

Article

# A Promising Energy Storage System Based on High-Capacity Metal Hydrides

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**Abstract:** In this paper, based on the study of hydrogen accumulation in the electrodes of nickel–cadmium batteries, a high-capacity hydrogen storage system (HSS) is proposed. It has been experimentally proven that hydrogen accumulates in the electrodes of nickel–cadmium batteries in large quantities over the course of their operation. It has been shown that hydrogen accumulates in metal–ceramic matrices of sintered oxide–nickel electrodes in the form of metal hydrides. The gravimetric capacity of the nickel matrix is 20.3 wt% and the volumetric capacity is 406 kg m<sup>−3</sup>. The obtained gravimetric capacities for metal–ceramic matrices exceed almost four times the criteria for onboard hydrogen storage systems established by the US Department of Energy (DOE), as well as previously obtained results for any reversible hydrogen accumulation materials. In addition, in our previous papers, it was proved that if we use thermal runaway for the desorption of hydrogen from metal hydrides then the kinetic and thermodynamic criteria established by the US DOE may be significantly exceeded. Thus, within the framework of the proposed HSS, using the electrochemical method of hydrogen accumulation and the thermal runaway process, one can not only achieve all of the criteria established by the US DOE for HSS but also significantly exceed them.

**Keywords:** energy storage systems; hydrogen storage; hydrogenation; dehydrogenation; thermal runaway



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## 1. Introduction

At present, renewable energy sources (RES) are rapidly developing, using, primarily, wind and solar energy [1,2]. This is due to the deterioration of the environmental situation and the depletion of traditional energy sources (coal, oil, etc.) [3,4]. However, energy production from these sources is highly dependent on the weather and the time of the day and year. Therefore, for the efficient operation of microgrids containing RES, reliable energy storage systems (ESS) are needed [5,6]. To do this, utility-scale energy storage systems use: compressed air energy systems, pumped-hydro systems, hydrogen storage systems (HSS), and battery systems [7,8]. In the onboard energy micro-networks of vessels and vehicles, etc., energy consumption is also highly dependent on their mode of operation. In smart energy microgrids of vessels [9] and vehicles, as energy storage systems, battery systems are mainly used but hydrogen storage systems can also be used. In utility-level HSS, hydrogen is stored in tanks at a pressure of approximately 50 MPa [7]. Hydrogen-based vehicles contain hydrogen in the tank at a pressure of 30–70 MPa. The presence of hydrogen tanks at such high pressures is extremely dangerous for both utility-level and onboard ESSs since any failure while using them will inevitably lead to an explosion and fire. In this paper, we consider the possibility of using HSS based on high-capacity metal hydrides. The use of these systems is completely safe.

Currently, many papers [10–15] are devoted to the study of this problem.

The US Department of Energy (DOE) has formulated the requirements for the onboard hydrogen storage system in the most detail [16]. The goal for 2020 was to achieve the following specific capacity parameters of 5.5 wt% and 40 kg m<sup>−3</sup> for a complete hydrogen storage system.

The US DOE criteria [16] for hydrogen storage systems have not been achieved so far. Although the modern US DOE criteria have been slightly reduced, we believe that the requirements [16] are the most optimal, since they are more consistent with similar specific parameters of the energy capacity of gas tanks found in modern cars [11–15].

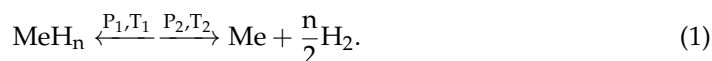
Currently, the most promising accumulators of hydrogen are considered to be light-element complex hydrides, nanostructured carbon materials, and hydrides of magnesium and its alloys. For example, the specific capacity parameters of  $\text{MgH}_2$  are  $110 \text{ kg m}^{-3}$  and 7.66 wt%. Theoretical specific capacity parameters of light-element complex hydrides are higher than that of  $\text{MgH}_2$  [10], however, their reversible specific capacity parameters are not greater than that of  $\text{MgH}_2$  [11].

It should be noted that, despite all the efforts of researchers, there is currently no hydrogen storage system that meets all of the requirements of the US DOE. It is this fact that is the main obstacle to the development of hydrogen energy.

Metal hydrides are currently prepared using three methods:

Firstly, metal hydrides can be prepared using chemical reactions [10]. However, only for a small number of metals can hydrides be obtained via this method, and they are irreversible [17]. This method is not used to produce hydrides in hydrogen storage systems.

