The thermal runaway is encountered in batteries of practically any electrochemical system. According to the standard point of view, the thermal runaway in accumulators goes on with the following scenario. In a case of an accumulator long recharging under constant voltage, so the thermal runaway is a result of positive feedback between a current and a temperature of accumulators during their charging under a constant voltage.

In a case of the thermal runaway initiation, a battery heats up till high temperature values; an electrolyte evaporates instantly; a battery is made by exothermic reactions of an oxygen cycle.

In our previous papers, it was shown that there are two processes of accumulation that step by step bring the nickel-cadmium batteries to the thermal runaway. Firstly, this is a process of a hydrogen accumulation inside of battery electrodes during their operation. Secondly, this is a process associated with a dendrites intergrowth through a separator. In the spot, where the dendrite is located, a distance between the electrodes gets cut to a large extent. As a result of this event, in this spot, current density will be much more than in other places on the electrodes. So this spot will be heated up much more intensively than other electrodes’ parts. This can be a reason of a thermal runaway exothermic reaction.

So the thermal runaway classical mechanism supposes that the reason for the thermal runaway is an acceleration of a battery charge reactions (on expense of its heating-up)

\[
\text{Ni(OH)}_2 + \text{OH}^- \rightarrow \text{NiOOH} + \text{H}_2\text{O} + e^- \quad [1]
\]

\[
\text{Cd(OH)}_2 + 2e^- \rightarrow \text{Cd} + 2\text{OH}^- \quad [2]
\]

or an acceleration of an electrolyte decomposition reactions

\[
2e^- + 2\text{H}_2\text{O} \rightarrow \text{H}_2 + 2\text{OH}^- \quad \text{(cathode)} \quad [3]
\]

\[
2\text{OH}^- \rightarrow 1/2\text{O}_2 + \text{H}_2\text{O} + 2e^- \quad \text{(anode)} \quad [4]
\]

as the thermal runaway takes place in cases of a long-time battery recharging.

In our previous papers, it was shown that a lot of experimental data exists that contradict to the generally accepted thermal runaway mechanism.

Firstly, according to the classical thermal runaway mechanism, a probability of the thermal runaway initiation should not depend on a battery operating life. Nevertheless, the available direct experimental data show that the thermal runaway initiation probability depends on the battery operating life to a large extent. Notably that in new Ni-Cd batteries, the thermal runaway is not encountered at all.

Secondly, according to the classical mechanism, the thermal runaway is connected with a battery charging reactions (Eqs. 1 and 2) intensification and an electrolyte decomposition (Eqs. 3 and 4) (in a case of a battery recharging) because of the battery heating up. Therefore at the thermal runaway from the battery, there can be released a steam and a small amount of hydrogen and oxygen in proportion 2:1. But the experimental measures show that as a result of a thermal runaway from a battery, there are released a steam (in amount approximately equal to an amount of an electrolyte in the battery) and a gas (95 to 97% of which is represented by the hydrogen).

Thirdly, according to the classical mechanism, the thermal runaway occurs on expense of an energy obtained by a battery from a recharger. But the direct experimental studies show that as a result of a thermal runaway, a battery releases energy approximately 140 times more than it obtains from the recharger.

Therefore, the thermal runaway is connected with a development of a powerful exothermic reaction. Though the thermal runaway classical mechanism does not suppose a development of some additional electrochemical reactions, except of one of battery charging and one of electrolyte decomposition (at battery recharging). Besides, there are a lot of other experimental facts contradicting to the thermal runaway classical mechanism.

