Int. J. Electrochem. Sci., 11 **(2016)** 7843 – 7848, doi: 10.20964/2016.09.49

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Communication

Hydrogen Amount Estimation in Electrodes of Nickel-Cadmium Batteries Depending on Their Operating Life

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Received: 7 June 2016 / *Accepted:* 15 July 2016 / *Published:* 7 August 2016

In this investigation, it was shown that hydrogen is absent in the electrodes of new nickel-cadmium batteries. However, during batteries operation, a lot of hydrogen is accumulated in their electrodes. The amount of hydrogen accumulated by the electrodes stops increasing after five years of service life.

Keywords: Hydrogen accumulation, battery, nickel–cadmium, thermal runaway

1. INTRODUCTION

A thermal runaway phenomenon occurs in batteries of all the electrochemical systems [1]. In the case of the thermal runaway occurrence, a battery heats up sharply and afterwards a battery body inflammation is possible followed by an explosion. In this case inevitably, a system contained the battery goes unserviceable.

Notwithstanding, in the international literature, investigations are very few of this dangerous phenomenon, especially in alkaline batteries. It should be noted that there exists quite a number of works investigating the thermal runaway in lithium-ion batteries [2-5]. Far less are works on a thermal runaway investigation in lead-acid batteries [6,7].

Alkaline batteries are installed in many systems of extra high hazard: aircrafts, railway transport, etc. In our opinion, the investigations lack on the thermal runaway in alkaline batteries can be assigned to two causes. Firstly, the thermal runaway is a very rare phenomenon. It does not constitute an everyday threat for systems comprising batteries. This is why batteries manufacturers do not invest any considerable finance in this phenomenon studying. Secondly, a mechanism of the

thermal runaway seems evident to many investigators [1], while till now there are neither direct experimental proves of this mechanism nor its artificial reproduction attempts.

In our previous papers [8-13], there was shown that as a result of the thermal runaway from nickel-cadmium (NC) batteries, a lot of hydrogen releases. In the papers [14,15], by means of thermal decomposition of such battery electrodes, it was proven that the hydrogen was present in electrodes of those batteries even before a thermal runaway.

In this paper, changes of the hydrogen amount are studied in electrodes of nickel-cadmium batteries with various operating life.

Theoretically, one may suppose two versions of hydrogen emergence in the nickel-cadmium batteries. Firstly, the hydrogen can appear in the battery electrodes because of some technological processes of the electrodes manufacturing. Then in new batteries, the hydrogen should be present in the same amount or more like in batteries featured with a rather long operating life. Secondly, it is possible that the hydrogen is accumulated in the electrodes of the NC batteries during their operation. For example, according to their service instruction, the battery KSL-15 is needed to be charged by the current 3.8 A during 6 hours. Hence, to this battery, 22.8 Ah are transferred, which exceeds 1.52 times the nominal capacity of the battery KSL-15. So, in the case of this battery, at its charging, about 7.8 Ah are spent for a water decomposition with the evolution of hydrogen and oxygen.

So, theoretically, as a result of a long operation of these batteries, a lot of hydrogen could be accumulated in their electrodes. If to accept that this presupposition is true, the hydrogen amount accumulated in the battery electrodes must depend on operating lives of these batteries. In this paper, the investigation is aimed at these hypotheses verification.

2. EXPERIMENTAL

For the experiments conducting, the batteries KSL-15 were selected (with sintered electrodes by capacity 15 Ah) with an operating life from 0 to 7.5 years and the batteries KPL-14 (with pocket electrodes by capacity 14 Ah) with operating lives from 0 to 10 years.

The experimental stand for the process investigation of the gas evolution from battery electrodes at their heating up was described in detail in the paper [13]. It was represented by a metal 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, while 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 entered into a measuring container.

As under the high temperature action, the observed electrode adhered to thermal chamber walls, for a convenience of its taking out after the experiment conduction, it was placed into a cartridge.

