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Analytical Model of Thermal Runaway in Alkaline Batteries

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In this study, there was first developed an analytical model of thermal runaway in alkaline batteries. The model was constructed based on the thermal runaway new mechanism experimentally deduced by us in our previous works proving that the thermal runaway was connected with initiation of a powerful exothermic reaction of atomic hydrogen recombination. It was shown that the equations obtained from the model for current and voltage changes on battery terminals during a thermal runaway correspond to experimental data with the relative error not more than 4.2%.

Keywords: model, thermal runaway, battery, nickel–cadmium, exothermic reaction

1. INTRODUCTION

It is a generally accepted concept [1] that the thermal runaway cause is battery self-heating in course of its charging at constant voltage or in course of its work in floating mode. Heating of a battery results in decreasing of its internal resistance and subsequently its charging current grows, which again increases the heat, etc. In this case, battery temperature goes up to high values; also inflammation and explosion are possible. Always any thermal runaway results in breakdown of a system containing this battery.

At present, the thermal runaway phenomenon in lithium-ion batteries is studied quite extensively [2-5]; not so lively the thermal runaway is studied in lead-acid batteries [6,7]; and near to zero is quantity of papers on investigation of the thermal runaway in alkaline batteries. But nickel-cadmium and nickel-iron batteries are used in a lot of systems of heightened danger: airplanes, railway, etc. In our opinion, such insufficient attention to researches of thermal runaway in batteries with aqueous electrolyte is explained by the fact that a thermal runaway initiating & studying is a very difficult task as this is very rare phenomenon. Besides, it seems to many researchers that the mechanism of the thermal runaway is evident [1]. However until now, there are no direct experimental proofs of this mechanism.

According to the traditional point of view [1], the thermal runaway takes place due to acceleration of batteries charging reactions

$Ni(OH)_2 + OH^- \rightarrow NiOOH + H_2O + e^-$, (1)

$Cd(OH)_2 + 2e^- \rightarrow Cd + 2OH^-$, (2)

or to acceleration of electrolyte decomposition reactions

$2e^- + 2H_2O \rightarrow H_2 + 2OH^-$ (cathode) (3)

$2OH^- \rightarrow 1/2O_2 + H_2O + 2e^-$ (anode) (4)

as the thermal runaway takes place in cases of a long-time battery recharging [1].

In papers [8,9], it was shown that at present, a lot of experimental facts exists contradicting to the thermal runaway generally accepted mechanism. For example, at a thermal runaway, energy is produced in amount 140 times more than at the same time the battery obtains from its recharger [9]. Besides, during a thermal runaway a lot of gas releases, 95% of which makes hydrogen [10,11]. Also a lot of other experimental facts [8-12] exists, which is impossible to be explained based on the electrochemical reactions (1-4).

In the paper [13] by experiments, it was shown that the thermal runaway is connected with an initiation of a powerful exothermic reaction of atomic hydrogen recombination:

$H_{ads\,Cd} + H_{ads\,Ni} \rightarrow H_2 \uparrow$, (5)

which proceeds on the basis of the electrochemical mechanism:

$H_2O + H_{ads} + e^- \rightarrow H_2 \uparrow + OH^-$ on a cathode (6)

$H_{ads} + OH^- \rightarrow H_2O + e^-$ on an anode (7)

The reaction (5) is the powerful exothermic reaction with heat dissipation in amount of 436 kJ/mole (hydrogen) [14].

So the thermal runaway proceeds according to the following scenario [13]. During a long-lasting batteries operation, into their electrodes, a lot of hydrogen is accumulated in the form of metal-hydrides [15,16] (i.e. in the atomic form [17]), while on cadmium electrode, dendrites are accumulated. In spots of dendrites penetration through a separator, the distance between the electrodes is reduced considerably. Hence in those spots, the current density of the batteries charge will be much higher than in neighboring areas of the electrodes [13]. A rate-limiting step for the electrochemical reactions (6,7) is the metal-hydrides decomposition step [13]. The metal-hydrides decomposition rate grows sharply with electrodes temperature growth. Thus in the dendrite location spot, an intensity of the reactions (6,7) will grow up. As the thermal runaway reaction (5) is an exothermic reaction, it will heat up the electrode even more. This will result in a more intensive metal-hydrides decomposition, etc. So the reactions (6,7) intensity will be rise steeply. This is exactly what we know as a thermal runaway process in alkaline batteries [13].

