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Short Communication

Investigation of Hydrogen Release Rate from Electrodes of Nickel-Cadmium Batteries at Their Thermal Decomposition

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In this paper, kinetics is examined of a hydrogen release at thermal decomposition of oxide–nickel and cadmium electrodes of nickel-cadmium batteries KSX-25 with operating life 6 years. The examination was conducted at fixed values of temperature: 480, 600, 800^{0}C (for cadmium electrodes) and 670, 840, 880^{0}C (for oxide–nickel ones). It was proved by experiments that in electrodes of nickel-cadmium batteries in a course of their long-lasting operation, a great amount of hydrogen is accumulated. The rate of the hydrogen release and the released hydrogen amount grow with decomposition temperature increase. Although at temperatures higher than 900^{0}C, the released hydrogen volume does not grow any longer. This fact shows that hydrogen atoms are contained inside of ceramic-metal matrix of electrodes in a potential hole, i.e. in their bound state. Energy values were found of hydrogen atoms activation for diffusion process in ceramic-metal matrices of oxide–nickel and cadmium electrodes; they are equal to 0.37 eV and 0.34 eV respectively.

Keywords: battery, nickel-cadmium, hydrogen accumulation, thermal runaway.

1. INTRODUCTION

In the papers [1-5], there was shown that at operation of nickel-cadmium batteries in the floating mode or at their charging under a constant voltage, an occurrence is possible of the thermal runaway phenomenon. In this case, a charging current in batteries grows sharply, while an electrolyte boils up instantaneously and turns into steam. Sometimes, there occurs abundant smoke formation, surface melting and rupture of battery plastic shell and even inflammation or explosion [6]. An analysis of the gas released as a result of the thermal runaway showed that 95-97% of the gas is represented by the hydrogen [1-4]. For example, at a thermal runaway of a nickel-cadmium battery

KSX-25, there releases about 140 liters steam (which is equal to an electrolyte volume), 280 liters hydrogen and 8.7 liters oxygen [7].

In the papers [8,9], by electrodes thermal decomposition, it was shown that hydrogen is accumulated in great amounts in electrodes of nickel-cadmium batteries in a course of their operation. For example, the batteries of the brand KSX-25 with their operating life more than 5 years contain about 800 liters hydrogen [9]. The specific capacity of an oxide–nickel electrode as a hydrogen accumulation unit was estimated as 13.4 wt% and 400 $\mathrm{kg \cdot m^{-3}}$ [8]. This result exceeds 2 times earlier results (obtained by traditional methods) for any revertible metal-hydrides including hydrides of magnesium and complex hydrides [10].

Batteries, in which the thermal runaway phenomenon is observed, are used in diverse technical devices of both domestic and special purpose: computers, telecommunications networks, aircrafts, etc.

As the thermal runaway occurs inadvertently and reasons of it are little-understood (till now), one should not rule out a possibility of its occurrence in a middle of an airplane flight. An airplane itself is a facility of a heightened danger; as for the occurrence of such uncontrolled wild process during a flight accompanied by smoke formation and possibly by a short circuit in an aircraft onboard system, etc., inevitably it would lead to a crisis situation with diverse subsequences.

This phenomenon arouses a great and purely theoretical interest. Perhaps, the thermal runaway is the only self-accelerating phenomenon in batteries, which occurs so wildly and independently of operating this battery personnel; besides it is accompanied with a lot of visual and thermal effects and practically uncontrollable. Notwithstanding, a publications analysis for the last 20 years showed that in the world literature, in actual fact, investigations are almost absent of this phenomenon in alkaline batteries. Meanwhile, as for thermal runaway investigations in lithium-ion batteries, there are rather a good deal of them [11-13].