On the basis of all the available experimental data in the papers, there was proposed the new thermal runaway mechanism. In these papers, there was shown that there are two processes of accumulation that step by step bring the nickel-cadmium batteries to the thermal runaway. Firstly, this is a process of a hydrogen accumulation inside of battery electrodes during their operation. Secondly, this is a process of dendrites accumulation on the cadmium electrodes of the nickel-cadmium batteries. In the papers there was shown that in a course of a long operation of the batteries KSX-25, in their electrodes, up to 800 liters hydrogen are accumulated. A thermal runaway initiation is connected with a dendrites intergrowth through a separator. In the spot, where the dendrite is located, a distance between the electrodes gets cut to a large extent. As a result of this event, in this spot, current density will be much more than in other places on the electrodes. So this spot will be heated up much more intensively than other electrodes’ parts. This can be a reason of a thermal runaway exothermic reaction initiation. This reaction will heat up the electrodes both in the dendrite location and in vicinity of this spot even more intensively, which will lead to even larger amount of hydrogen release, and so on.
down separator as well as between the electrodes after an electrolyte evaporation. Secondly, this is hydrogen exhaustion in the electrodes in the thermal runaway location.

Hydrogen is present inside of battery electrodes in a form of metal-hydrides, i.e., in atomic form. After the atomic hydrogen release from the electrodes, its recombination occurs:

\[ H + H \rightarrow H_2 \]  \[ \text{[5]} \]

The reaction (Eq. 5) is a powerful exothermic reaction with heat dissipation in amount of 436 kJ/mole (hydrogen). This heat buildup is more intensive than in a case of hydrogen combustion reaction in oxygen, which makes 285.8 kJ/mole (hydrogen). \[ H_2 + \frac{1}{2} O_2 \rightarrow H_2O \] \[ \text{[6]} \]

It is the atomic hydrogen recombination reaction (Eq. 5), which is the thermal runaway exothermic reaction in question. In the paper, there was proved that the exothermic reaction of the thermal runaway (Eq. 5) proceeds via electrochemical mechanism. Indeed, in a case of a thermal runaway initiation, the battery charging current rises steeply, while the voltage on battery terminals tumbles down approximately to 0.55 V (Fig. 2 and paper).

Such a sharp voltage drop cannot be explained only by the decrease in internal resistance of the battery due to increase in temperature. Actually, this voltage is even less than the OCV for the reactions (Eqs. 1 and 2) and (Eqs. 3 and 4), i.e., under the voltage 0.55 V on the battery terminals these reactions would not take place at all. 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. 1 and 2) and (Eqs. 3 and 4).

In this manuscript by experiments we study thermal runaway electrochemical reactions on a cathode and anode in alkaline batteries.

### Experimental

**Examination of electrochemical reactions on nickel hydride.**— In the papers, it was shown that as a result of a long-term operation of alkaline batteries, in their electrodes, a lot of hydrogen accumulates. So sintered matrices of long-life alkaline battery electrodes represent metal hydrides with a very high content of hydrogen. Subsequently, in order to understand the thermal runaway mechanism, one needs to know, which electrochemical reactions take place on metal hydrides in the charge process of the alkaline batteries. In this section, we shall study an electrochemical behavior of the nickel hydride, which forms metal-hydride matrices of positive electrodes of nickel-cadmium batteries with a long period of operation.

In this paper, the electrochemical behavior of the nickel hydride was examined in an electrolyte of an alkaline battery. This is the solution KOH (Reagent) by density 1.20 g cm\(^{-3}\) with addition of 20 g l\(^{-1}\) of LiOH. In our investigation, a plate of the electrolytic nickel was used by square 1 cm\(^2\). For creation of a reproducible surface, the plate was electropolished during 30 s in a 60% solution of H\(_2\)SO\(_4\) at an anode current density \( i = 5000\ \text{A m}^{-2}\). Then the plate was washed with bidistilled water and dried up with an absorbent paper. For the nickel hydride formation, the plate was placed in a cell with solution of H\(_2\)SO\(_4\) in concentration 1N with addition of 0.2 g l\(^{-1}\) thiourea. The nickel hydride formation process takes place at cathode current density \( i = 500\ \text{A m}^{-2}\) during one hour. In this case, according to the data, in the plate, \( \beta \)-phase of the nickel hydride formed. Then the electrode was washed with bidistilled water and carried over into the working cell for an examination. The working cell was placed under nitrogen atmosphere (99.999%) for avoiding of an electrode oxidation. A potential of a working electrode was found versus a silver chloride electrode and then it was recalculated based on the standard hydrogen electrode (SHE).