With time, the thermal runaway process stops because of a gas lock formation between electrodes, which interrupts the electrochemical reactions (6,7), physically. The gas lock is formed because of a release of a lot of hydrogen in the spot of the thermal runaway (5) and electrolyte evaporation as a result of the high temperature.

In this paper based on the found mechanism of the thermal runaway [13], the analytical model of this process is developed. It should be noted that currently there is no reliable model of thermal runaway in alkaline batteries. This paper continues our works on analytical modeling of various processes taking place in batteries [18-20].

2. ANALYTICAL MODEL OF THERMAL RUNAWAY

From the moment of the thermal runaway initiation, the reactions (6,7) rate grows up as an avalanche. Indeed, the more current of the thermal runaway reactions (6,7), the more temperature in the spot of the thermal runaway (by virtue of the fact that the thermal runaway reaction (5) is exothermic) and so the more hydrides decomposition rate and the more rate of hydrogen release. The metal-hydrides decomposition reaction is the rate-limiting step for a generalized reaction of the thermal runaway (5) [13]. As (according to the study [13]) the hydrides decomposition reaction is a reaction of the first order, the following equation must be correct for the thermal runaway reaction rate.

$$\frac{dI_{tr}}{dt} = kI_{tr} \ , \qquad (8)$$

where I_{tr} is current of thermal runaway and k is the thermal runaway reaction rate constant. From the Equation (8), it follows that from the thermal runaway initiation moment, the current will grow up exponentially

$$I_{tr} = A\exp(kt) \ . \qquad (9)$$

Now let us take into consideration a blocking of the thermal runaway reaction by a gas lock being created in burned-down separator [9] in the spot of the thermal runaway due to the hydrogen release and the electrolyte evaporation because of the very high temperature of the thermal runaway. The thermal runaway reaction rate constant k must depend on a volume V of the gas lock as it blocks the place of the thermal runaway and makes difficult or completely interrupts the thermal runaway reactions (6,7) on separate spots. Notably, the more volume of the gas lock is (i.e. the more spacious thermal runaway area is blocked), the less the reaction rate constant k must be. When the gas lock volume reaches some value V_0, the current rise rate dI_{tr}/dt must become equal to zero. Thereafter the thermal runaway current must diminish – i.e. $dI_{tr}/dt < 0$. Hence, the thermal runaway reaction rate constant must take the form:

$$k = k_0(V_0 - V(t)), \qquad (10)$$

where $V(t)$ is the gas lock volume. In its turn, the gas lock volume must be in proportion with a volume of the gas released, which is proportional to an electricity amount spent on the thermal runaway reaction, i.e.

$$V(t) = A\int_{t0}^{t} I_{tr}(t)dt, \qquad (11)$$

where $t0$ is time moment of thermal runaway initiation and A is proportionality constant.

This way with a due account of the ratios (10,11) from the Equation (8), we obtain the equation describing thermal runaway current change in view of the blocking gas lock formation:

$$\frac{dI_{tr}}{dt} = k_0(V_0 - A\int_{t0}^{t} I_{tr}(t)dt)i_{mp}(t). \qquad (12)$$

This equation is differential-integral one and for its solving, it is convenient to convert it into a purely differential equation. With this purpose in mind, in the right part of the Equation (12), we take the integral separately and differentiate the obtained ratio. We'll obtain the differential equation:

$$I_{tr}\frac{d^2 I_{tr}}{dt^2} - \left(\frac{dI_{tr}}{dt}\right)^2 = BI_{tr}{}^3, \qquad B = k_0 A. \qquad (13)$$

In the peak point of the thermal runaway current $t = t_k$, the following conditions must be correct:

$$I_{tr}(t)\Big|_{t=t_k} = I_{\max},$$
$$\left.\frac{dI_{tr}}{dt}\right|_{t=t_k} = 0. \qquad (14)$$

Let us solve the Equation (13) at the boundary conditions (14). For the thermal runaway current change, we obtain the following expression:

$$I_{tr}(t) = I_{\max}\left(1 - th^2\left(\sqrt{\frac{I_{\max}B}{2}}(t - t_k)\right)\right) \qquad (15)$$

Qualitatively, the theoretical curve of the thermal runaway current change (15) corresponds quite well to the experimental data obtained in the works [9,21].

