Research into storage processes in batteries to create highly efficient reversible hydrogen storage

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Abstract. This paper has experimentally proved that hydrogen accumulates in large quantities in metal ceramic electrodes of alkaline accumulators during their operation. It has been found that hydrogen is not present in the metal ceramic electrodes of alkaline accumulators not yet in operation. It is shown that in alkaline accumulators with a service life of more than five years, the largest amount of hydrogen is present in their electrodes. Hydrogen is found to accumulate in oxide-nickel electrodes of alkaline accumulators, which have hydrogen absorption capacity of 13.4 wt%. Sintered nickel matrix of oxide-nickel electrode of alkaline accumulator was considered. The values of hydrogen absorption in this matrix are 20.2 wt%, the stored energy density is 44.018 kJ/g. The results obtained in the operation are three times higher than the previously obtained data, which are based on the use of traditional methods for reversible metal hydrides, such as magnesium hydride and complex hydrides. In addition, the results obtained exceed the values announced in the criteria for hydrogen storage systems developed by the US Department of Energy.

1. Introduction
Finding an optimal method of storing hydrogen in hydrogen power is the most important and technically difficult task [1-4]. Currently, the best method of storing hydrogen in terms of safety and efficiency is considered to be the use of sorbing materials and metal hydrides [1-8]. The main problem of reversible hydrogen storage is the achievement of optimal indicators for the capacity of accumulated hydrogen. It is insufficient for modern consumers in terms of practical use [1-15].

The U.S. Department of Energy (DOE) most definitely formed criteria for portable hydrogen storage systems as part of the country’s hydrogen energy development program. These criteria were developed taking into account the requirements of the U.S. automotive industry [16]. The main criterion is the specific capacity of the system. Here, the main indicator is the achievement by 2020 of gravimetric capacity parameters of more than 5.5 wt%, and by volume capacity more than 40 kg m\(^{-3}\). Kinetic and thermodynamic parameters of the system are also taken into account.

As part of the problem discussed, research has been carried out in the world over the past 10 years on mainly nanostructured carbon materials and complex hydrides of the light elements of the periodic system.

If we consider all common hydrides, then in terms of volume and gravimetric capacity, magnesium hydrides of MgH\(_2\) and its alloys have the highest values: 110 kg m\(^{-3}\) and 7.66 wt%, respectively. From the point of view of theoretical parameters of gravimetric capacity of some complex hydrides, they can exceed values of magnesium hydride [1]. However, if we consider this issue from a practical point of view and in terms of the reversibility of the vessel after use, then complex hydrides are inferior to magnesium hydride MgH\(_2\) in this indicator [2].
Unfortunately, despite the large amount of work done, the researchers failed to develop an optimal portable hydrogen storage system that meets the criteria formulated by the US Department of Energy for the automotive industry. In this regard, it was not possible to create portable hydrogen storage systems with the necessary parameters for the automotive industry, which is an obstacle to the widespread introduction of hydrogen energy into the global economy.

Currently, three technologies for the production of metal hydrides are used in the world.

1. Chemical method of producing hydrides. Here, metal hydrides are synthesized by chemical interactions [1], but this can be realized only for a limited amount of hydrides [17]. The disadvantage of this method of producing hydrides is the irreversibility of this process. Fundamentally, the process of regenerating the starting hydrides for their use in chemical reactions is possible, but not practical, based on economic considerations. Because of this, the method discussed is considered unacceptable for portable hydrogen storage systems.

2. A thermochemical method that allows the accumulation of hydrogen in metal hydrides. This method causes the hydrogenation/dehydrogenation process to set certain hydrogen pressures and temperatures.

3. Electrochemical method, which is caused by the process of hydrogen accumulation in metal hydrides by decomposition of the electrolyte. Hydrogen, which is released as a result of the reaction, is adsorbed at the cathode. Then, most of it leaks into the atmosphere. A small part of hydrogen penetrates into the depth layers of the cathode. First, hydrogen is present inside the cathode in an unbound state as an α-phase. With a long electrolysis process, hydrogen over time forms bound states with the cathode metal in the form of a β-phase. Metal hydrides [1, 18] are thus formed. During electrolysis for a short period of time in a small period of time, hydride is formed in the thinnest layer of the cathode [18]. This reaction proceeds on the order of several hours, but the gravimetric capacity of the cathode in this case as a hydrogen storage tank is small. The considered method of hydrogen accumulation at the cathode is not new [1], however, the electrochemical method has never been used for hydrogen accumulation in hydrogen storage systems. However, taking into account our studies of thermal acceleration in alkaline accumulators and obtaining positive results in this direction, it was possible to prove the effectiveness of the above method for hydrogen accumulators [18-20].