A decomposition of every electrode was conducted at the temperature 800^0C. This temperature was chosen based on the following considerations. In our preliminary experiments, it was found that for a cadmium electrode, a remarkable gas release starts at 340^0C, while for oxide-nickel one at 660^0C.

For both oxide-nickel and cadmium electrodes, an essential gas release starts at temperatures more than 740^0C. Thus the temperature 800^0C was chosen as an optimal one for the thermal decomposition for both cadmium and oxide-nickel electrodes.

The thermal decomposition process stopped when a daily gas release stayed less than 4 mL/g (of an electrode). For example, for a battery KSL-15 with a long operating life, the thermal decomposition took in average 12 days for a cadmium electrode and 14 days for oxide-nickel one, on a basis of 11 hours-long working day. Daily from a cadmium electrode, not less than 3.5 L released on first days and up to 100-110 mL gas on last days, while for an oxide-nickel electrode, the amount made not less than 5.5 L on first days and up to 100-110 mL on the last days.

A quantitative determination of the released gas composition was made with aid of the gas analyzer VOG-2M.

The results of the experimental investigations for the battery KSL-15 are represented in the Table 1, while for the battery KPL-14 in the Table 2. To the thermal decomposition, one electrode was subjected, which preliminary was rolled up in a form of a tube and placed into the cartridge.

At the thermal decomposition of both oxide-nickel and cadmium electrodes, from new batteries KSL-15, the gas mixture release in amount about 180-192 mL. This volume falls within the device accuracy limits. The point is that at an initial moment at electrodes heating up in the thermal chamber, the air enters into the measuring container because of air thermal expansion in the thermal chamber itself. Then, with the thermal chamber heating up, from the electrodes, the gas starts releasing and together with the hot air it enters into the measuring container. So it was very difficult to determine an entrance moment of the gas released from the electrodes into the measuring container.

Table 1. Dependence of average volume of gas released (from one electrode) on operating lives of batteries KSL-15 at thermal decomposition of oxide-nickel and cadmium electrodes

No. of the accumulator	1	2	3	4	5	6	7	8	9
Period of operation (years)	New	1	1.5	3.5	4	5	5.5	6	7.5
Amount of gas released (Ni) (l)	0	13	16.7	26.3	29.9	32	31.5	31.6	31.9
Amount of gas released (Cd) (l)	0	11	12.8	16.1	18.7	20	19.5	19.5	19.8

Table 2. Dependence of average volume of gas released (from one electrode) on operating lives of batteries KPL-14 at thermal decomposition of oxide-nickel and cadmium electrodes

No. of the accumulator	1	2	3	4	5	6	7	8
Period of operation (years)	New	1	2	4.8	6	7	8	10
Amount of gas released (Ni) (l)	0	19.9	30.9	37	36.9	37.1	36.8	36.9
Amount of gas released (Cd) (l)	0	7.7	17.2	26.1	25.9	26.1	25.8	25.9

The relative error of the data in the Tables 1,2 is 5-6 %.

This is why a set of experiments was conducted on heating up of an empty thermal chamber to various temperature values. When the empty thermal chamber was heated up to the temperature 800^0C,

into the measuring container, air in amount of about 180-190 mL entered. So in connection with the air heating up in the thermal chamber, we let out the first 210 mL gas into the atmosphere, while the left gas was collected and analyzed.

The analysis of the gas released from the electrodes of both types with aid of the gas analyzer VOG-2M showed that the released gas consists only of the hydrogen. The absolute error in the percentage concentrations is 0.3-0.5.

3. RESULTS AND DISCUSSION

The results of the conducted experiments (Tables 1 and 2) show clearly that the hydrogen is accumulated in oxide-nickel and cadmium electrodes in proportion to the batteries operation duration as the hydrogen amount in the oxide-nickel and cadmium electrodes grows with batteries operating life duration increase. Notably that new oxide-nickel and cadmium electrodes do not contain any hydrogen at all.