In our previous papers [3,4] by experiments, it was proved that the reason of a thermal runaway initiation in alkaline batteries is a powerful exothermic reaction of recombination of atomic hydrogen, which is accumulated in electrodes during batteries operating life

$$\mathrm{H}_{ads\mathrm{Cd}} + \mathrm{H}_{ads\mathrm{Ni}} \rightarrow \mathrm{H}_2 \uparrow . \qquad (1)$$

The reaction (1) runs in line with the electrochemical mechanism:

$$\mathrm{H_2O} + \mathrm{H}_{ads} + \mathrm{e}^- \rightarrow \mathrm{H}_2 \uparrow + \mathrm{OH}^- \quad \text{(cathode)},$$

$$\mathrm{H}_{ads} + \mathrm{OH}^- \rightarrow \mathrm{H_2O} + \mathrm{e}^- \quad \text{(anode)} \; .$$

The reaction (1) is the powerful exothermic reaction with heat dissipation in amount of 436 kJ/mole (hydrogen) [10]. A rate of the reaction (1) is determined by a rate of hydrogen release from electrodes, which depends on an electrodes temperature and an energy value of atomic hydrogen binding inside of electrodes sintered matrices.

In this respect, this paper is aimed at a) the rate investigation of hydrogen release from electrodes under various temperatures and b) hydrogen activation energy assessment. This work became a continuation of started in papers [14,15] researches on modeling of various processes in electrochemical batteries.

2. EXPERIMENTAL

For the examination, nickel-cadmium batteries KSX-25 were chosen with sintered electrodes with capacity 25 ampere-hours.

The experimental installation for investigating of the gas release process from electrodes of batteries in a case of their heating-up was described in details in the papers [7,8]. It is represented by a metal thermal chamber 1.8 m long and 2.5 cm in diameter. A sealed end of the thermal chamber was placed into a muffle furnace, while through the other end, the gas withdrawal was arranged. Considering that as a rule under the action of the high temperature, such electrode is melted partially and adheres to the walls of the thermal chamber, it was placed into a cartridge for its extraction convenience after the experiment conducting. For heat exchange decrease in the thermal chamber, above the cartridge, a round porous ceramic plug was inserted 20 cm long.

For the examination, the batteries were chosen with their operating life 6 years as a top amount of hydrogen is accumulated in electrodes after 3 to 5 years of operation [7,8]. Then gradually, the oxide–nickel and cadmium electrodes were thermally decomposed in the above described installation. To the cadmium electrodes, the following temperatures were applied: 480, 600, 800^0C, while to the oxide–nickel ones the temperatures were chosen 670, 840, 880^0C.

The temperature values for the electrodes decomposition were chosen based on the following considerations. In our preliminary experiments, there was found that an initiation of a noticeable gas release starts from 340^0C for a cadmium electrode and from 660^0C for an oxide–nickel one.

A rate of the gas release was estimated based on a released gas volume for five minutes. The gas release rate measuring was conducted every hour.

3. RESULTS AND DISCUSSION

The experimental results in the form of diagrams for three values of temperature are represented in the Figures 1,2. From the diagrams on the Fig. 1,2, it is seen that the gas release process at the thermal decomposition of the electrodes takes in average 140 hours for an oxide–nickel electrode and 78 hours for a cadmium electrode. With time, the rate of the gas release decreases exponentially. Per a day from an electrode, the following amount of gas was released: for a cadmium electrode not less than 175 ml/g (milliliters of gas per one gram of an electrode weight) in first days and down to 4 ml/g in the last days; while for an oxide–nickel electrode from 250 ml/g down to 4 ml/g. The process of the thermal decomposition stopped, when daily gas release became less than 4 ml/g.

The gas analysis was conducted with aid of the gas analyzer VOG-2M. The performed analysis showed that the gas released as a result of electrodes thermal decomposition is represented by the hydrogen in total.

It is interesting to note that as a result of the electrolyte decomposition (in a course of battery charging), gases released are hydrogen and oxygen. But as it was shown by the experimental investigations [7,8], in electrodes, only the hydrogen is accumulated, while the oxygen leaves a battery. This is connected with the fact that the hydrogen possesses a very high diffusional penetrability. The diffusion coefficient of hydrogen atoms in metals is many times higher than a diffusion coefficient of any other atoms including oxygen atoms, too. For example, at the temperature 20^0C, the hydrogen diffusion coefficient in nickel is approximately 10^{10} times higher than the diffusion coefficient of nitrogen or oxygen [10].

