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Short Communication

Processes of Hydrogen Release Relaxation at Thermal Decomposition of Electrodes of Nickel-Cadmium Batteries

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In this study, it is shown that processes of hydrogen release relaxation at thermal decomposition of sintered electrodes of nickel-cadmium batteries are conditioned by the combination of the following factors. Firstly, this is the distribution of atomic hydrogen all around the entire volume of a ceramic-metal matrix of an electrode. Secondly, this is the very low diffusion coefficient of the atomic hydrogen in ceramic-metal matrices, which is connected with the fact that inside of the ceramic-metal matrix of the electrode, the atomic hydrogen is found in its bound state (β-phase). Thirdly, this is a large concentration of the atomic hydrogen in the ceramic-metal matrix of the porous electrode: the atomic hydrogen is accumulated in such electrodes in a course of batteries long-term operation.

Keywords: relaxation, hydrogen accumulation**,** thermal runaway, battery, nickel–cadmium

1. INTRODUCTION

The thermal runaway occurs in nickel-cadmium, lead–acid, lithium-ion, nickel-metal hydride, etc. batteries, which is to say that the thermal runaway is a phenomenon inherent in batteries of practically all the electrochemical systems.

This phenomenon emerges spontaneously irrespective of qualities of employees maintaining the batteries. The alkaline batteries are installed in many systems of heightened danger: airplanes, railway vehicles, etc. However until now yet, this phenomenon nature is understudied. In a case of a thermal runaway, a battery heats up sharply; and upon that its inflammation and explosion are possible. In this case inevitably, a system containing battery goes unserviceable. In connection with this in aviation always, the thermal runaway causes emergency situations of all kinds of complexity degrees.

However in the world literature, there are very few studies of this dangerous phenomenon, and especially scarce is its investigation for alkaline batteries.

While studying the thermal runaway in the nickel-cadmium batteries [1-3], it was shown that there are two accumulation processes, which bring batteries step-by-step to the thermal runaway. First process is one of a hydrogen accumulation in electrodes of nickel-cadmium batteries. Second one is accumulation process of dendrites on cadmium electrodes. The hydrogen accumulation process goes on during a long batteries operation due to the electrolyte decomposition. At charging, all batteries are recharged approximately 1.5 times larger as compared to their nominal capacity. Overcharging is needed for the batteries full charge. However meanwhile, there takes place a decomposition of an electrolyte on hydrogen and oxygen. The oxygen escapes from batteries completely, while the hydrogen releases from the batteries only partially and partially it is accumulated in their electrodes [4-6]. This phenomenon is connected with the fact that the hydrogen has the very high diffusional penetrability. For example, at the temperature 20^0C, the coefficient of hydrogen diffusion in nickel is approximately 10^{10} times larger than the nitrogen or oxygen diffusion coefficients [7]. The high diffusional penetrability of the hydrogen is determined by the small size of its atoms, by their little mass and by structural features of metal-hydrogen systems [8,9]. That is why at electrolyte dissociation in batteries, only the hydrogen is accumulated in electrodes, while the oxygen passes to the atmosphere [10,11].

In the papers [1,10,11], with use of a thermal decomposition of electrodes of nickel-cadmium batteries KSX-25, it was shown that after five years of operation in the electrodes of those batteries, about 800 liters hydrogen are accumulated. Notably, a gravimetric capacity of ceramic-metal matrix of an oxide-nickel electrode as a hydrogen accumulating unit is equal to 20.1 wt% [11]. These values exceed thrice all the earlier data obtained for any reversible metal hydrides (including magnesium hydride or complex hydrides) obtained using traditional methods [7,12].

In this paper, there is studied and modeled the dynamics of hydrogen release from electrodes of nickel-cadmium batteries at their thermal decomposition. This work became a continuation of started in papers [13-16] researches on modeling of various processes in electrochemical batteries.

2. EXPERIMENTAL

The electrodes thermal decomposition was performed in the thermal chamber made in the form of a tube 1.8 meter long and 2 centimeters in diameter. A tube sealed end was inserted into a muffle furnace, while into the other tube end a rubber plug was inserted with a tube for gas withdrawal. The hydrogen getting released as a result of the electrodes thermal decomposition passed through a standard coil and got into a metering container. An electrode from a battery being in a rolled-up state was placed into a metal cartridge, which then was inserted into the thermal chamber. The use of the cartridge allowed very easy withdrawing of the electrodes from the thermal chamber. Above the cartridge in the thermal chamber, a porous ceramic plug 20 cm long was placed. It diminished convection inside of the thermal chamber and prevented any considerable heating of the rubber plug equipped with the tube for the gas withdrawal. The experimental installation was described in detail in the paper [4].