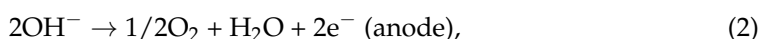
Secondly, the thermo-chemical method for preparing metal hydrides is now generally accepted. Using this method, hydrogenation occurs at elevated hydrogen pressure and metal temperature ( $P_1, T_1$ ), followed by its cooling, and dehydrogenation occurs at reduced hydrogen pressure and elevated metal temperature ( $P_2, T_2$ ). For example:



However, this method is inertial, since it takes a significant amount of time to heat and cool the hydrides. In addition, this method requires additional energy consumption for heating and cooling hydrides.

Using this method, high temperatures are required in order to achieve the desired kinetic parameters set by the US DOE which is not acceptable from the point of view of the thermodynamic parameters set by the US DOE. Therefore, within the framework of the thermo-chemical method, hydrides that meet all the requirements of the US DOE have not yet been found.

Thirdly, metal hydrides can be prepared using the electrochemical method. For example, when decomposing an alkaline electrolyte in nickel–cadmium batteries, hydrogen accumulates in their electrodes:



Atomic hydrogen formed as a result of electrolyte decomposition penetrates the battery electrodes (because of its high diffusion permeability [10]) and forms metal hydrides [10,18]. With one battery charge, hydrides are formed only in a very thin surface layer of the electrodes [18]. Therefore, with one battery charge, a small amount of hydrides accumulates in the electrodes. This method has never been used in hydrogen storage systems.

However, by studying the thermal runaway in alkaline batteries [18–22], we were convinced that during the long-term operation of batteries, a very large amount of hydrogen can accumulate in their electrodes [23–27].

Thermal runaway can occur in the case of a battery charging at a constant voltage or during its operation in a floating mode [28]. During thermal runaway, fire and explosion of the battery are possible [19–22].

In more detail, the reasons for the accumulation of hydrogen in electrodes in large volumes (using the electrochemical method of accumulation) were studied in [23,26,29–31].

It should be noted that in our previous experiments in paper [27], 284 L of hydrogen was released during thermal runaway from a KSX-25 (25 Ah) battery. This amount of

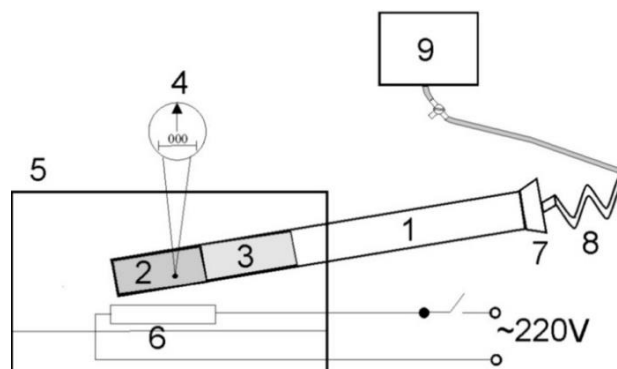
hydrogen is more than that found in the electrolyte (180 mL) battery when it is decomposed into hydrogen (about 224 L) and oxygen. In addition, 152 mL of electrolyte was released in the form of vapor. Consequently, hydrogen was in the battery electrodes even before the thermal runaway.

The purpose of this paper is to study a hydrogen storage system based on high-capacity metal hydrides using an electrochemical method for the hydrogenation of metal hydrides, and the process of thermal runaway for dehydrogenation.

## 2. Experimental

For an experimental study of the accumulation of hydrogen in the electrodes during the electrochemical decomposition of the electrolyte (2, 3), nickel–cadmium batteries KSL-12 (12 Ah) and KSH-40 (40 Ah) were used. The KSL-12 batteries were charged with a current of 3 A for six hours. The KSH-40 batteries were charged first with a current of 15 A for two hours, and then with a current of 10 A for three hours.

The amount of accumulated hydrogen was determined by the thermal decomposition of the electrodes. The thermal decomposition of the electrodes was carried out in heating chamber 1 (Figure 1) in the form of a seamless steel tube 1.8 m long and 2 cm in inner diameter (wall thickness 2.5 mm), of which one of the ends was hermetically sealed. The rolled-up electrode was placed in cartridge 2 (for ease of removal) which was then placed in a heating chamber. The cartridge was in the form of a seamless steel tube with a length of 15 cm and an outer diameter of 1.9 cm (wall thickness 0.5 mm). After placing the electrode in the cartridge, it was closed on both sides with steel plugs in the form of screws (0.5 cm thick) with 1 mm holes for a gas outlet.