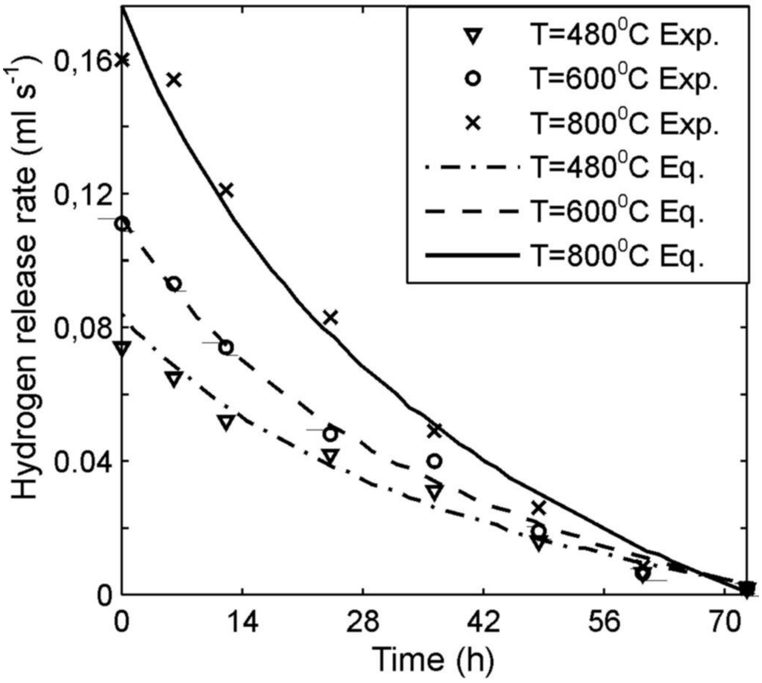

Figure 1. Rate variations of hydrogen release in a course of thermal decomposition of cadmium electrodes of battery KSX-25 at heating-up different temperatures: Exp – experimental data, Eq – Cottrell's equation (7) with parameters from Table 1

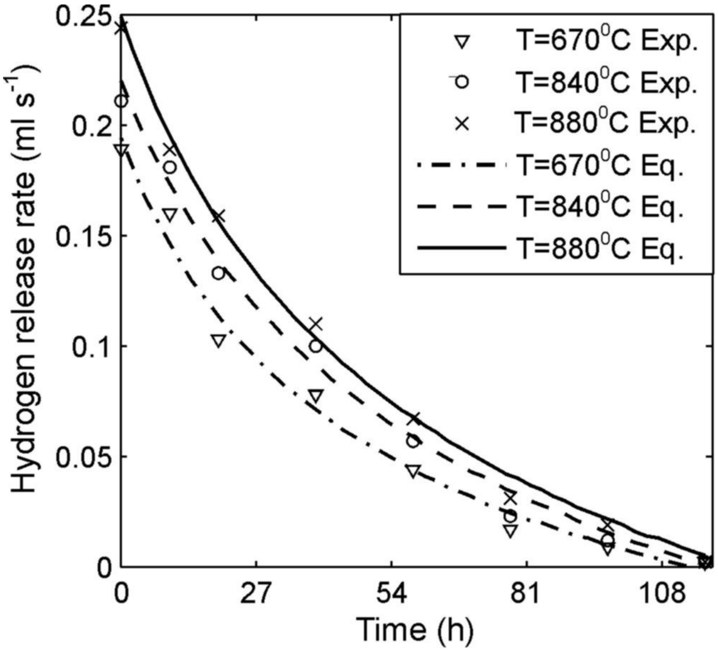

Figure 2. Rate variations of hydrogen release in a course of thermal decomposition of oxide–nickel electrodes of battery KSX-25 at heating-up different temperatures: Exp – experimental data, Eq – Cottrell's equation (7) with parameters from Table 2

The precision of the measurements of the released hydrogen total volume is about 200 ml. The point is that in an initial moment of heating-up into the gas receiver of the thermal chamber, air enters because of a thermal expansion in the thermal chamber itself. Then in proportion to thermal chamber heating-up time, from electrodes, the hydrogen starts releasing and together with heated-up air, it enters into the gas receiver. In connection with this, it is hard to fix a moment of arrival of the released-from-the-electrodes gas into the receiver. That is why a set of experiments was conducted on heating-up of an empty thermal chamber up to various temperature values. As a rule, at heating-up of the empty thermal chamber up to temperature value 800^{0}C, into the receiver, about 200 ml air entered.