At a rather short operating life, a content of hydrogen in electrodes varies very much. Apparently, it is connected with different conditions of various batteries operation. At great operating lives (more than five years), the hydrogen content in the electrodes is approximately the same.

In batteries with a long operating life, a really great amount of the hydrogen is accumulated. So, for example, the battery KSL-15 comprises 5 cadmium and 6 oxide-nickel electrodes. Hence, in one battery KSL-15 (No. 6, Table 1), the hydrogen amount makes approximately 292 L. The battery KPL-14 comprises 4 cadmium and 5 oxide-nickel electrodes. Hence in one battery KPL-14 (No. 4, Table 2), the hydrogen content makes approximately 289 L. These values correspond to values obtained previously for other types of nickel-cadmium batteries [13-15].

From the following calculations, the fact is seen that in the course of the batteries operation, this amount of hydrogen accumulation is possible:

According to the technical operation manual of the batteries KSL-15, they are charged with the current 3.8A during 6 hours. Therefore, these batteries are recharged 1.52 times more as compared with their nominal capacity. The recharging is needed for batteries' complete charging. So at the charge, almost 7.8 Ah is spent on the electrolyte decomposition with the evolution of hydrogen and oxygen.

So, at one act of charging of the battery KSL-15, up to 3 liters hydrogen and up to 1.5 liters oxygen are released. Thus, the found 292 liters hydrogen in the batteries KSL-15 electrodes can be obtained after 98 charge-discharge cycles. Close to its operating life finish, a battery KSL-15 has been subjected to a number of charge-discharge cycles being ten times greater. This is why, theoretically, the battery can accumulate the found amount of the hydrogen. The battery KPL-14 is charged with the current 2.5A during 10 hours. Similar calculations for the battery KPL-14 show that the found content of the hydrogen could be accumulated by it for as little number of the charge-discharge cycles as 67.

At charging of the nickel-cadmium batteries with the direct current, the water decomposition takes place with the evolution of hydrogen and oxygen. Nevertheless, the experiments (Tables 1, 2) show that no oxygen is accumulated in the electrodes, while hydrogen is. And moreover, the latter is

accumulated in very big amounts both in an oxide-nickel and cadmium electrodes. This is connected with the fact that the hydrogen possesses a very high diffusion permeability. For example, at the temperature 20^0C, a diffusion coefficient of the hydrogen in nickel is approximately 10^{10} times higher than the diffusion coefficient of the nitrogen or the oxygen [16]. This way, at electrolyte decomposition onto hydrogen and oxygen, only the hydrogen penetrates into the electrodes and is accumulated inside of them, while the oxygen exits into the atmosphere. In the paper [15], it was shown that the gravimetric capacity of hydrogen accumulation in a ceramic-metal nickel matrix of an oxide-nickel electrode can reach 21%. This value of the gravimetric capacity exceeds thrice all previously obtained values for any reversible metal hydrides including magnesium hydrides or complex hydrides (obtained with use of traditional methods). [16,17].

4. CONCLUSIONS

At batteries charging, the hydrogen release on the cadmium electrodes. Nevertheless, as the experimental studies show (Tables 1,2), although the hydrogen is accumulated both in cadmium and oxide-nickel electrodes. In the battery KSL-15 the electrodes are densely packed. So the hydrogen released on the cadmium electrodes can get easily on the oxide-nickel electrodes and be accumulated inside of them. In batteries of greater capacity, pocket electrodes are placed freely. Notwithstanding, our experiments shows that at batteries charging, the hydrogen released on the cadmium electrodes reaches the oxide-nickel electrodes and is accumulated in them in the same manner as in the batteries with a dense electrodes packing. This fact requires separate both theoretical and experimental researches.

ACKNOWLEDGEMENTS
This work was supported by the grant of the President of the Russian Federation for state support of young scientists (No. МК-4969.2016.8)

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