At first, polarization curves were defined of non-hydrogenated nickel in the alkaline battery electrolyte at cathode and anode polarizations (Fig. 3). Hydrogen and oxygen evolution on metals adheres well to the Tafel’s equation:

\[ E = A + B \cdot \log (i) \]

where \( E \) – potential; \( i \) – current density on working electrode; \( A, B \) – empiric constants. The inclination of the cathode polarization curve on the Fig. 3 is equal to 0.12 V, which corresponds to the hydrogen evolution reaction on the cathode:

\[ \text{H}_2\text{O} + \text{e}^- \rightarrow \text{H}_{\text{ads}} + \text{OH}^- \]

The inclination of the anode polarization curve on the Fig. 3 is equal to 0.04 V, which corresponds to the oxygen evolution reaction on the anode:

\[ 2\text{OH}^- \rightarrow \text{H}_2\text{O} + \text{O}_{\text{ads}} + 2\text{e}^- \]

The similar form is taken by the polarization curves also in a case that in the nickel there is only a free chemically not fixed hydrogen (\( \alpha \)-phase of nickel hydride).

Then polarization curves were obtained on a nickel hydride in a case of presence of chemically fixed hydrogen in the metal (\( \beta \)-phase of nickel hydride) (Fig. 4). The working samples were prepared in...
accordance with above described method. The polarization curves were obtained by the way of polarization multistage increase with the pitch of 0.02 V in the same alkaline battery electrolyte. On the chart represented in the Fig. 4, it is seen that on both cathode and anode branches of the polarization curves, limiting currents are observed. This is typical for the β-phase of the nickel hydride. On the non-hydrogenated nickel as well as on the α-phase of the nickel hydride, they are absent (Fig. 3).

On the cathode branch, the limiting current is observed in area of potentials from −0.65 V to −1.00 V. Afterwards the chart takes a form of a straight line with the angular inclination 0.12 V, which corresponds to hydrogen evolution in concord with the reaction (Eq. 8) (Ref. 15). This is to say that in this area, the hydrogen evolves from the nickel hydride exactly in the same way as on a common nickel.

On the anode branch, the limiting current is observed in the area of the potentials from −0.35 V to 0.7 V. Then the chart has a form of an approximately straight line corresponding to the line of the oxygen evolution on the Fig. 3.

For a better understanding of the cathode and anode processes taking place on the nickel hydride, let us consider a dependence diagram of the nickel hydride potential from time duration (Fig. 5) in a case of a current absence in the cell. On the parts 1 and 2 of Fig. 5 chart, some relaxation processes take place connected with hydrogen transposition from the nickel hydride into the solution. Then the potential comes to equilibrium (part 3 Fig. 5).

The hydrogen can arrive to the electrode surface from the α-phase of the nickel hydride, i.e. on expense of free chemically non-fixed hydrogen atoms with aid of the diffusion in solid. Moreover, from the β-phase of the nickel hydride, with the preliminary step of its decomposition,

\[ \text{NiH}_x \rightarrow \text{Ni} + \text{H}_2. \]  

Our additional studies at lower concentrations of alkalis (Fig. 5 and others) showed that balance potential \( E_r \) grows linearly with pH decrease and with inclination 0.06 V, i.e.

\[ E_r = E_o - 0.06 \cdot \text{pH} \]  

Besides, an extrapolation of the dependence (Eq. 11) onto the ordinate axis leads to a potential of the hydrogen electrode at pH = 0. So \( E_r \) on a nickel hydride coincides with the potential of the hydrogen electrode.\[13,16\]

\[ \text{H}_2\text{O}_x + \text{OH}^- \leftrightarrow \text{H}_2\text{O} + e^- \]  

For the further investigations, it is important to know that relaxation processes – connected with the potential coming into equilibrium condition (Eq. 12) after placing of electrode in the solution being under studying – continue approximately for 38 minutes (Fig. 5).

For working out in more detail, it is necessary to clarify some points. Firstly, what electrochemical reactions proceed in the cases of cathode and anode polarization of the working nickel-hydride electrode? Secondly, what steps those reactions pass? Thirdly, which of them is a rate-limiting step, i.e. a step responsible for an emergence of limiting cathode and anode currents?