In proportion to decomposition temperature growth, a gas release rate grows (Fig. 1,2). That is, the higher the temperature, the higher the gas release rate in any moment of time of the electrodes decomposition and hence the more hydrogen can be extracted from the electrodes. To this conclusion, one can come also by the way of calculating of the areas under every diagram on the Fig. 1,2, which are equal to the volumes (*V*) of the gas released as a result of the electrodes thermal decomposition (Table 1,2). But at the temperature values higher than 900^{0}C, as a matter of fact, the volume of the released hydrogen does not grow any longer already.

This result can be explained with a supposition that the hydrogen atoms in electrodes are contained in a potential hole, i.e. in their bound state. Then according to Boltzmann distribution, the higher temperature is, the more hydrogen molecules amount is able to leave the potential hole. But at the temperatures higher than 900^{0}C, the entire accumulated hydrogen has already left the electrodes. This fact is very important for understanding of the form, in which the hydrogen is contained in electrodes of nickel-cadmium batteries.

The gas release at electrodes thermal decomposition is conditioned by diffusional processes; that is why it should be described by the Cottrell's equation [16]

$$j = \frac{C_H SD}{\sqrt{\pi D t}} \quad , \tag{2}$$

$$\gamma = \sqrt{\pi D t} \, , \tag{3}$$

where *j* – hydrogen atoms flow from electrode, C_H - hydrogen volume concentration in electrode, *S* – electrode surface area, *D* - effective diffusion factor of hydrogen atoms in ceramic-metal matrix of electrode, γ - diffusion boundary layer thickness in ceramic-metal matrix of electrode.

In the equation (2) at $t \to 0$, the hydrogen atoms flow from electrode tends to infinity, which is physically meaningless. In our experiments, we started measuring the hydrogen flow from the thermal chamber, when a temperature inside of the thermal chamber reached the necessary value. Hence by the experiment beginning, the diffusional boundary layer will have the thickness

$$\gamma_0 = \sqrt{\pi D t_0} \tag{4}$$

So if to measure the hydrogen atoms flow from an electrode from the time moment t_0, the equations (2,3) are necessary to be written in the form:

$$j = \frac{C_H SD}{\sqrt{\pi D (t + t_0)}} \quad , \tag{5}$$

$$\delta = \sqrt{\pi D (t + t_0)} \, . \tag{6}$$

It is important to take into account also a possible reverse flow of the hydrogen from the thermal chamber into the electrode. In the thermal chamber, the constant temperature and the constant pressure [8,9] are kept; hence the reverse flow j_b must be also constant. With due consideration of the hydrogen reverse flow, the equation (5) will have the form:

$$j = \frac{A}{\sqrt{t + t0}} - j_b\,, \qquad (7)$$

where

$$A = C_H S \sqrt{\frac{D}{\pi}}\,. \qquad (8)$$

With use of the experimental data (Fig.1,2), let's find parameters for the Cottrell's equation (7) applying the least-squares procedure and Levenberg–Marquardt's optimization procedure [17]. The results are represented in the Tables 1,2, while the theoretical curves based the Cottrell's equation (7), with parameters from the Tables 1,2 are represented on the Figures 1,2.

Table 1. Optimal values for parameters cadmium electrode in Cottrell's equation

Parameters	T=480^{0}C	T=600^{0}C	T=800^{0}C
A (ml(H$_2$) s$^{-1/2}$)	57.04	74.977	122.51
$t0$ (h)	29.72	28.48	29.217
j_b (ml(H$_2$) s^{-1})	0.091	0.122	0.202
δ (%)	8	5	6
V(l)	8.181	10.649	16.05
D (cm^2 s^{-1})	4.217×10^{-8}	7.287×10^{-8}	1.946×10^{-7}

Table 2. Optimal values for parameters oxide–nickel electrode in Cottrell's equation

Parameters	T= 670^{0}C	T= 840^{0}C	T=880^{0}C
A (ml(H$_2$) s$^{-1/2}$)	113.73	164	172.776
$t0$ (h)	29.16	39.42	37.03
j_b (ml(H$_2$) s^{-1})	0.157	0.216	0.225
δ^a (%)	5	5	6
V(l)	25.24	31.78	36.60
D (cm^2 s^{-1})	5.144×10^{-8}	1.069×10^{-7}	1.187×10^{-7}

δ – relative error of experimental data for Cottrell's equation (7) (Fig. 1 и 2).