For research by experiments, the nickel-cadmium batteries KSX-25 were used by capacity 25Ah with ceramic-metal (sintered) electrodes inside of them. According to our previous studies [10,11], a top amount of hydrogen is accumulated in electrodes of batteries of the kind after five years of their operation. That is why in the experiments, batteries were used with their operation period equal to seven years. The electrodes thermal decomposition took place at the temperature 800^0C as an essential hydrogen release would start for oxide-nickel and cadmium electrodes at temperature values more than 740^0C. The process of the thermal decomposition was stopped when the amount of gas released during a 24 h period was less than 100 ml.

A gas release velocity was determined on a base of an escaped gas volume during 5 minutes. Measuring of the gas release velocity was performed every hour.

The thermal decomposition of the cadmium electrodes was performed during 72 to 84 hours, while the same of the oxide-nickel electrodes during 130 to 140 hours. The process used to be performed for 10 to 13 hours per day. Then for a night, the process used to be interrupted for 11 or 14 hours and restored next day. Notably, at a moment of an installation turning-on on a next day, always, the gas release velocity was much higher than the same at a moment of an installation shutdown.

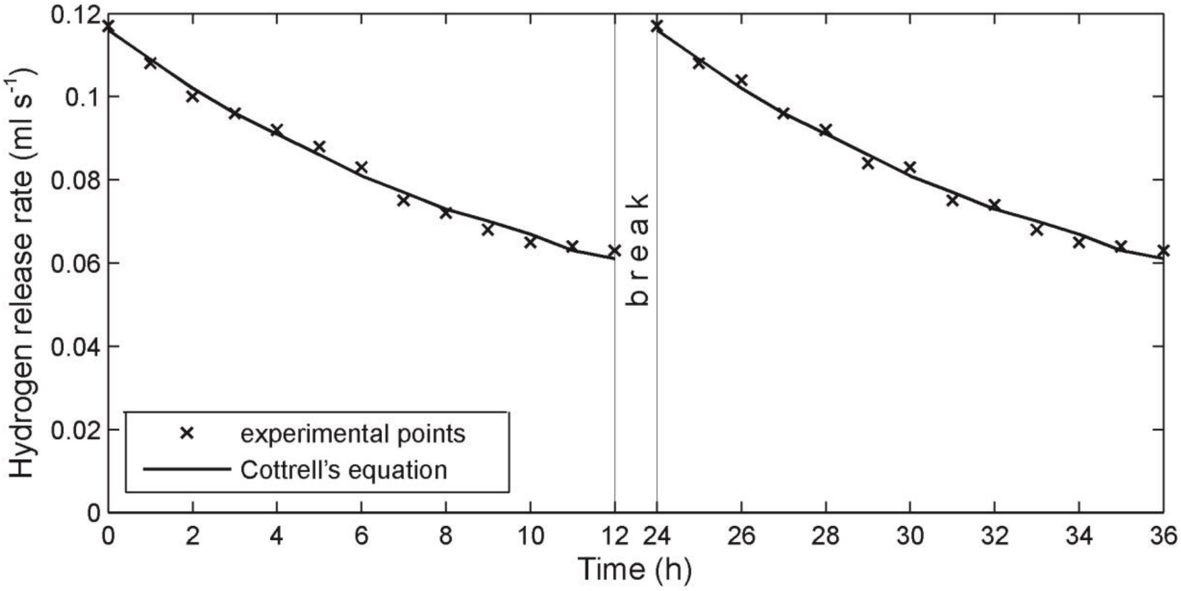

Figure 1. Process of hydrogen release relaxation at thermal decomposition of an oxide-nickel electrode of a battery KSX-25 at the temperature 800^0C.

