodes (Figs. 3 and 4) indicates that in this area a very powerful exothermic process took place.

From the point of view of the standard mechanism of the thermal runaway, also the shape cannot be understood of the separator burning-through areas looking like correct circles. A conclusion can be made that a local heating-up of the electrodes during the thermal runaway is connected with a non-uniformity of a charge current density on the electrodes surfaces. This non-uniformity can be connected, for example, with a non-uniformity in a distribution of dendritic crystals in the separator on the electrodes surfaces or with some other ageing processes of separators and electrodes, as a number of colleagues supposed in a private conversation. But no mentioned above reason can constantly result in forming of the powerful local current density in the shape of the correct circles. It is as if the thermal runaway is initiated from a point on a surface and then similarly to the fire growth process it is uniformly distributes radially from this initial point.

Thirdly, according to the standard mechanism, the thermal runaway takes place on expense of the energy, which the accumulator obtains from the recharger. Calorimetric analysis showed, that in the result of thermal runaway the energy equal to 5012 kJ (relative error 7%) released from the accumulator. Meanwhile the accumulator receives from charging device the energy equal to 33.7 kJ (Ref. 2) (during the process thermal runaway). This fact can be explained only from an assumption that the thermal runaway is accompanied by a powerful exothermic reaction. Moreover, this reaction must be a basis of the mechanism of the thermal runaway.

Fourthly, the standard mechanism of the thermal runaway supposes that the thermal runaway is connected only with an intensification of an accumulator charge reaction (on expense of internal resistance decreasing) and possibly also of an electrolytic solution decomposition reaction as the thermal runaway takes place in case of a long recharging of the accumulators. If this is the case, a hydrogen/oxygen ratio in the liberated gas must be 2 : 1. Nevertheless the experiment shows that the liberated gas mixture contains more than 95% of hydrogen.

Fifthly, current $I$ rises sharply when thermal runaway initiates, and consequently the temperature of the electrodes increases sharply. In order to gain insight into the causes for the increase in current, we measured the voltage $U$ at the battery terminals, Fig. 1.

The charging current and voltage of the charging device are correlated by the following equation:

$$ I = \frac{U - E}{r_a + r_f}, $$

where $I$ is the charge current, $U$ is the voltage maintained by the charging device, $E$ is the battery open circuit voltage (OCV), $r_a$ is the resistance of the connecting leads and shunt, $r_f$ is the battery internal resistance. The resistance $r_f$ is nonlinear one; it takes into account not only ohmic resistance of electrolyte but also all other nonlinear processes depending on current and influencing voltage on battery terminals $U$ and in particular the activation processes on the electrode-electrolyte border.

Voltage at the battery terminals can be equated as follows:

$$ U_t = E + I \cdot r_f. $$

According to the standard point of view, the cause of thermal runaway in the given mechanism is related to the decrease of internal resistance of the batteries due to their heating. Let us analyze the curves in Fig. 1 for the change of current and voltage during thermal runaway.

During the charging of Ni–Cd batteries the following reaction takes place at the positive electrode:

$$ \text{Ni(OH)}_2 \cdot \text{OH}^- \rightarrow \text{NiOOH} + \text{H}_2\text{O} + \text{e}^- $$

and the following reaction takes place at the negative electrode:

$$ \text{Cd(OH)}_2 + 2\text{e}^- \rightarrow \text{Cd} + 2\text{OH}^- $$

OCV corresponding to reactions (Eqs. 3 and 4) shall be $E = 1.26 \text{--} 1.44 \text{~V, depending upon the charge state of the electrodes and their type.}$

The thermal runaway reported takes place due to long overcharging of batteries. The only reaction at this moment can be the decomposition of water into hydrogen and oxygen.