When charging some types of nickel-cadmium accumulators using a constant voltage, as well as during the floating charge process, an effect can occur, which is called thermal acceleration [20]. When this effect occurs in the battery, the charge current increases sharply, which leads to evaporation of the electrolyte of the battery into steam. Sometimes there were cases of fire and explosion of the battery or melting of the body [18-20].

In a number of works [13, 15] on a research of non-stationary process of thermal dispersal on the basis of alkaline batteries of KSX-25 brand with a capacity of 25 of Ah with the baked electrodes the received results of experimental researches showed that at thermal dispersal there is a release of the gas mix consisting approximately of 284 liters of hydrogen and 13 liters of oxygen.

Based on your reviewed data and theoretical research, it can be assumed that hydrogen accumulates in the electrodes of the batteries as their useful life increases and accordingly the longer this time, the more hydrogen can accumulate in them. If we accept this assumption as the main hypothesis, then the amount of hydrogen accumulated in the electrodes of the batteries will be determined primarily by the value of their life on the site. This hypothesis needs to be tested in the work.

2. Experimental

In order to carry out experimental studies on the above mentioned issues, KSL-15 batteries with a capacity of 15 Ah were used as the object of the study. These batteries included sintered electrodes. The period of operation of the considered batteries was ranked in the range from 0 to 7.5 years. In addition, the experimental part used KPL-14 grade batteries with a capacity of 14 Ah with another type of electrodes - lamellar. These batteries had service life in the range from 0 to 10 years.

The experimental part of the study was carried out on a laboratory bench designed to control the gas release process during the thermal decomposition of electrodes from various batteries. For more
information on the work of the laboratory stand, refer to [19]. The laboratory stand consists of a metal chamber, where the electrode for thermal decomposition is placed, the chamber has a cylindrical shape. The length of the chamber is 1.8 m, its 0.02 m. On one side, the chamber is sealed. Because the sealed side of the metal chamber was placed for heating in the muffle furnace. The other side of the metal chamber was connected to the measuring vessel through a rubber plug with a tube for discharging the released gas mixture.

At the next stage of the experiment on a laboratory bench, the electrode was heated in a thermal chamber. The gas mixture released during heating was cooled by a standard coil when passing through it into a measuring vessel. The electrode in the thermal chamber was exposed at a high temperature because of this it adhered to the walls of the thermal chamber. In order to avoid this problem, the electrode was placed in a special cartridge.

Each electrode in the thermal chamber was decomposed under the influence of a temperature of 800°C. The choice of such a decomposition temperature of the electrode was not random. In a number of our studies on thermal acceleration, it was found that the gas release during thermal separation of the cadmium electrode from the nickel-cadmium battery begins to be recorded at a temperature of 340°C. Gas release during thermal separation from the oxide-nickel battery of the same battery is recorded at a temperature of more than 740°C. In accordance with this, the operating temperature value for decomposition of battery electrodes was chosen to be 800°C. This temperature value was used as the optimal thermal decomposition of cadmium and oxide-nickel electrodes.

The experiment related to the thermal decomposition of the electrodes of the batteries was stopped at gas release values of at least 4 ml of the gas mixture from one electrode in one day of the experiment. One day of the experiment was 11 hours of continuous thermal decomposition of the electrode. If we consider in detail the object of study - a battery of the KSL-15 brand with a significant service life, more than 5 years, then the process of thermal decomposition of cadmium electrodes took place on average over 12 days of the experiment. The nickel oxide electrode was thermally decomposed in 14 days. Every day, during the experiment on the thermal decomposition of the cadmium electrode, at least 3.5 liters of the gas mixture was separated from it at the initial stage of the experiment and at least up to 100-110 ml of the gas mixture at the final stage. The daily volume of gas release from the oxide-nickel electrode above the battery under consideration was at least 5.5 liters during the initial period of experimental studies and at least 100-110 ml per-switch.

The qualitative composition of the separated gas mixture was determined by the gas analyzer VOG-2M.