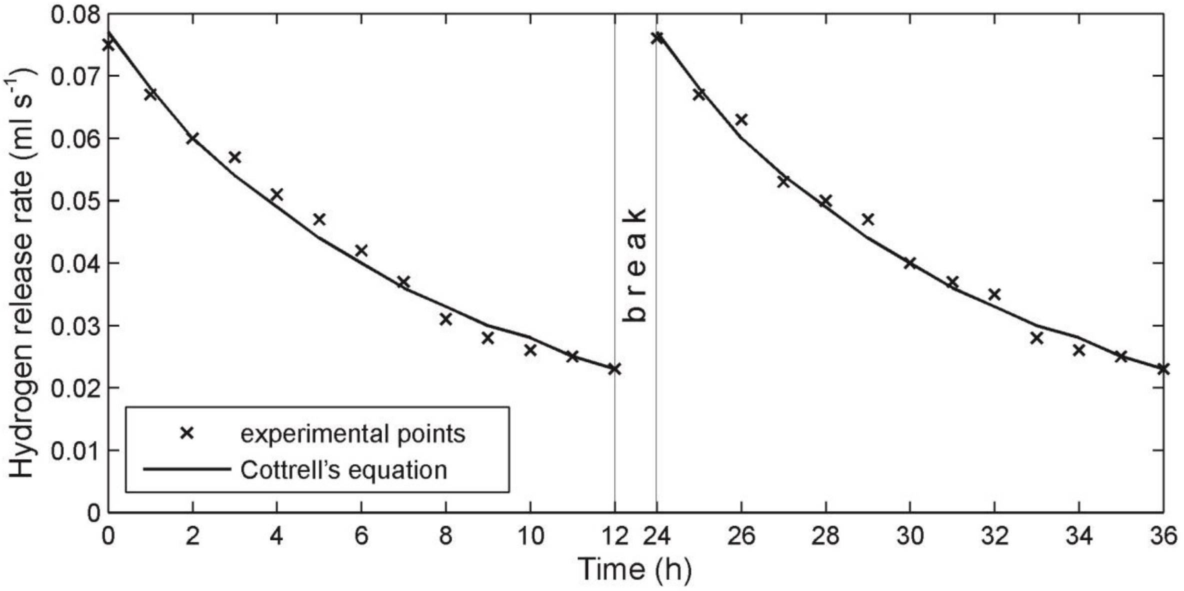

Figure 2. Process of hydrogen release relaxation at thermal decomposition of a cadmium electrode of a battery KSX-25 at the temperature 800^{0}C.

Table 1. Content of hydrogen in oxide-nickel and cadmium electrodes of a battery KSX-25

Type of electrode	Ni	Cd
Period of operation (years)	7	7
Electrode size (cm)	7.3 × 13.6 × 0.081	7.1 × 13.6 × 0.065
Amount of hydrogen released (l) [a]	35.9	18

[a] The relative error in the data in Table 1 is 5–7%.

The results of the dynamics measuring of the gas release from the electrodes at their thermal decomposition for first two days&nights are represented in the Figures 1 and 2. The total amount of the gas released from an oxide-nickel electrode and a cadmium one is represented in the Table 1. An analysis of the gas released – performed with aid of the gas analyzer VOG-2M – showed that the gas consisted only of hydrogen.

3. RESULTS AND DISCUSSION

In the paper [11], it was shown that the hydrogen is accumulated only in a ceramic-metal matrix of an electrode. This feature of the gas release (Fig. 1 and 2) testifies that in an electrode, hydrogen is distributed on the entire volume of a ceramic-metal matrix of an electrode. Then as a result of the gas release in boundary layers of the ceramic-metal matrix of the electrode, a hydrogen concentration decreases step-by-step, so the gas release velocity drops. During interruptions of the experiment, due to diffusion processes, leveling of hydrogen concentration takes place on the entire volume of the porous matrix. Then next day at the moment of the installation turning-on, the concentration of the hydrogen in surface layers of the electrode ceramic-metal matrix will be higher than at the moment of the installation shutdown. Just this can be an explanation of the considerable increase of the gas release velocity at the moment of the repeated installation turning-on. Notably, this pattern of the gas release is possible only in the case that a hydrogen diffusion velocity in the electrode ceramic-metal matrix is very low, while its amount is very large.

Let us evaluate parameters of the hydrogen diffusion in the electrodes. As the process of the gas release at the thermal decomposition of electrodes is conditioned by diffusion processes, changes of a hydrogen flow from the electrodes in the course of time must be described by the Cottrell's equation [17]:

$$j_d = \frac{C_H S D}{\sqrt{\pi D t}} \quad , \qquad (1)$$

where j_d – hydrogen atoms flow from an electrode, C_H – per-unit-volume concentration of hydrogen atoms in the electrode, S – electrode surface area, D - diffusion coefficient of hydrogen atoms in a ceramic-metal matrix of an electrode.