At the cathode:

$$ 2\text{e}^- + 2\text{H}_2\text{O} \rightarrow \text{H}_2 + \text{OH}^- $$

At the anode:

$$ 2\text{OH}^- \rightarrow 1/2\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- $$

Thus, in formulas (Eqs. 1 and 2) $E$ shall be the OCV of a hydrogen--oxygen element, i.e. the difference between the standard potentials of hydrogen and oxygen electrodes in the given electrolyte, which is equal to 1.229 V. (Ref. 11)

Let us examine the initiation of the thermal runaway process. When it starts, the voltage at the battery terminals drops sharply to approximately 0.55 V (Fig. 1). Such a sharp drop in voltage, according to Equation 2 cannot be explained by only the decrease in internal resistance of the battery due to increase in temperature. Actually, this voltage is even less than the OCV for the above reactions (Eqs. 3 and 4) and (Eqs. 5 and 6). This voltage drop can only be explained by the decrease in OCV during the process of thermal runaway. It is possible only if the thermal runaway process is related with the initiation of a new potent electrochemical reaction, with much lower difference ($\Delta E$) in the standard potentials for the anode and cathode, as compared to reactions (Eqs. 3 and 4) and (Eqs. 5 and 6).

The generally accepted mechanism for thermal runaway assumes, that during the thermal runaway, just as before it starts, the electrochemical reaction for the decomposition of water as in Equations 5 and 6 is underway but much more intensely due to decrease in the internal resistance of the battery. However, neither the reaction for the decomposition of water (Eqs. 5 and 6), nor the battery charging reaction (Eqs. 3 and 4) can’t proceed at a battery terminal voltage of 0.5 -- 0.6 V during thermal runaway.

It is worth mentioning, that the parameter $E$ decreases with the rise in battery temperature for reactions (Eqs. 5 and 6) approximately...
according to the equation\(^{12,13}\)

\[
E = 1.229(1 - 0.0003(T - 298)) \tag{7}
\]

where \(T\) is the battery temperature.

However, it shall can reach a voltage of 0.5–0.6 V only when the temperature rises to 2000 K. Thermal runaway in the battery as seen from Figure 1, started at a temperature of approximately 373 K at the positive terminal of the battery. The temperature is much higher than 373 K (Ref. 2), but much lower than 2000 K at the point of thermal runaway at the electrodes.

Hence, the analysis unequivocally shows that the thermal runaway is not related with the intensification of the reactions (Eqs. 3-6) due to self-heating of the batteries, but from a new electrochemical reaction proceeding with a much lower difference in standard potentials \(\Delta E\) between the anode and the cathode, than for reactions (Eqs. 3 and 4) and (Eqs. 5 and 6).

The given analysis confirms the conclusions made on the basis of thermal runaway energy balance in our earlier manuscript,\(^2\) that the thermal runaway is related with the initiation of a new potent exothermic reaction.

The sharp decrease in OCV \((E)\) and battery resistance \(r_\beta\) during thermal runaway, according to Equation 1, should produce a sharp growth in the charging current, as is observed in the experiment.

Further, the internal resistance of the battery sharply increases, due to evaporation of the electrolyte, and the charging current sharply drops to very small values as in Fig. 1.

On the basis of all the obtained experimental data, the following mechanism of the thermal runaway in the nickel-cadmium accumulators can be proposed.\(^6\)

As during the thermal runaway a great mass of the hydrogen is released from the accumulators for 3–5 minutes,\(^2,5\) the assumption can be made that the hydrogen is an active participant of the thermal runaway process and of the exothermic reaction accompanying this process. But the hydrogen is accumulated in the accumulator electrodes only in proportion to their operation life,\(^{2,3,6}\) Hence if the assumption is correct that the hydrogen is the active participant of the thermal runaway process, then the thermal runaway probability must grow so far as the hydrogen is accumulated, or, which is the same, so far as the accumulator spends its operation life, which exactly corresponds to the experimental data.\(^6\) The other process of ageing step-by-step leading the accumulator to the thermal runaway is the process of collection of dendritic crystals in the separator.