The obtained results from experimental studies on the basis of KSL-15 grade batteries are presented in Table 1, and on the basis of KPL-14 grade batteries are presented in Table 2. Each electrode was folded into a tube and placed in a cartridge prior to thermal decomposition.

In an experiment on the thermal decomposition of oxide-nickel and cadmium electrodes removed from new and non-used KSL-15 grade batteries, a gas release of the order of 180-192 ml of the gas mixture was observed. The volume of the gas mixture obtained is comparable to the accuracy limits of this process in the gas storage container. The obtained gas volume is recorded at the initial moment during the experiment due to the fact that when the plant is heated, the air in the sealed chamber expands and begins to enter the gas storage tank. Typically, in the next step, the thermal decomposition of the electrode begins to release the gas mixture in combination with hot air from the thermal chamber. In reality, it is very difficult to estimate the moment when it is the gas mixture obtained during the thermal decomposition of the electrodes into the storage vessel that begins to enter.

To solve the above problem, a series of experiments was carried out related to the heating of a thermal chamber without electrodes. Heating was carried out at different temperatures. It was found that when heating an empty thermal chamber at a temperature of 800°C, gas release associated with expansion of heated air was observed in the volume of the order of 180-190 ml. In connection with this established fact, the presence of heated air in the thermal chamber in the volume of 200 ml was
taken into account. Therefore, this amount of gas mixture was not taken into account in experimental studies. It was simply released into the atmosphere. The following volumes of the gas mixture obtained by thermal decomposition of the electrodes have already been recorded and analyzed and collected in a storage vessel.

Obtained as a result of experimental studies on thermal decomposition of electrodes of different types, the gas mixture was analyzed by a gas analyzer VOG-2M with absolute error in percentage concentrations of 0.3-0.5. The results of the analysis proved the presence of hydrogen in the electrodes. It has been found that the thermal decomposition gas mixture consists almost entirely of hydrogen.

Table 1. Quantitative parameters of thermal decomposition of electrode from batteries of grade KSL-15

| Battery number | 1   | 2   | 3   | 4   | 5   | 6   | 7   | 8   | 9   |
|----------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Service life (years) | New | 1   | 1.6 | 3.4 | 4.2 | 5.1 | 5.3 | 6.2 | 7.5 |
| Amount of gas (Ni) (liters) | 0   | 11  | 16.3| 25.2| 28.7| 33.0| 31.6| 31.0| 31.1|
| Amount of gas (Cd) (liters)  | 0   | 11  | 12.8| 15.4| 18.3| 20.6| 19.5| 20.9| 21.2|

Table 2. Quantitative parameters of thermal decomposition of electrode from batteries of grade KPL-14

| Battery number | 1   | 2   | 3   | 4   | 5   | 6   | 7   | 8   |
|----------------|-----|-----|-----|-----|-----|-----|-----|-----|
| Service life (years) | New | 1   | 2.1 | 4.4 | 6.2 | 7.1 | 8.4 | 10.1|
| Amount of gas (Ni) (liters) | 0   | 18.4| 31.3| 36.1| 36.3| 36.3| 35.8| 37.5|
| Amount of gas (Cd) (liters)  | 0   | 7.5 | 16.3| 24.6| 27.1| 27.5| 27.0| 27.9|

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

3. Results and discussion

In the course of the conducted experiments on thermal decomposition of electrodes of the analyzed types, the data are presented in Tables 1 and 2, which show a direct proportional relationship between the amount of hydrogen released from the electrodes and the period of operation of the studied batteries in enterprises. It is also worth noting that during the thermal decomposition of the above mentioned types of electrodes, hydrogen is not released from new and non-previously operated accumulators.

It is also worth noting that with rather small battery life, the amount of hydrogen accumulated in their electrodes varies quite significantly from battery to battery, presumably this can be due to different operating conditions of the batteries. With rather long battery life, more than five years, the amount of hydrogen accumulated in the electrodes is on average approximately the same.

In batteries with long service lives, a really large amount of hydrogen can accumulate. So, for example, in the battery of the brand KSL-15 contains 5 cadmium and 6 oxide-nickel electrodes. From this, it can be found that in one battery of grade KSL-15 (No. 6, Table 1) the total amount of accumulated hydrogen is approximately 292 liters. For a battery of grade KPL-14 with 4 cadmium and 5 nickel oxide electrodes in its composition (No. 4, Table 2), the hydrogen content is approximately 289 liters.

