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Ni-Cd Batteries as Hydrogen Storage Units of High-Capacity

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In this study, it has been experimentally proven that the electrodes of the Ni-Cd batteries in the process of their operation absorb hydrogen in large quantities. There is no hydrogen inside the electrodes of new batteries, but after five years of service life the electrodes reach their maximum hydrogen capacity. The capacity of an oxide-nickel electrode as a hydrogen absorber was quantified as 13.4 wt% and 400 kg · m^{-3}. These values exceed twice the earlier data obtained for any reversible metal hydrides, obtained using traditional methods.
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Hydrogen storage is one of the most challenging technical barriers for the implementation of a hydrogen-based energy economy.[1–4] The safest and most effective method to store hydrogen is by using solid media, such as sorbent materials and hydrides.[3–8] However, the specific capacity indexes for reversible hydrogen storages are not yet sufficient for practical use. Today many publications are devoted to solve this problem.[2–9] During the past decade, MgH_2 and light-element complex hydrides were the focus of intense interest.[2,4,9] Among the common hydrides, magnesium and its alloys are the best candidates for hydrogen storage because of their high volumetric and gravimetric capacity (110 kg m^{-3} and 7.66 wt% for MgH_2). Some complex hydrides have theoretical gravimetric capacity more than MgH_2.[9] But in practice, the reversible capacitances of those complex hydrides are less than that of magnesium hydride.[2] Presently, in spite of all the efforts made, there is a need to increase the capacity and improve the kinetic and thermodynamic features of the hydrides meant to be used as hydrogen storage substrates.

In our earlier study it was determined, that a huge amount of hydrogen evolved as a result of the nickel-cadmium battery thermal runway.[1] The thermal disintegration of the electrodes also demonstrated, that hydrogen was present inside the electrodes even before the thermal runway, and the amount was much higher than that from a usual thermal runaway. The present study aims to study the hydrogen accumulation in the electrodes of the Ni-Cd batteries during their operation, and to evaluate the capacity of the electrodes as hydrogen absorbers. Nickel cadmium batteries having sintered electrodes were used. The electrodes have had various capacities and modes of discharges.

Experimental

For the experiments, KSX-25 batteries with sintered electrodes were used. The detailed description for the installation and experimental procedures are reported.[1] The hydrogen desorption from the electrodes, when heated was investigated in an air-tight chamber under the temperature of 800°C. Hydrogen desorption was performed in average: for cadmium electrode within 7 days, and for oxide-nickel electrode within 13 days, during 11 hours daily. Process of thermal decomposition stopped, when the daily hydrogen emission remained lower than 100 ml. To carry out the experiment, five KSX-25 accumulators with a long service life were chosen at random. One cadmium and one nickel electrode were taken from each accumulator. Then the above electrodes were subjected to thermal decomposition in the described installation. The experiment was repeated three times for each battery. Table I demonstrates the average values calculated for three experiments for the amount of hydrogen inside an electrode for each type of electrodes.

To test the gas, a VOG-2M volumetric and optical gas analyzer was used. The absolute error in the percentage concentrations is 0.3–0.5. Analysis of the gas released from both electrodes showed that it consisted of at least 99% hydrogen.

Results and Discussion

Table I (accumulators No. 3-6) demonstrates that the electrodes of the KSX-25 batteries with long service life contain a huge amount of hydrogen.

Hydrogen is absent in the electrodes of new nickel-cadmium batteries, but during its service life the amount of hydrogen inside the electrodes increases (Table I, accumulators No. 1-3). The amount of hydrogen absorbed by the electrodes stops increasing after five years of service life, i.e., the maximum capacity of the electrodes for hydrogen storage is reached after that time (Table I, accumulators No. 4-6).

The data in Table I relate to one accumulator electrode. In a KSX-25 accumulator there are 14 cadmium and 15 nickel electrodes. Therefore, in one KSX-25 accumulator there are approximately 820 *l* of hydrogen (Table I, accumulator No. 2).

The 20KSX-25 batteries according to their use and maintenance manual overcharge by 1.6 times as compared to their nominal capacity. Overcharge is required for complete charging of the batteries. Consequently, one charging of a KSX-25 battery produces 6 *l* of hydrogen and 3 *l* of oxygen. Thus, the discovered 820 *l* of hydrogen may have been accumulated during 137 charging-discharging cycles. By the end of its life span, a KSX-25 battery is likely to have gone through ten times as many charging-discharging cycles. Therefore, it can, in principle, accumulate the discovered amount of hydrogen.