In a location area of a dendritic crystal, a distance is essentially decreased between the electrodes. This event results in the occurrence that in this area the charge current density will be much more than in other locations of the electrodes. Hence this place will be heated up much more vigorously than the other locations of the electrodes.

When the cadmium electrode is heated up to 340\(^{\circ}\)C, a remarkable hydrogen release is initiated from it,\(^5\) but even at temperatures at least one and half less, a minor hydrogen release is already initiated from it. This can be a reason of the exothermic reaction initiation of the thermal runaway. This reaction will heat up the electrodes even harder in the location of a dendritic crystal and in neighboring areas around it, which will lead to even greater hydrogen release and so on.

Thus the exothermic reaction will outspread from the location of the dendritic crystal radially and so it will burn the separator through in the shape of the correct circles (Figs. 3 and 4). There are two factors, which can prevent outspreading of this exothermic reaction on the entire electrode surface. Firstly, it is the gas lock, which is formed in the hole of the burnt-through separator and between the electrodes after the electrolytic solution evaporation. Secondly, it is hydrogen depletion in the electrodes in the area of the thermal runaway.

The dendritic crystals emerge in the separators in random locations; this can be an explanation of absolutely random location of burnt holes of the separators in different accumulators (Figs. 3 and 4).

Hydrogen is located inside of electrodes of the accumulators in the form of metal hydrides i.e. in an atomic form.\(^{5,14}\) At an output of atomic hydrogen from electrodes occurs its recombination.

\[
H + H \rightarrow H_2 \tag{8}
\]

Reaction (Eq. 8) is powerful exothermic reaction with a thermal emission 436 kJ/mol (hydrogen).\(^{15}\) This thermal emission is more than at reaction of burning of hydrogen in oxygen 285,8 kJ/mol (hydrogen).\(^{16}\)

On the basis of recombination of atomic hydrogen (Eq. 8), hydrogen welding is based. It is capable to create a flame with temperature 3700\(^{\circ}\)C. While oxygen-hydrogen welding (Eq. 9) is capable to create a flame with temperature only 2500\(^{\circ}\)C. (Ref. 17)

As a result of the thermal runaway (Fig. 1), 270 l of hydrogen are released. Thus, if hydrogen in the electrode is in atomic phase, in case of its recombination and evolving of 270 liters of hydrogen, the energy of 5207 kJ shall release. This value well corresponds to the above experimental value.

Thus, in all probability, it is a recombination reaction of atomic hydrogen with exothermic reaction of thermal runaway in alkaline batteries.

It is interesting to note the change in the charging current in KSX-25 batteries as shown in Fig. 2. Such a discontinuous variation of current can indicate that the thermal runaway can initiate and decay in batteries repeatedly and spontaneously. Indeed, initiation and decay of thermal runaway at a particular point of an electrode shall initially bring a sharp growth of the charging current and then to similar drop due to evaporation of the electrolyte and consequent formation of a gas plug in the separator burn through hole. It shall, in turn increase the average current density at other points of the electrodes, which may result in initiation of the thermal runaway at another point, possibly between another pair of electrodes, etc. This can explain the stepwise nature of the current in Fig. 2.

Conclusions

The recombination reaction of atomic hydrogen (Eq. 8) is full exothermic reaction of thermal runaway in alkaline batteries. According to researches (Figs. 1 and 2), the reaction (Eq. 8) must pass through electrochemical process. Undoubtedly, investigation of this complicated and poorly studied mechanism of the electrochemical process requires further researches conclusion, both theoretical and experimental ones. However, preliminary experiments have shown that the electrochemical reaction (Eq. 8) takes place precisely at a voltage of 0.5–0.6 V.

Undoubtedly the proposed mechanism of the thermal runaway should be considered only as a possible hypothesis requiring separate additional both experimental and theoretical researches. Nevertheless it allows explaining all available at the moment experimental data.

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