Next, we consider calculations showing that during the operation of the battery it is possible to accumulate such a volume of hydrogen.
You can see from the maintenance manual of KSL-15 batteries that they are charged with current 3.8 A for 6 hours. Therefore, to fully charge these batteries, they must be charged 1.52 times their nominal capacity. Thus, when charging batteries of this brand, almost 7.8 Ah is spent on the decomposition of electrolyte water into hydrogen and oxygen.

So during the experiment, during one cycle of charging the battery of the brand KSL-15, up to 3 liters of hydrogen and up to 1.5 liters of oxygen were released. Therefore, it can be assumed that the amount of hydrogen equal to 292 liter stored in the electrodes of the batteries of the grade KSL-15 can be accumulated over 98 charge-discharge cycles. As a rule, at the enterprise, KSL-15 class batteries can be subjected to more charge and discharge cycles at their service life set by the manufacturer at five years. Moreover, this number of charge-discharge cycles in practice can be tens of times more and therefore the theoretically studied battery can accumulate the amount of hydrogen obtained in the experiment. If we consider a battery of the grade KPL-14, which is charged with current 2.5 A for 10 hours, it can also be argued here that the accumulated amount of hydrogen in the electrodes of this battery can be accumulated over the order of 67 charge-discharge cycles.

As is known, when charging nickel-cadmium batteries with direct current, water decomposes into hydrogen and oxygen, but experiments conducted (Tables 1, 2) show that oxygen does not accumulate in electrodes, only hydrogen. Moreover, hydrogen accumulates in oxide-nickel and cadmium electrodes in very large quantities, due to the fact that hydrogen has a very high diffusion permeability. It is known that at a temperature of 20°C, the diffusion coefficient of hydrogen in nickel is about 10^10 times greater than nitrogen or oxygen [1].

The next step is to evaluate the parameters of the sintered nickel matrix of the nickel oxide electrode as a hydrogen accumulator. According to the data obtained from experiments (No. 6, Table 1), approximately 32 liters of hydrogen can be accumulated in a matrix consisting of sintered nickel over a long period of operation of KSL-15 grade batteries. The weight of the oxide-nickel electrode is 21.3 grams, including a mass of the active substance of 7.15 grams. It is obtained that gravimetric capacity of oxide-nickel electrode for hydrogen absorption is 13.4 wt%, and gravimetric capacity of sintered nickel matrix of oxide-nickel electrode for hydrogen absorption as its accumulator is 20.2 wt%. The data obtained as a result of the study exceeds all the previously obtained results using the traditional thermochemical method by 4 times for any previously considered reversible metal hydrides: magnesium hydride or complex hydrides [1,2].

Hydrogen is present in the electrodes of the accumulator battery in the form of metal hydrides, that is, it is present there in atomic form [1], and after its separation from the electrodes of the accumulator battery, its recombination occurs:

\[ \text{H+H} \rightarrow \text{H}_2 \]  
(1)

The reaction (equation 1) presented above is intensive and exothermic with dissipation of a large amount of heat, of the order of 436 kJ/mol (hydrogen) [18]. As a result of this reaction, the amount of heat dissipates more than in the case of the reaction when hydrogen is burned in oxygen - 285.8 kJ/mol (hydrogen) [17].

Now, knowing the numerical values from the gravimetric capacity and hydrogen recombination energy, we can calculate the stored energy density in the metal-ceramic matrix of the oxide-nickel electrode of the battery, which is 44.018 kJ/g.

4. Conclusions
It has been shown that when charging batteries, hydrogen is released on cadmium electrodes, and it has been experimentally established (Table 1, 2) that hydrogen can accumulate in cadmium and in oxide-nickel electrodes of batteries. If we consider a battery of the brand KSL-15 in which the electrodes are in a dense package, this is possible, since hydrogen released on cadmium electrodes can easily get into the nickel oxide electrodes and accumulate there. In batteries having a large capacity, lamellar electrodes are used, which are placed freely inside the battery. However, despite this fact, experiments carried out in the framework of this work show that when charging batteries, hydrogen, which is released on cadmium electrodes, also enters and accumulates in oxide-nickel electrodes, as in
batteries with a dense package of electrodes. This interesting fact requires separate attention in further theoretical and experimental studies.

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