Cathode process on nickel hydride.— Let us study the cathode process on the nickel hydride. The atomic hydrogen being formed as a result of nickel hydride disintegration diffuses to the electrode surface and is adsorbed on it. Hence, as the electrochemical step at the case of the cathode process, only the step of the electrochemical desorption of the atomic hydrogen adsorbed on the electrode surface can be.\[13,15\] i.e.

\[ \text{H}_2\text{O} + \text{H}_x + e^- \rightarrow \text{H}_2 + \text{OH}^- \]  

Now let us find out, which step of the cathode process on the nickel hydride is the limiting one, i.e. one responsible for the limiting cathode
Voltammetry (CV). In the Fig. 6, the nickel hydride CV is represented step (Eq. 10) and the step of the atomic hydrogen diffusion to the electrode surface.

Differences of these steps can be highlighted with aid of cyclic voltammetry (CV). In the Fig. 6, the nickel hydride CV is represented. The cyclic voltammogram was taken in the potentials area from $-0.98 \text{ V}$ to $-0.53 \text{ V}$, which just covers the area of the limiting cathode current (Fig. 4). The scanning speed $v = 0.001 \text{ V s}^{-1}$.

From the Fig. 6, it is seen that the limiting cathode current lowers with a cycle number increase. Such CV change is typical, where a previous chemical reaction is slowed down in relation to the main electrochemical reaction proceeding on the electrode. In the above consideration by us cathode process, this previous chemical reaction can be only the reaction of the nickel hydride disintegration (Eq. 10).

It is possible to give also other pro arguments for this statement. For kinetics clarifying of the previous limiting step, there was taken the cathode chronocoulometric diagram of the nickel hydride, i.e. the dependence between the carried over cathode charge $q$ and time (Fig. 7). With this purpose, in every CV cycle, a coulometer was used for finding out of a negative charge $q^-$ consumed for the electrochemical desorption of the hydrogen (Eq. 13). This diagram was obtained as a result of cycling in the potentials area from $-1 \text{ V}$ to $-0.53 \text{ V}$ (scanning speed 0.001 V s$^{-1}$). From the Fig. 7, it is seen that our experimental points are well approximated with a straight line.

If to suppose that the limiting step is the one of the atomic hydrogen diffusion, from the Cottrell’s equation for the dependence of the limiting cathode current from time, we shall obtain the equation

$$i_k = nFCE\sqrt{\frac{D}{\pi t}}.$$  

After this, equation integration on time, we shall obtain

$$q^- = 2nFCE\sqrt{\frac{Dt}{\pi}}.$$  

Thus in this case the dependence $q^-(t)$ must be linearized in the coordinates $q^-$ vs. $\sqrt{t}$, which does not correspond to the experiment (Fig. 7).

If to suppose that the limiting step is the one of the nickel hydride disintegration (Eq. 10), then according to studies, this is a chemical reaction of the first order. For the chemical reactions of the first order, a linear dependence is inherent in the coordinates $q^-$ vs. $t$ extrapolated into zero of the coordinate system, which indeed is observed in the experiment (Fig. 7). Thus the limiting step of the cathode process on the nickel hydride is the step of the nickel hydride disintegration.

**Anode process on nickel hydride.**— Now let us investigate the anode process on the nickel hydride. For clarifying of a nature of the proceeding electrochemical reaction, there was taken the dependence of the electrode potential from time at the anode current density $i_a = 0.5 \text{ A/m}^2$ (Fig. 8). In all the described below experiments, preliminary, the electrode was exposed to the electrolyte action during 40 minutes with a purpose of excluding of relaxation processes (parts 1 and 2, Fig. 5).

From the Fig. 8, it is seen that during the first 8 to 10 minutes, the potential rises steeply approximately by 0.24 V; then about 220 subsequent minutes it continues its growth but very slowly; then again it rises steeply up to the oxygen evolution potential value.