**Figure 1.** Schematic diagram of the installation for thermal decomposition of metal hydrides: (1) heating chamber, (2) cartridge, (3) porous ceramic plug, (4) thermocouple, (5) muffle furnace, (6) heater, (7) rubber plug with a tube for gas extraction, (8) standard coil, and (9) measuring container for released gas.

To reduce convection in the heating chamber, and to make the temperature of the cartridge constant along its entire length, a porous ceramic plug 3 (20 cm) was tightly inserted into the heating chamber above the cartridge. The ceramic plug 3 was custom-made from heat-resistant ceramic, commonly used for thermal insulation in various technical heating devices. The gas released from the electrodes when the heating chamber was heated passed through a standard coil 8 (Figure 1) and cooled (while the steam was converted to water and remained in the standard coil). Then, the already clean gas entered the measuring container 9. This installation was also used in [23,26,27,29–31] to determine the amount of accumulated hydrogen in various metal hydrides and carbon materials.

The decomposition of the electrodes in the heating chamber took place at a temperature of 800 °C since preliminary experiments showed that a significant evolution of hydrogen from cadmium and oxide–nickel electrodes begin at temperatures above 740 °C.

On average, electrodes with a long service life (more than 5 years) decomposed in 8 days (Cd) and 12 days (Ni) (with thermal decomposition at 11 h a day). The experiments were stopped when the daily gas release from the electrodes became less than 4 mL/g (electrode).

The gas analyzer VOG-2M (Workshops of VGSC, Leninsk-Kuznetsky, Russia) was used to determine the quantitative composition of the released gases (accuracy: percentage concentration  $\Delta c = \pm 0.2\text{--}0.3\%$ ). Gas analyzer VOG-2M determined the concentration of gases: H<sub>2</sub>, O<sub>2</sub>, CO, CO<sub>2</sub>, and CH<sub>4</sub> in the gas mixture.

### 3. Results

#### 3.1. Accumulation of Hydrogen in Electrodes by Electrochemical Method

In the experiments, we used two groups of nickel–cadmium batteries (KSL-12 (12 Ah) and KXS-40 (40 Ah)) with eight batteries in each group, with sintered electrodes with a service life of 0 to 7 years. All of the batteries were operated under the same conditions. For the thermal decomposition of the electrodes at the installation (Figure 1), three cadmium and three oxide–nickel electrodes were taken from each battery. The experimental results are presented in Tables 1 and 2. Tables 1 and 2 show the average amount of gas released from the three electrodes (Cd and Ni separately) for each battery at 25 °C. The VOG-2M gas analyzer showed that the released gas contained only hydrogen (0.2–0.3% is the absolute error of percentage concentrations).

**Table 1.** Dependence of the amount of accumulated hydrogen in the electrodes on the service life of the KSL-12 batteries at 25 °C<sup>1</sup>.

No. of the Battery	1	2	3	4	5	6	7	8
Period of operation (years)	New	1	1.7	3.2	4.1	5	6	7
Amount of gas released (Ni) (L)	0	12.0	17.0	25.8	30.1	31.8	31.7	31.7
Amount of gas released (Cd) (L)	0	10.3	13.0	15.9	18.5	19.8	19.8	19.9

<sup>1</sup> The relative error of the measured gas volumes is 4%.

**Table 2.** Dependence of the amount of accumulated hydrogen in the electrodes on the service life of the KXS-40 batteries at 25 °C<sup>1</sup>.

No. of the Battery	1	2	3	4	5	6	7	8
Period of operation (years)	New	1	1.9	3.1	4.6	5	6	7
Amount of gas released (Ni) (L)	0	13.1	20.0	27.0	33.1	36.1	36.0	36.1
Amount of gas released (Cd) (L)	0	11.1	14.0	16.1	18.1	20.2	20.1	20.2

<sup>1</sup> The relative error of the measured gas volumes is 4%.

It should be noted that experiments with an empty heating chamber showed that, due to the expansion of the gas in the heating chamber at a temperature of 800 °C, approximately 200 mL of gas additionally entered the measuring container. Therefore, the first 200 mL of gas in Tables 1 and 2 were not counted.

From the results obtained (Tables 1 and 2), it follows:

Firstly, there was no hydrogen in the electrodes of the new batteries.

Secondly, as the battery life increased, hydrogen accumulated in their electrodes.

Thirdly, after about five years of battery operation, the amount of hydrogen in their electrodes ceased to increase, that is, the maximum possible accumulation of hydrogen in the electrodes was achieved.

