Short Communication

Study of Effect of Batteries Capacity on Probability of Thermal Runaway Occurrence

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In this study, it was shown that an occurrence probability of a thermal runaway in nickel-cadmium batteries with sintered electrodes falls down with decrease of batteries capacity, while other parameters necessary for thermal runaway process occurrence such as dendrites density on cadmium electrode and gravimetric capacity of a hydrogen accumulation in electrodes do not depend on the batteries capacity.

1. INTRODUCTION

The thermal runaway can occur in a case of constant-voltage batteries recharging or in a case of their work in float mode [1]. According to the generally accepted point of view, the thermal runaway is connected with electrochemical reactions acceleration in batteries due to their self-heating [1]. The thermal runaway is a phenomenon common to batteries of practically all electrochemical systems. At the present time, this phenomenon is studied quite intensively in lithium-ion batteries [2-4], but desperately scantily in batteries with aqueous electrolyte [5]: especially few such studies are there for alkali batteries.
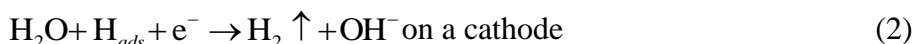
In the papers [6,7], it was shown that at the present time, a lot of experimental facts exist contradicting to the generally accepted mechanism of the thermal runaway. For example, in a course of a thermal runaway, an energy release is 140 times higher than energy amount that at the same time the battery receives from its recharger [7]. Besides, during a thermal runaway, a great deal of gas releases, 95% of which is the hydrogen [8,9]. Also a lot of other experimental facts [6-10] exist, which are

impossible to be explained on a base of electrochemical reactions of batteries charging and electrolyte decomposition.

In the work [11] by experiments, it was proved that two processes of accumulation leads batteries to the thermal runaway step-by-step. Firstly, this is the hydrogen accumulation process in electrodes [12,13]. Secondly, this is the process of dendrites accumulation on a cadmium electrode. In the paper [11], it was also proved that the thermal runaway is connected with an initiation of the powerful exothermic reaction of the atomic hydrogen recombination

$$H_{ads\,Cd} + H_{ads\,Ni} \rightarrow H_2 \uparrow \ , \qquad\qquad (1)$$

which runs in line with electrochemical mechanism

$$H_2O + H_{ads} + e^- \rightarrow H_2 \uparrow + OH^- \text{ on a cathode} \qquad (2)$$

$$H_{ads} + OH^- \rightarrow H_2O + e^- \text{ on an anode} \qquad (3)$$

The reaction (1) is a powerful exothermic reaction with heat dissipation in amount of 436 kJ/mole (hydrogen) [14].

In spots of dendrites' penetration through a separator, a distance between electrodes decreases significantly. Hence in these places, current density of batteries charging will be much higher than in neighboring parts of the electrodes [11]. The rate-limiting step for the electrochemical reactions (2,3) is the stage of metal-hydrides decomposition [11]. Metal-hydrides decomposition velocity increases sharply with growth of electrodes temperature. Hence in a dendrites location, a power of the reactions (2,3) will grow. As the reaction (1) is an exothermic reaction, it will heat up the electrode even higher. This will lead to even more intensive metal-hydrides decomposition, and so on. This way, a power of the reactions (2,3) will rise steeply. This is exactly, what the thermal runaway process in alkali batteries is. [11]

In the paper [6] by experiments it was proved that a thermal runaway probability grows with increase of charge voltage, ambient temperature and operating life of batteries. This work is aimed at studying an effect of batteries capacity on occurrence probability of the thermal runaway.

2. EXPERIMENTAL

In the experiments, there were used the nickel-cadmium batteries KSX-25, KSX-6 and KSX-3.5 (NIIHIT, Saratov, Russia) by capacity 25, 6 and 3.5Ah respectively. These batteries had sintered electrodes of the same construction, were equal in thickness and differed only in surface area.

Cycling was fulfilled for a group of ten same parallel connected batteries. This allowed obtaining a large volume of statistical data for a less time interval. Between the batteries, there were inserted heat-insulating wood block fillers two centimeters thick. So in a case of a thermal runaway occurrence in one battery, it could not influence an occurrence probability of the thermal runaway in neighboring batteries on expense of their additional heating-up.

According to our previous studies [6], a thermal runaway occurrence probability grows with increase of batteries operating life and charging voltage. That is why in the experiments, the batteries were used with their operating life seven years, and as for charging, it was done at the voltage 2V [6]

during ten hours. Battery discharging was performed in accordance with the instructions to the batteries (Tab. 1).

Table 1. Batteries cycling modes

Batteries	KSX-25	KSX-6	KSX-3.5
Charge voltage (V)	2.2	2.2	2.2
Charge time (h)	10	10	10
Discharge current (A)	10	2	1.4
Final voltage (V)	1	1	1

Each batteries group was charged and discharged 80 times. So for each batteries type, there were performed 10*80=800 charging-discharging cycles. These batteries cycling results are represented in the Table 2.