Thus, unequivocally, the nickel hydride chronopotentiogram shows that in the area of the potential value $-0.6 \text{ V}$, some electrochemical reaction takes place. Let us find parameters of this reaction. Let’s make use of the equation built for potential change on the chronopotentiogram from the paper:

$$E = \frac{-RT}{\beta F} \ln \left( \frac{nFCEK}{i} \right) = \frac{-RT}{\beta F} \ln \left( 1 - \sqrt{\frac{t}{t_c}} \right).$$  

From this equation under $r = 0$, we’ll obtain the dependence of the electrode potential from the anode current value in the form of the Tafel’s equation:

$$E = -\frac{2.3RT}{\beta F} \log(nFCEK) + \frac{2.3RT}{\beta F} \log(i).$$  

**Figure 6.** Cyclic voltammograms for nickel hydride in alkaline battery electrolyte obtained in potentials area from $-0.98 \text{ V}$ to $-0.53 \text{ V}$; scanning speed is 0.001 V s$^{-1}$; 1, 2, 3 – cycle numbers.

**Figure 7.** Cathode chronocoulometric diagram for nickel hydride in alkaline battery electrolyte obtained in cycling in the potential area from $-1 \text{ V}$ to $-0.53 \text{ V}$.

**Figure 8.** Chronopotentiogram for nickel hydride in alkaline battery electrolyte under anode current density $i_a = 0.5 \text{ A/m}^2$, with preliminary electrode exposition in electrolyte during 40 minutes.
The dependence $E$ vs. $\log(i)$ for the Equation 17 was obtained experimentally. With this purpose, a number of chronopotentiograms was taken at different values of the anode current density $i$. The data obtained were represented on a chart in coordinate system $E$ vs. $\log(1 - \sqrt{t/\text{tc}})$ according to the Equation 16. An extrapolation of these straight lines onto the ordinate axis ($t = 0$) gives potentials $E$ corresponding to initial hydrogen concentrations in nickel hydride at different $i$ values. The results are represented in the Fig. 9.

For inclination angle of the polarization straight line (Fig. 9), there is obtained the classical Tafel’s value $0.12 \pm 0.005$ V. From this and from the Equation 17 for the anode coefficient $\beta$, we obtain the value $\beta \approx 0.5$. Both obtained values correspond to electrochemical step of hydrogen ionization.\(^{13,15}\)

$$\text{H}_{\text{ads}} \rightarrow \text{H}^+ + e^-.$$ \hspace{1cm} [18]

As an alkaline environment, immediately, protons interact with ions $\text{OH}^-$, the reaction (Eq. 18) is necessary to be written down in the form

$$\text{H}_{\text{ads}} + \text{OH}^- \rightarrow \text{H}_2\text{O} + e^-.$$ \hspace{1cm} [19]

which does not change the sense of the proceeding electrochemical reaction.

Now let us give a consideration to the following question: what step of the anode process going-on on the nickel hydride is the limiting step? Only two steps take precedence of the anode electrochemical step of the anode process going-on on the nickel hydride is the limiting reaction.\(^{16-18}\)

According to the study,\(^{19}\) the chemical reaction of the nickel hydride disintegration (Eq. 10) is found from a number of chronopotentiograms similar to Fig. 8 at different current densities on the formula\(^{14}\)

$$K = \frac{\lim_{t \to 0} (t^{1/2})}{\lim_{t \to \infty} (t^{1/2})} = \frac{1}{10.5 \pm 1.2}.$$ \hspace{1cm} [21]

The chemical reaction of the nickel hydride disintegration (Eq. 10) can be found from a number of chronopotentiograms similar to Fig. 8 at different current densities on the formula\(^{14}\)

$$(\text{Eq. } 10)$$ and the step of the atomic hydrogen diffusion to the electrode surface.

These steps differences can be found with aid of the cyclic voltammetry (CV). With this purpose, the cyclic voltammogram of the nickel hydride was taken in the potential area from $-0.55$ V to $0.05$ V, which just covers a part of the area of the limiting anode current ($-0.35 \ldots + 0.65$). The potential scanning speed was $v = 0.05$ V s$^{-1}$ Fig. 10.