Thus, after long-term operation, approximately 238 L of hydrogen accumulated in the electrodes of the KSL-12 battery, since these batteries have four cadmium and five oxide–nickel electrodes. The KXS-40 batteries accumulated approximately 1274 L of hydrogen in the electrodes (these batteries had 22 cadmium electrodes and 23 oxide–nickel electrodes).

This amount of hydrogen can accumulate in the electrodes of the KSL-12 and KXS-40 batteries during their long-term operation (more than 5 years).

Indeed, KSL-12 batteries are charged with a current of 3 A for six hours, i.e., a recharge of 6 Ah over their nominal capacity. A recharge is required to fully charge the batteries. However, this released approximately 2.3 L of hydrogen and 1.15 L of oxygen. Therefore, theoretically, 238 L of hydrogen could be accumulated by the battery KSL-12 in 104 charge–discharge cycles. For five years of operation, these batteries go through about ten times more charge–discharge cycles. Consequently, the detected amount of hydrogen could well have accumulated in the electrodes of the KSL-12 batteries.

The situation is similar for KSX-40 batteries. The KSX-40 batteries are charged first with a current of 15 A for two hours and then with a current of 10 A for three hours, i.e., a recharge of 20 Ah over their nominal capacity, producing approximately 8.2 L of hydrogen and 4.1 L of oxygen. Therefore, theoretically, 1274 L of hydrogen in the KSX-40 battery could accumulate in 155 charge–discharge cycles. Therefore, over five years of operation, these batteries can actually accumulate 1274 L of hydrogen because, during this time, these batteries go through about ten times more charge–discharge cycles.

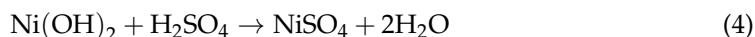
The experiments carried out show that only hydrogen accumulated in the electrodes but the electrolyte decomposed into hydrogen and oxygen. This is due to the fact that the diffusion coefficient of atomic hydrogen in metals is  $10^{10}$  times higher than the diffusion coefficient of atomic oxygen [10]. Therefore, only hydrogen accumulated in the electrodes (and also released into the atmosphere), and only oxygen was released into the atmosphere.

### 3.2. Accumulation of Metal-Hydrides in Electrodes

An oxide–nickel electrode consists of two substances: a metal–ceramic nickel matrix and an active substance (nickel hydroxide  $\text{Ni}(\text{OH})_2$ ). In this section, we will determine where the hydrogen accumulates: in the active substance or in the metal–ceramic matrix of the electrode.

First, we investigated the possibility of hydrogen accumulation in nickel hydroxide.

If an oxide–nickel electrode is placed in sulfuric acid, then a soluble  $\text{NiSO}_4$  salt is formed:



Therefore, if hydrogen accumulates in nickel hydroxide (in a free state or weakly bound to a nickel hydroxide state, soluble in sulfuric acid) then it will be released in the amount specified in Tables 1 and 2 as in the thermal decomposition of the oxide–nickel electrode in general.

If hydrogen forms strong chemical bonds with nickel hydroxide that are not destroyed by sulfuric acid, then the weight of the oxide–nickel electrode after etching in sulfuric acid will be greater than the weight of the new metal matrix.

Let us now experimentally test these two possible variants of hydrogen accumulation in the active substance of the oxide–nickel electrode.

First of all, we determined the etching time of nickel hydroxide in 22.6% sulfuric acid. It was found that the mass of the oxide–nickel electrode ceased to decrease after 20 min of etching in sulfuric acid. In our experiments, in order to ensure the removal of nickel hydroxide from the oxide–nickel electrode completely, we used an etching time of 30 min.

In addition, direct experimental studies have shown that the sintered nickel matrix does not dissolve well in this sulfuric acid since its weight did not change after 200 min of etching in acid (accuracy of the weights used  $\pm 5$  mg). Hydrogen was also not released at the same time within the measurement accuracy of  $\pm 5$  mL.

Experimental studies were carried out using eight oxide–nickel electrodes. The electrodes were taken from KSX-40 batteries with a service life of six years under the same conditions.

Before the experiment, the electrodes were washed in distilled water, dried, and weighed. Then, the electrodes were placed in sulfuric acid (in a sealed container with a tube for gas removal in measuring container 9 (Figure 1)). After 30 min of etching in sulfuric acid, the electrodes were washed again in distilled water, dried, and weighed. The results are presented in Table 3.