Firstly, we evaluate the specific parameters of an oxide-nickel electrode as a hydrogen absorber. An oxide-nickel electrode accumulates approximately 36 liters of hydrogen during the long service life of a KSX-25 battery (Table I). The weight of the electrode is 24 grams. Hence, the specific mass capacity of an oxide-nickel electrode as a hydrogen absorber equals to 13.4 wt%. The obtained result exceeds the earlier obtained results for nickel hydride (obtained using traditional methods) by 10 times,[10] and for any reversible metal hydrides, including magnesium hydride or complex hydrides by 2 times.[2,9]

Considering that the physical dimensions of an oxide-nickel electrode of a KSX-25 battery equal to 7.3 × 13.6 × 0.081 cm, we obtain that the specific volume capacity of an oxide-nickel electrode as a hydrogen absorber equals to 400 kg · m^{-3}. According to this parameter, the obtained result exceeds the earlier obtained results for any reversible metal hydrides by more than 3 times.[9]

The reasons for such high specific parameters of an oxide-nickel electrode are not yet quite clear. Thus, numerous experimental and theoretical researches are required to reveal the above mentioned reasons. However, it must be noted that in an oxide-nickel electrode there are a number of factors present, which contribute to hydrogen accumulation. At present, these factors are under intensive research.

First, the nickel oxide electrode in a KSX-25 battery is metal-ceramic, made from finely divided nickel powder with strongly collapsed crystalline structure. Any imperfections of metal crystalline

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Table I. Hydrogen content in oxide-nickel and cadmium electrodes of the KSX-25 batteries with a different service life.[a]

No. of the accumulator	1		2		3		4		5		6	
Period of operation (years)	new		1		4.5		5.3		7		6.1	
Type of electrode	Ni	Cd	Ni	Cd	Ni	Cd	Ni	Cd	Ni	Cd	Ni	Cd
Amount of gas released, liters	0	0	19	13	32	13	35.8	19.6	35.7	20	36	20

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

structure (particularly dislocations) are traps for hydrogen, as they decrease the energy of hydrogen atom as compared to their location in normal interstice. Besides they are the centers of hydrogen absorption, and also contribute to hydrogen penetration into the metal depth. Hence, imperfections of the metal crystalline structure cause sharp rise of hydrogen miscibility in it. The hydrides used in the modern methods of preparation are ground down in ball mills with the above mentioned purpose.[5,6]

Secondly, an oxide-nickel electrode contains nickel oxides. It is a well known fact that the oxides of transition metals act as catalysts of hydrogen accumulation.[7,8]

Thirdly, the electrodes are densely packed. Thus, hydrogen evolved at the cadmium electrode during charging of the battery may penetrate into the pores of both the oxide-nickel, and cadmium electrodes. Hence, in all probability, the oxide-nickel electrode accumulates hydrogen not electro-chemically, but due to the high capillary pressure. According to works[11,12] the amount of hydrogen C accumulated in metal is related to external pressure of hydrogen P by the formula $C = K\sqrt{P}$.

Capillary pressure in the electrode pores is inversely proportional to pore radius R, i.e.

$$P = A/R \qquad [1]$$

$A = 0.2$ μm MPa – proportionality constant for the given electrolyte. In porous electrode the main pores have the average radius of the order of several dozens of microns. However the finely divided powder, used for manufacturing of metal-ceramic matrix of the electrodes, have the micro fissures with dimensions from several hundreds of angstrom to the size of crystalline lattice of the metal.[13] Thus, hydrogen accumulating in the micro fissures as the result of electrolyte decomposition may have the pressure of up to 100 MPa and higher (Eq. 1).

Lastly, the process of hydrogen accumulation in the batteries' electrodes takes place all through their service life. This is more than five years in the present study. With the modern methods, the process of hydrides preparation could take from several minutes to several hours. Analysis of hydrides' research works for approximately last 20 years showed, that most probably there were no experiments for obtaining transition metals hydrides at high external hydrogen pressures lasting for extremely long time periods. However exposure to external pressure is a significant factor at any processes of penetration of one substance into another. Especially when the penetration process is extremely slow as in our case

Conclusions

It appears that the high capillary pressure of hydrogen acting through the exceedingly long time on the strongly destroyed crystalline structure of the electrodes' metal over the catalyst (oxide of transition metal) allowed to accumulate 10 times more hydrogen as compared to the traditional methods of hydrides preparation. This supposition, of course, requires a separate experimental as well as a theoretical research.

It must be noted, that an oxide-nickel electrode by its specific parameters of hydrogen accumulation exceeds the requirements of the US Department of Energy.[14] However, due to the high temperature of hydrogen desorption and low speed of absorption/desorption the given hydrides cannot be used as hydrogen accumulators for future hydrogen-fueled vehicles. Nevertheless, their use in stationary devices cannot be excluded.

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