On the CV, there are well seen the limiting anode currents higher than the potential value $-0.35$ V; those currents lower with a cycle number increase. Such CV behavior is typical, where a previous chemical step is slowed down in relation to the main electrochemical reaction.\(^{17}\) In the case of the considered anode process, this can be only the chemical reaction of the nickel hydride disintegration (Eq. 10).

For a further clarifying of the previous limiting step, for the nickel hydride, there was also taken the anode chronocoulometric diagram, i.e. the dependence of carried-over anode charge $q^+$ from time (Fig. 11). With this purpose in every CV cycle with aid of coulometer, there was found the positive charge $q^+$ consumed on hydrogen ionization (Eq. 19). This diagram was obtained at the cycling process in the potential area from $-0.55$ V to $+0.5$ V. The scanning speed was $0.05$ V s$^{-1}$. From the Fig. 11, it is seen that the experimental points are well approximated by a straight line.

So if to suppose that the limiting step is one of the diffusion of the atomic hydrogen, then dependence $q^+(t)$ must be linearized in the coordinates system $q^+$ vs. $\sqrt{t}$ according to the Equation 15, which does not correspond to the experimental data (Fig. 11).

According to the study,\(^{20}\) the chemical reaction of the nickel hydride disintegration (Eq. 10) is found from first order. For chemical reactions of the first order, the linear dependence $q^+$ on time is typical extrapolated onto zero of the coordinates system.\(^{21}\) Exactly such dependence is observed in the experiment (Fig. 11). Thus also for the anode process on the nickel hydride, the limiting step is one of the nickel hydride disintegration (Eq. 10). A speed of the nickel hydride disintegration reaction calculated on a curve inclination (Fig. 11) is equal to

$$\frac{dq^+}{dt} = 0.81 \text{ A m}^{-2}$$ \hspace{1cm} [20]

Figure 9. Anode polarization dependence for nickel hydride in alkaline battery electrolyte.

Figure 10. Cyclic voltammograms for nickel hydride in alkaline battery electrolyte obtained in cycling in potential area from $-0.55$ V to $+0.5$ V.

Figure 11. Anode chronocoulometric diagram for nickel hydride in alkaline battery electrolyte obtained in cycling in potential area from $-0.55$ V to $+0.5$ V.
i.e. the reaction balance (Eq. 10) is shifted to the right. Notably that, as the additional analysis shows, after the chronopotentiograms obtaining, the electrolyte does not contain any nickel. Hence in these experiments, only hydrogen is ionized, while the nickel stays in the crystal lattice.

**Results and Discussion**

First of all, we would like to draw attention to a feature of electrochemical reactions (Eqs. 13 and 19). These electrochemical reactions do not depend on a specific metal. This is why they will proceed on any metals able to form hydrides. Of course, speeds of these reactions on various metals will be different as they depend on disintegration rate of specific hydrides (Eq. 10) and on a speed of hydrogen atoms diffusion in these metals.

In electrodes of long-life nickel-cadmium batteries, a lot of hydrogen is accumulated. For example, in the batteries KSX-25 with operation period more than 5 years, the hydrogen is contained in amount of approximately 800 liters. So metal sintered matrices of electrodes of the nickel–cadmium batteries will be built of metal hydrides.

A thermal runaway occurs in batteries in a case of their long-time recharge. Therefore, at the moment of recharging of batteries, the following electrochemical reactions will proceed: main reactions of electrodes charging (Eqs. 1 and 2); reactions of electrolyte decomposition (Eqs. 3 and 4) and reactions taking place on metal hydrides (Eqs. 13 and 19).

Let’s give consideration to electrochemical reactions (Eqs. 13 and 19) in more detail. During the charge of the nickel–cadmium batteries, the electrochemical reaction (Eq. 13) will proceed on the cadmium electrode, while the reaction (Eq. 19) on oxide-nickel one. An overall reaction for them will be the following electrochemical reaction:

\[ \text{H}_2\text{ads}_\text{Cd} + \text{H}_2\text{ads}_\text{Ni} \rightarrow \text{H}_2 \uparrow \]  \hspace{1cm} (22)

i.e. the electrochemical reaction of the atomic hydrogen recombination (Eq. 5).