**Table 3.** Results of etching in sulfuric acid of oxide–nickel electrodes battery KSX-40.

No. of the Electrode	1	2	3	4	5	6	7	8
Initial mass, g	24.10	23.95	24.00	23.95	23.95	23.95	24.10	24.00
Final mass, g	16.00	15.85	16.00	15.85	15.85	15.85	16.00	15.90
Mass loss, g	8.1	8.1	8	8.1	8.1	8.1	8.1	8.1
Mass loss, %	33.6	33.8	33.3	33.8	33.8	33.8	33.6	33.7
Amount of hydrogen, mL	0	0	0	0	0	0	0	0

From the experimental data (Table 3), the following conclusions can be drawn:

Firstly, hydrogen does not accumulate in nickel hydroxide either in the free or in the weakly bound state since hydrogen is not released when the electrodes are etched within the measurement accuracy of  $\pm 5$  mL.

Secondly, according to the factory of the KSX-40 batteries' manufacturer, the active substance of oxide–nickel electrodes contains 33–36% nickel hydroxide and 2–3% cobalt hydroxide.

The weight of the oxide–nickel electrode was 24 g (Table 3). For six years of operation of the KSX-40 battery, 36 L of hydrogen accumulated in the oxide–nickel electrode (Table 2, point 7) or  $36 \times 2/22.4 = 3.2$  g of hydrogen (22.4 L is the volume of a mole of hydrogen, and 2 g is its weight). Therefore, the weight of the oxide–nickel electrode without accumulated hydrogen was  $24 - 3.2 = 20.8$  g. The weight loss of the oxide–nickel electrode as a result of its etching in sulfuric acid (i.e., the weight of the active substance of the electrode) was 8.1 g (Table 3). Thus, the active substance in the new oxide–nickel electrode was  $(8.1/20.8) \times 100 = 38.9\%$ . In the experiments shown in Table 3, the percentage of active substance in the oxide–nickel electrode varies from 38.5% to 39%.

The values obtained fully correspond to the data of the manufacturer of the KSX-40 batteries. Consequently, hydrogen does not accumulate in nickel hydroxide in the form of tightly bound compounds. Thus, hydrogen does not accumulate in nickel hydroxide in any form.

Therefore, based on experimental data (Table 3), it can be assumed that hydrogen accumulates in the metal–ceramic matrix of the electrode as this also occurs in other transition metals used for hydrogen storage [11,32,33].

Now, let's test this assumption experimentally:

Verification of hydrogen accumulation in nickel matrices of positive electrodes was also carried out by a direct method at the installation (Figure 1). For this, we took 12 positive electrodes from KSX-40 batteries with a service life of six years under the same conditions (after removing the active substance from the electrodes by etching in sulfuric acid (4)). Then, the nickel matrices were thermally decomposed in the installation (Figure 1) according to reaction (1). The amount of hydrogen that evolved was the same as shown in Table 2 (No. 6) within a relative experimental error of 4%.

Consequently, hydrogen accumulates in the metal–ceramic matrices of the electrodes.

Thus, during the thermal decomposition of a metal–ceramic matrix (oxide–nickel electrode), only hydrogen was released from it, and only nickel remains. Thus, this experiment directly proves that the metal–ceramic matrix consists of two substances: hydrogen and nickel, that is, nickel hydride.

## 4. Discussion

### 4.1. Analysis of Electrodes Hydrogenation by Electrochemical Method

Using the data in Tables 2 and 3, we calculated the gravimetric and volumetric capacities of the electrodes of the tested batteries in order to compare them with the US DOE criteria.

The average mass of the nickel matrix of the positive electrode of the KSX-40 battery was 15.9 g (Table 3) and the physical size was  $7.3 \text{ cm} \times 13.6 \text{ cm} \times 0.08 \text{ cm}$ . It accumulated about 36.1 L of hydrogen (Table 2 column 6) or  $36.1 \times 2/22.4 = 3.22$  g of hydrogen (22.4 L is the volume of a mole of hydrogen, and 2 g is its weight). Hence the gravimetric capacity of the nickel matrix was 20.3 wt% and the volumetric capacity was  $406 \text{ kg m}^{-3}$ .

The average mass of the nickel matrix of the positive electrode of the KSL-12 battery was 14.08 g. Considering that 31.7 L of hydrogen was accumulated in this nickel matrix (Table 1 № 6) or  $31.7 \times 2/22.4 = 2.83$  g, then, for the gravimetric capacity of the matrix, we obtained the value 20.1 wt%. Thus, the maximum gravimetric capacities of the nickel matrices of the investigated KSX-40 and KSL-12 batteries coincided with the limits of a relative experimental error of 4%.