Along with it, a diffusion boundary layer thickness in the ceramic-metal matrix of the electrode is set by the equation:

$$\delta = \sqrt{\pi D t} \ . \qquad (2)$$

In our experiments (Fig.1 and 2), we started measuring of the hydrogen flow parameters not from the moment of time, when the thickness of the diffusion boundary layer is equal to zero (as in the equations (1,2)), but instead from the moment, when the temperature in the thermal chamber would reach the value 800^{0}C. So at the moment of the experiment start (Fig.1,2), already, the diffusion boundary layer had some thickness. In order to take this factor into account, we shall rewrite the Cottrell's equation in the following form:

$$j_d = \frac{C_H S D}{\sqrt{\pi D (t + t0)}} \quad , \qquad (3)$$

$$\delta = \sqrt{\pi D (t + t0)} \ . \qquad (4)$$

where *t0* – empiric parameter needed for taking into account the diffusion layer thickness at the moment of the experiment start.

Besides, a reverse flow is possible of hydrogen from a thermal chamber into an electrode. As in a thermal chamber (in a course of a thermal decomposition of an electrode), there is maintained the constant temperature (T=800^{0}C) and the constant pressure (equal to the atmospheric pressure) [4], hence the reverse flow j_b must also be constant. So the equation for the hydrogen cumulative flow from an electrode will take the form:

$$j_s = \frac{C_H S D}{\sqrt{\pi D (t + t0)}} - j_b \qquad (5)$$

With a purpose of a comparison convenience reaching of the Cottrell's equation (5) with our experimental data, we shall rewrite it in the following form:

$$j_s = \frac{A}{\sqrt{t+t0}} - j_b\,, \qquad (6)$$

where

$$A = C_H S \sqrt{\frac{D}{\pi}}\,. \qquad (7)$$

We shall find parameters for the Cottrell's equation (6) from the requirement of the best coincidence of the equation with the experimental data (Fig.1 and 2) with aid of the method of least squares and the optimization procedure by Levenberg–Marquardt. The optimization results are represented in the Table 2. Besides, using the data from the Tables 1 and 2, it is possible to find diffusion coefficients for hydrogen atoms in oxide-nickel and cadmium electrodes from the equation (7).

The found diffusion coefficients (Table 2) are much less than the diffusion coefficients of free atoms of hydrogen in any metals [18]. A decrease of the diffusion coefficients is possible only in the case that the hydrogen inside of the electrodes is not in its free state (α-phase) but instead in its bound state, i.e. in the β-phase. If an atom of the hydrogen is there in its bound state (in a potential hole), a probability of hydrogen atom transmigration from one potential hole into another one will decrease accompanied with the connection strength growth. Hence, upon the same gradient of concentration, a diffusion coefficient will decrease, while the connection strength will grow.

The found by us diffusion coefficient for hydrogen atoms in nickel matrix of an oxide-nickel electrode is about 10^6 times less than the diffusion coefficient of free hydrogen atoms in nickel at the temperature 800^0C [19]. Thus, the hydrogen atoms are connected inside of the ceramic-metal matrices of porous electrodes of nickel-cadmium batteries to a large extent.

Table 2. Optimal values for parameters in Cottrell's equation

Parameters	Figure 1	Figure 2
A (ml(H_2) $s^{-1/2}$)	37.985	20.141
$t0$ (h)	11.607	6.458
j_b (ml(H_2) s^{-1})	0.070	0.055
δ^a (%)	2	4
C_H (ml(H_2) cm^{-3})	4.464×10^3	2.868×10^3
D (cm^2 s^{-1})	5.769×10^{-9}	4.154×10^{-9}

δ^a – relative error of experimental data for Cottrell's equation (6) (Fig. 1 and 2)

4. CONCLUSION

Thus, processes of hydrogen release relaxation at a thermal decomposition of sintered electrodes of nickel-cadmium batteries are determined by the following features of the hydrogen inside of the ceramic-metal matrices: those features are, firstly, a distribution of atomic hydrogen all around the entire volume of the ceramic-metal matrices of the electrodes and, secondly, the fact that the atomic hydrogen is found inside of the electrodes in its bound state, i.e. in the β-phase. These facts matter much for understanding reasons of hydrogen accumulation in very large amounts in electrodes of nickel-cadmium batteries in a case of their long-time operation [10,11]. Although this problem requires further both theoretical and experimental studies.

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