Based on the electrochemical reaction (Eq. 22), it is possible to explain the experimental facts highlighted in the beginning of the paper, which are impossible to be understood in frame of the generally accepted thermal runaway mechanism. Let’s consider changing of the main parameters of the nickel–cadmium battery (Fig. 2) in the course of the thermal runaway from point of view of electrochemical reaction process (Eq. 22). To a moment of a thermal runaway initiation in the battery KSX-25, the recharging current was very small, about 0.38 A (Fig. 2). Dominantly, it was consumed on electrolyte decomposition, i.e. on electrochemical reactions (Eqs. 3 and 4) and in much less percentage on the battery charge (as it was mode of recharging), i.e. on electrochemical reactions (Eqs. 1 and 2). At common temperatures, a speed of electrochemical reactions (Eqs. 13 and 19) is not high (8.1 \times 10^{-5} A cm^{-2}) (Eq. 20). Providing that electrodes square is equal to 7.3 × 13.6 cm and in the battery KSX-25, 14 cadmium and 15 oxide-nickel electrodes are situated, for reactions (Eqs. 13 and 19) maximal current, we obtain the value 0.22 A. This current is defined by hydrides disintegration speed (Eq. 10) and does not depend on electrodes porosity. It is worth to be mentioned that at new batteries KSX-25 in similar charge modes (under constant voltage), typically, recharging current is equal to 0.15–0.18 A. In new alkaline batteries, the hydrogen in electrodes is absent at all\(^2,3\) and therefore the reactions (Eqs. 13 and 19) are absent under the batteries charging. In the batteries KSX-25 featured with an operation long time and thus inclined to a thermal runaway,\(^4\) typically, the recharging current is equal to 0.37–0.40 A. The conducted analysis shows that the reason of the recharging current value growth is connected with electrochemical reactions occurrence (Eqs. 13 and 19).

In the paper it was shown that by taking only electrochemical reactions (Eqs. 1–4) into consideration, it is impossible to explain changes of charging current and voltage on battery terminals under thermal runaway (Fig. 2). Though with taking the electrochemical reactions (Eqs. 13 and 19) into account, such parameters change of nickel-cadmium battery becomes evident.

In proportion to nickel-cadmium batteries operation years number, in their separators, dendrites are accumulated that cut essentially a distance between electrodes exactly in the spots, where they grow. This leads to the situation that at a moment of batteries charge under constant voltage, in these spots, charging current density will be many times higher than in any places of the same electrodes. Indeed, a local density of a charging current on electrodes in spots of dendrites growth will be:

\[ i_{\text{loc}} = \frac{U_0}{L \epsilon} \]  \hspace{1cm} (23)

where: \( U_0 \sim \) voltage on battery terminals, \( \rho \) - electrolyte specific resistance, \( \epsilon \) - distance between a dendrite and counter electrode. This charging current local density \( i_{\text{loc}} \) will exceed much the charging current average density \( i_{\text{av}} \) on electrodes as

\[ \frac{i_{\text{loc}}}{i_{\text{av}}} = \frac{L}{\epsilon} \]  \hspace{1cm} (24)

where \( L \) - distance between electrodes. The distance \( \epsilon \) between a dendrite and a counter-electrode can be tens and hundreds times less than the distance \( L \) between the electrodes. Hence, also the charging current local density in spots of dendrites growth can be tens and hundreds times more than the charging current average density on the electrodes. In its turn, it will lead to a strong local overheating of those spots on both battery electrodes.