In the paper [11], it was shown that two processes of accumulation leads batteries to a thermal runaway step-by-step. Firstly, this is the process of dendrites accumulation on a cadmium electrode. Secondly, this is the hydrogen accumulation process in electrodes.

Visual inspections of the electrodes of the batteries KSX-25, KSX-6 and KSX-3.5 after seven-years-long operation showed that the dendrites density on cadmium electrodes of these batteries is approximately the same. Theoretically, this result follows from the fact that the current density on these batteries electrodes during their operation is approximately the same. Besides, the electrodes of those batteries are the same in their construction and differ only with their surface area. Thus, the first necessary condition for thermal runaway occurrence in all investigated batteries is the same.

Table 2. Batteries cycling results

Batteries	KSX-25	KSX-6	KSX-3.5
Charge voltage (V)	2.2	2.2	2.2
Period of operation (years)	7	7	7
Number of charge-discharge cycles	800	800	800
Number of thermal runaways	3	0	0

That is why by experiments we studied the second necessary condition for a thermal runaway occurrence. With this purpose, we evaluated a gravimetric capacity of hydrogen accumulation on electrodes of those batteries.

For hydrogen volume determination in battery electrodes, the stand was used described in detail in the paper [8]. It was represented by a thermal chamber in a form of a tube 1.8 m long and 2 cm in diameter. A sealed end of the tube was placed into a muffle furnace. Into the other end, a rubber

plug with a pipe for gas withdrawal was inserted. As a result of the electrode heating up in the thermal chamber, the gas released from it cooled down partially passing through a standard coil and then it entered into a measuring container. The electrodes were placed into a cartridge, which was inserted into the thermal chamber. This allowed easy taking the electrodes out after the experiment conduction. For convection decrease in the thermal chamber, above the cartridge, a porous ceramic plug 20 cm long was placed into the thermal chamber. In common with the papers [12,13], an electrodes decomposition in the thermal chamber took place at the temperature 800^0C. The electrodes decomposition process stopped, when daily gas release became less than 4 mL/g (of an electrode). Hydrogen desorption was performed in average: for cadmium electrode within 7 days, and for oxide-nickel electrode within 13 days, during 11 hours daily.

For the experimental studies in a random manner, there were selected three batteries of the above-specified types. From each battery, one cadmium and one nickel electrode were taken out. Then these electrodes were subjected to thermal decomposition on the above-described stand. In the experiments, to the thermal decomposition at the same time, the electrodes were subjected in number from one to three, which was determined by a cartridge capacity.

Based on the results of three experiments for each electrode type and for each battery type, an average gas volume in an electrode was found. Then the data were recalculated for all the battery electrodes. The results of these experiments are represented in the Table 3.

Table 3. Hydrogen average content in oxide-nickel and cadmium electrodes

Batteries	KSX-25		KSX-6		KSX-3.5	
Period of operation (years)	7		7		7	
Type of electrode	Ni	Cd	Ni	Cd	Ni	Cd
Amount of gas released from battery (l)	537	274	129	67	75	38
Gravimetric capacity (wt%)	13.3	10.3	13.4	10.4	13.2	10.2

Our analysis of the released gas with use of the gas analyzer VOG-2M showed that the gas consisted only of hydrogen. The absolute error in the percentage concentrations was 0.3-0.5.

Knowing the electrodes number in the batteries and their weight (before their thermal decomposition), it is possible to find a gravimetric capacity of hydrogen accumulation in the electrodes. For example, the battery KSX-25, contains 15 oxide-nickel electrodes weighing 24 g each and 14 cadmium electrodes weighing 17 g each. Thus, the gravimetric capacity of hydrogen accumulation for oxide-nickel electrodes of the batteries KSX-25 is equal 13.3wt%. This value corresponds to the value earlier obtained in the paper [12].

So from the Table 3, it is seen that with a growth of batteries capacity, an accumulated in it hydrogen volume grows in proportion, too, as electrodes mass grows. But the specific mass capacity of hydrogen accumulation is approximately the same at all the investigated batteries (Table 3). Hence

also the second necessary condition for a thermal runaway occurrence [11] is the same on all the investigated batteries.

3. RESULTS AND DISCUSSION

The results of the conducted experiments (Table 2) show expressly that the probability of a thermal runaway depends on a battery capacity. Indeed, all the batteries were cycled at the same ambient temperature and at the same charge voltage. Besides, they had the same operating life in similar conditions. It means that the batteries were subjected to action of the same external factors influencing their thermal runaway occurrence probability [12]. Nevertheless, in the batteries KSX-6 and KSX-3.5 of the small capacity, no thermal runaway occurred, while in the batteries KSX-25 of larger capacity thermal runaway occurred three times (Table 2). Thus the establishment of the relationship between the capacity of nickel-cadmium batteries and the probability of occurrence of thermal runaway is the main result of this experimental work.