Besides from the equation (8) with use of the data of the Table 3, it is possible to find effective diffusion factors of hydrogen atoms in oxide–nickel and cadmium electrodes (Tables 1,2).

The found values of the diffusion factors (Tables 1,2) represent an average effective estimation for the diffusion factors of hydrogen atoms in the electrodes during the entire process of the electrodes thermal decomposition.

Diffusion coefficients of hydrogen atoms in solid bodies at different temperatures are well-characterized by Arrhenius equation $D=D_0 \cdot \exp(-E/RT)$ [18]. Using this equation and the experimental data (Fig. 1,2), it is possible to find the hydrogen atoms activation energy E for the diffusion process. On the Fig.3, there is represented the dependence diagram ln(D) vs. (1/T). From the Fig.3, it is seen that the experimental data show a good correspondence to a straight line, which confirms the applicability of the Arrhenius equation. The calculated values of the activation energy for oxide–nickel and cadmium electrodes are represented in the Table 3. These values are indicative of the fact that the hydrogen is bound quite strongly inside of a ceramic-metal matrix of a porous electrode [9].

Table 3. Parameters of oxide–nickel and cadmium electrodes of a battery KSX-25

Type of electrode	Ni	Cd
Period of operation (years)	6	6
Electrode size (cm)	7.3 × 13.6 × 0.081	7.1 × 13.6 × 0.065
Top amount of hydrogen released (l)[a]	36.60	16.05
Hydrogen concentration in electrodes (ml(H_2) cm^{-3})	4.477×10^3	2.549×10^3
Activation energy (eV)	0.37	0.34

[a] The relative error in the data in Table 3 is 5–7%.

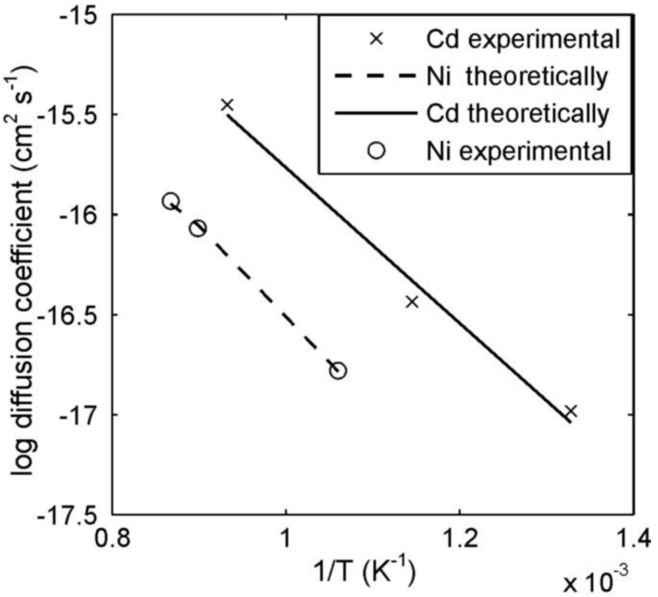

Figure 3. Dependence of hydrogen diffusion coefficient on temperature for oxide–nickel and cadmium electrodes

4. CONCLUSION

The investigations conducted show that in a course of a long-lasting operation of the nickel-cadmium batteries KSX-25, in their ceramic-metal electrodes, a great amount of hydrogen is accumulated. The hydrogen atoms are contained inside of the electrodes' ceramic-metal matrix [9] in a bound state (β-phase). Notably, the connection is quite strong as the hydrogen atoms activation energy for a diffusion process is equal approximately 0.35 eV. This can serve as an explanation of the very low diffusion coefficient of hydrogen atoms in ceramic-metal nickel matrix of electrodes (Table 2) as compared with the diffusion coefficient of non-bound hydrogen atoms (α-phase) in nickel [18]. In whole, the problem of the big deal of hydrogen accumulation in electrodes of electrochemical batteries at their long operation requires further both theoretical and experimental investigations.

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