As it was highlighted in the papers [9,10,21], often at a thermal runaway, not one but several current bursts are observed, which correspond to upraise and dying out of various focal points of a thermal runaway during batteries recharging. Most often, there can be one or two current bursts but it is possible to observe up to five of them. In this case, the thermal runaway total current will look like:

$$I_{tr}(t) = \sum_{j=1}^{n} I_{j,\max}\left(1 - th^2\left(\sqrt{\frac{I_{j,\max}B_j}{2}}(t - t_{j,k})\right)\right), \qquad (16)$$

where n is thermal runaway bursts number at batteries recharging.

The thermal runaway in batteries occurs in a case of their recharging at constant voltage [1]. In this case, the voltage on the batteries terminals during the thermal runaway will look like as follows:

$$U(t) = U_0 - R \cdot I_{tr}(t), \qquad (17)$$

where U_0 is constant voltage of battery charge and R is resistance of supply lines and an instrument shunt [9]. Finally with due account of the Equation (16) for voltage change on battery terminals, we shall obtain the expression:

$$U(t) = U_0 - R \cdot \sum_{j=1}^{n} I_{j,\max}\left(1 - th^2\left(\sqrt{\frac{I_{j,\max}B_j}{2}}(t - t_{j,k})\right)\right). \qquad (18)$$

3. EXPERIMENTAL

In order to compare the obtained models (16,18) with the experimental data, the nickel-cadmium batteries KSX-25 (by capacity 25 Ah) with long operating life (more than 6 years) were used. Notably, batteries' cycling was performed in severe conditions. This allowed increasing probability of a thermal runaway emergence [8]. Batteries' charging was performed during 10 hours at high constant voltage 1.87V. Then discharging was performed by the current 10 A down to the voltage value 1V. At the same time, ten parallel-connected batteries were cycled – for obtaining of greater amount of statistical data. Between the batteries, wooden spacer plates (two centimeters thick) were inserted. This allowed excluding a thermal mutual influence between the batteries.

The current was measured with aid of shunts (with resistance 0.001 Ohm) fastened to negative terminals of batteries. As a result of the cycling, there were performed 800 charge-discharge cycles. Notably, only in two cases, the thermal runaway was observed. The obtained experimental values for current and voltage changing are marked in Fig. 1 and 2 by crosses and points respectively.

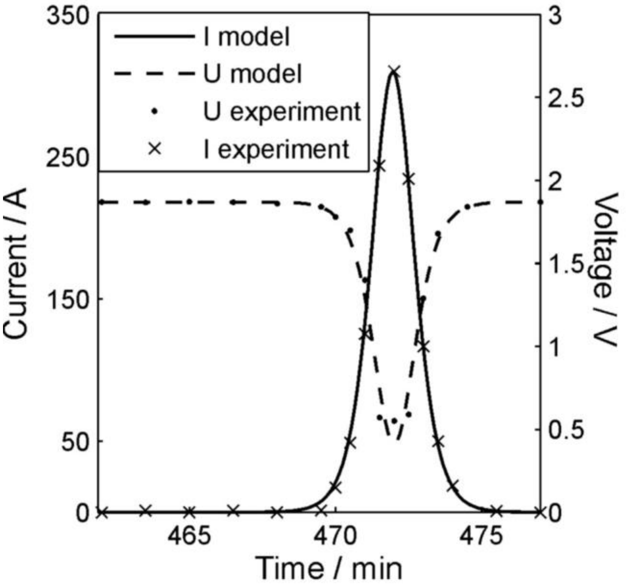

Figure 1. Comparison between analytical models for current and voltage changing and experimental data for the battery KSX-25 (No. 1) during thermal runaway: model – theoretical curves (16,18), experiment – experimental data

4. RESULTS AND DISCUSSION

For Equations (16,18) verification, the experimental data were used for changes of current and voltage on battery terminals during the thermal runaway (Fig. 1,2). The empiric constants (t_k, I_{max}, B, U_0, R) for these equations were found based on the requirement of the best coincidence of the Equations (16,18) with the experimental data, for this the least squares method and Levenberg–Marquardt optimization procedure were used. The optimization results are represented in the Table 1.