For more than 25 years of thermal runaway studying in alkali batteries, never have we coped initiating a thermal runaway in batteries by capacity less than 12 Ah. Thus, batteries capacity influences a thermal runaway occurrence probability significantly.

From the point of view of the thermal runaway mechanism represented in the paper [11], this dependence can be explained by influence of the following factors.

Firstly, the more batteries capacity, the more their mass, and hence, the worse a heat-removal from internal electrodes. So (during charging at the same voltage), internal electrodes located inside of batteries of a large capacity will be heated up more than internal electrodes of batteries of a small capacity. However, according to investigations described in the paper [8], with electrodes temperature growth, a thermal runaway occurrence probability grows as well.

Secondly, at the same charging voltage and hence at the same charging current density (as electrodes of the batteries in question are the same constructively), batteries of larger capacity are charged with large total current. In a case of a short circuit, through a dendrite, the large total current of charge will allow concentrating a larger local current in this spot and hence heating up this electrode part more intensively than in batteries of a small capacity. Undoubtedly, both these factors promote a thermal runaway initiation.

4. CONCLUSIONS

Thus, in this study, for the first time proved experimentally**,** that an occurrence probability of a thermal runaway in nickel-cadmium batteries with sintered electrodes falls down with decrease of batteries capacity**.** However, based on the conducted experimental studies, a categorical affirmation about impossibility of thermal runaway in batteries of small capacity is, of course, premature as the studying of three batteries type does not provide us with a sufficient statistical material. Besides, the conducted experimental researches show that in the batteries KSX-25, KSX-6 and KSX-3.5, in equal

measures, accumulation processes are present (of hydrogen in electrodes (Table.3) and of dendrites on cadmium electrode) necessary for a thermal runaway process occurrence. Hence, according to the thermal runaway mechanism [11], in all the studied batteries, a thermal runaway process occurrence is possible. Although in batteries of a small capacity, in virtue of a better heat-removal from internal electrodes and lower charging total current, it is needed to use more severe charging conditions in order to obtain a thermal runaway process occurrence. For example, it is needed to use a higher charging voltage or a higher ambient temperature [8]. However, this assumption requires separate both theoretical and experimental researches.

References

1. Y. Guo, in: J. Garche (Ed) *Encyclopedia of Electrochemical Power Sources, vol. 4,* Elsevier, Amsterdam (2009) 241
2. S.J. Lee, C.Y. Lee, M.Y. Chung, Y.H. Chen, K.C. Han, C.K. Liu, W.C. Yu and Y.M. Chang, *Int. J. Electrochem. Sci.,* 8 (2013) 4131
3. J. Li, J. Chen, H. Lu, M. Jia , L. Jiang, Y. Lai and Z. Zhang, *Int. J. Electrochem. Sci.,* 8 (2013) 5223
4. X. Feng, M. Fang, X. He, M. Ouyang, L. Lu, H. Wang and M. Zhang, *J. Power Sources*, 255 (2014) 294
5. F. Torabi and V. Esfahanian, *J. Electrochem. Soc.*, 158 (2011) A850
6. N.E. Galushkin, N.N. Yazvinskaya, D.N. Galushkin, and I.A. Galushkina, *J. Electrochem. Soc.,* 161 (2014) A1360
7. N.E. Galushkin, N.N. Yazvinskaya, and D.N. Galushkin, *J. Electrochem. Soc.,* 162 (2015) A749
8. D.N. Galushkin, N.N. Yazvinskaya and N.E. Galushkin, *J. Power Sources,* 177 (2008) 610
9. N.E. Galushkin, N.N. Yazvinskaya, D.N. Galushkin and I.A Galushkina, *Int. J. Electrochem. Sci.*, 9 (2014) 3022
10. 10. N.E. Galushkin, N.N. Yazvinskaya, D.N. Galushkin and I.A Galushkina, *Int. J. Electrochem. Sci.*, 10 (2015) 6645
11. N.E. Galushkin, N.N. Yazvinskaya, and D.N. Galushkin *J. Electrochem. Soc.,* 162 (2015) A2044
12. N.E. Galushkin, N.N. Yazvinskaya and D.N. Galushkin, *ECS Electrochem. Lett.*, 2 (2012) A1
13. N.E. Galushkin, N.N. Yazvinskaya, D.N. Galushkin and I.A Galushkina, *Int. J. Hydrogen Energy*, 39 (2014) 18962
14. S.J. Blanksby and G.B. Ellison, *Acc. Chem. Res.,* 36 (2003) 255.