As it was shown in the paper,\(^2\) under electrodes temperature growth, metal hydrides disintegration speeds (Eq. 10) will rise steeply. For a cadmium electrode at temperatures higher than 340 °C, a rapid disintegration of cadmium hydrides starts, while as for oxide-nickel electrodes, at temperatures higher than 660 °C (Ref. 2) and even at temperatures twice as less, the hydrides disintegration speed is considerably high. The hydrides disintegration (Eq. 10) (according to the above studies) is a limiting step for electrochemical reactions (Eqs. 13 and 19). So the speeds of the electrochemical reactions (Eqs. 13 and 19) can increase hundreds times in proportion to the metal hydrides disintegration growth speed. The mentioned above high enough temperatures are not impossible for the nickel–cadmium batteries. For example, the temperature evaluation in the spots of the thermal runaway as judged by thermal traces on the electrodes (Fig. 1) showed that during the thermal runaway in these spots, the temperature was much higher than 700 °C. So the role of the electrochemical reactions (Eqs. 13 and 19) can become determinative (during batteries charging) at high temperatures that can be created in local spots on electrodes on expense of dendrites intergrowth.

The electrochemical reactions taking place on metal hydrides (Eq. 22) is the exothermic reaction proceeding with very high heat production (436 kJ/mole) (hydrogen).\(^5\) This is why its initiation in a spot of a dendrite intergrowth will lead to even higher electrodes local heating-up in those spots; and in its turn this will lead to even more mass disintegration of hydrides on both electrodes and thus to reactions speeds increase (Eqs. 13 and 19). The exothermic reaction (Eq. 22) requires new hydrides for its continuation. In a spot of the reaction initiation (Eq. 22), they will be exhausted; and reaction will shift radially from this point burning a separator in a form of regular circles, which indeed is observed in the experiments (Fig. 1 and paper\(^6\)).

An interruption of the electrochemical reactions of the thermal runaway (Eqs. 13 and 19), in our opinion, is connected with electrolyte evaporation between electrodes (as a result of high temperature) as well as with a gas lock formation between those electrodes (from the steam evolved and the hydrogen). This gas lock will physically interrupt any electrochemical reactions (Eqs. 13 and 19). As long as the formation of the gas lock being sufficient for electrochemical reactions interruption (Eqs. 13 and 19) is dominantly a random process, hence also the radii of separator burning-out will be various, in concord with the experimental results.\(^7\)
As for the thermal runaway process, the electrochemical reactions (Eqs. 13 and 19) become determinative, while other reactions (Eqs. 1–4) contributions are desperately insignificant, so on battery terminals, an electric potential difference will be established corresponding to proceeding of namely these reactions. According to the above studies, during the electrochemical reaction (Eq. 19), the potential of the positive electrode will be equal in average to −0.6 V vs. SHE according to the chronopotentiogram (Fig. 8). If to take a similar chronopotentiogram for the cathode current direction, during first 5–8 minutes, the potential will tumble sharply about by 0.2 V starting from the balance potential −0.852 V (Fig. 5), then slowly decrease along of the cathode branch (Fig. 3). So during the electrochemical reaction (Eq. 13), the potential of the negative electrode will be in average equal to −1.08 V vs. SHE (Figs. 3 and 4). So this electric potential difference between anode and cathode for the reactions (Eqs. 13 and 19) coincides with the experimental voltage value on battery terminals during a thermal runaway (Fig. 2), reactions (Eqs. 1–4) will not proceed at all.7

Based on the electrochemical reaction (Eq. 22), it is also possible to explain other earlier difficult for understanding results connected with the thermal runaway. In the paper,7 by means of the calorimetric measurement, it was shown that during the thermal runaway (Fig. 2) from the battery, the energy is produced in amount of 5207 kJ. Notably that during the thermal runaway the amount of the energy produced exceeds the energy amount received by the battery from a recharger 140 times.7 This experimental fact can be explained in no way by the generally accepted thermal runaway mechanism,1 which takes into account no other electrochemical reactions except of the reactions (Eqs. 1–4). Based on the exothermic reaction (Eq. 22), this fact has quite natural explanation. So the electrochemical reaction (Eq. 22) explains the entire complex of the experimental studies connected with the thermal runaway.

Conclusions

Undoubtedly, the proposed mechanism of the thermal runaway phenomenon requires further investigations both experimental and theoretical. Nevertheless, it allows explaining all the available at the moment experimental data.

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