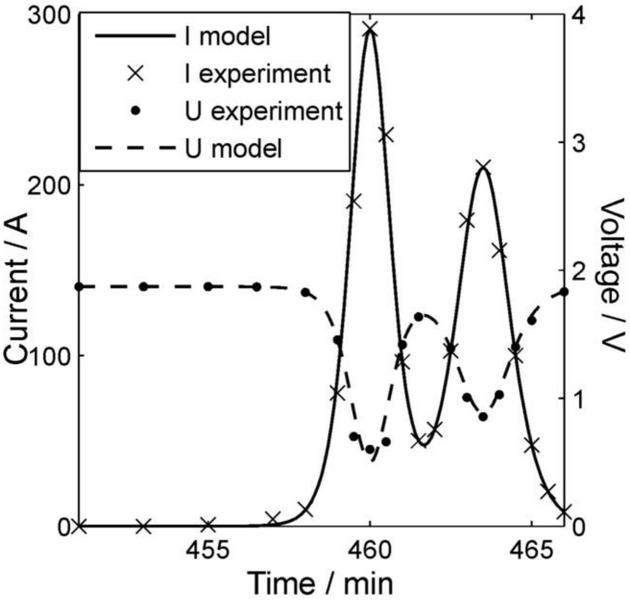

Figure 2. Comparison between analytical models for current and voltage changing and experimental data for the battery KSX-25 (No. 2) during thermal runaway: model – theoretical curves (16,18), experiment – experimental data

Thus, the obtained Equations (16,18) match well with the experimental data for current and voltage changes during a thermal runaway as the relative error of experimental data simultaneous approximation by the Equations (16,18) on the Figs. 1 and 2 makes not more than 4.2%

Table 1. Optimal values for parameters in Equations (16,18).

Parameters	Figure 1	Figure 2	
n	1	1	2
t_k (min)	472	460	463.5
I_{max} (A)	310	290	210
B (A^{-1} min^{-2})	0.007	0.01	0.008
U_0 (V)	1.87	1.87	1.87
R (Ω)	0.0047	0.0047	0.0047
δ (%)	3.7	4.2	

n is a sequence number of a current burst on Figs. 1 and 2. δ is relative error of experimental data simultaneous approximation by the Equations (16,18) on Figs. 1 and 2.

It should be observed that experimental investigation of batteries parameters changing (current/voltage on batteries terminals, temperature) in course of thermal runaways, was fulfilled by us in a lot of previous works [9,10,21]. However, constructing of the model of this dangerous and interesting phenomenon becomes possible only in this paper. The point is that as for true mechanism of the thermal runaway in alkaline batteries, we managed establishing it experimentally only in the paper [13]. In that paper, there was experimentally proved that the thermal runaway in alkaline batteries is connected not with an acceleration of the traditional electrochemical reactions (1-4) due to batteries self-heating (as it was considered previously [1]) but instead with initiation of the new powerful exothermic reaction of the recombination of atomic hydrogen (5) accumulated in battery electrodes during their operation. Based on the thermal runaway established mechanism [13], in this work for the first time, the model of this dangerous phenomenon (Fig.1 and 2) was constructed corresponding closely to the experimental data.

5. CONCLUSIONS

Perhaps, the thermal runaway is the only phenomenon in batteries emerging absolutely sporadically regardless of a maintaining team and being accompanied with powerful energetic and visual effects. In this work for the first time, there was developed the analytical model of this unique from electrochemical point of view phenomenon on the basis of the recently confirmed thermal runaway mechanism in batteries with aqueous electrolyte [13]. Undoubtedly, this phenomenon requires further both theoretical and experimental studies.

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