The negative electrodes of the KSX-40 and KSL-12 batteries were plastic bonded and had weights of both 17 g and 16.2 g, respectively. The maximum amount of accumulated hydrogen in these electrodes was 20.2 L (Table 2 column 6) and 19.8 L (Table 1 column 6). Consequently, the maximum gravimetric capacity of the negative electrodes of these batteries was 10.6 wt% and 10.9 wt%, respectively (Tables 1 and 2).

For our research, the most interesting aspect was the accumulation of hydrogen in sintered metal matrices, i.e., in metal hydrides. This was the purpose of this article's research. Therefore, in this article, we did not investigate the accumulation of hydrogen in the negative electrodes (which do not contain sintered metal matrices) since these were plastic-bound electrodes.

In the negative electrodes of KSX-40 and KSL-12 batteries, hydrogen accumulated in spongy cadmium and graphite powder. However, this is a topic for a separate study.

The obtained gravimetric capacities for sintered metal matrices exceeded almost four times the criteria for onboard hydrogen storage systems established by the US DOE [16], as well as previously obtained results for any reversible materials used in hydrogen storage systems.

It should be noted that when using the electrochemical method of hydrogen accumulation in battery electrodes, many methods are automatically used that allow an increase in the accumulation of hydrogen in metal hydrides (which are widely used in modern hydrogen storage systems) [23,26,29–31].

Firstly, the nickel matrix was made by sintering finely divided nickel powder. In [32,33], it was proved that grinding a metal powder in ball mills led to a significant increase in the accumulation of hydrogen in it.

Due to the fact of an increase in the accumulated hydrogen with an increase in the number of dislocations and micro-defects in the electrodes, we tested experimentally on batteries.

To verify this fact, half of the standard oxide–nickel electrodes in the KSL-12 battery were removed. Then, the solid nickel electrodes were inserted in their place. Moreover, solid nickel electrodes had the same mass and surface area as standard oxide–nickel electrodes. After a year of battery charging with a current of 1 A, the amount of hydrogen accumulated in the electrodes was determined as usual on the installation (Figure 1). The solid nickel electrode had the same weight of 14.08 g as the weight of the nickel matrix for the KSL-12 battery. It accumulated 1.422 L of hydrogen in this experiment. The experimental result showed that the gravimetric capacitances of solid nickel electrodes and the metal–ceramic nickel matrices of the oxide–nickel electrode were 0.9 wt% and  $20.2 \pm 0.1$  wt%, respectively. Consequently, the presence of pores and dislocations in the electrodes strongly affected the gravimetric capacitance of the electrodes as hydrogen accumulators.

In the metal–ceramic electrodes, there were a large number of dislocations and other micro-defects at the atomic level, and it was in them that a large amount of atomic hydrogen accumulated. In [10,32,33], in order to accumulate a large number of dislocations in metal powders, they are ground in ball mills, which led to a sharp increase in their gravimetric capacity as hydrogen accumulators.

We have proved the relationship between the number of dislocations in electrodes and their gravimetric capacity by direct experiments using transmission electron microscopy and scanning electron microscopy. For example, using Scanning Electron Microscopy of the solid nickel electrodes (used in the experiment), it was found that the more splits and other micro-defects on the surface of the electrodes, the more these electrodes accumulated hydrogen. Then, using Transmission Electron Microscopy, it was found that in the studied solid nickel electrodes, the number of dislocations (from the minimum value to the maxi-

imum value) differed four times. In this case, the amount of accumulated hydrogen in the electrode increased by a factor of 4.1 in proportion to the number of dislocations.

Secondly, the capillary pressure in the small pores of the sintered electrode matrix can reach a pressure of up to 100 MPa and higher [19], and the amount of hydrogen accumulated in the metal increases in proportion to the root of the hydrogen pressure [34,35]. Therefore, capillary pressure should be of great importance for the accumulation of hydrogen in sintered nickel matrices.

Thirdly, in the batteries under study, the electrodes were densely packed. Therefore, hydrogen released at the negative electrode can penetrate the pores of the nickel matrix of the positive electrode and can accumulate in this matrix due to the high capillary pressure.

Fourthly, in [36], it was theoretically proved that the specific capacity of hydrogen accumulation in porous media increases with decreasing pore diameter down to 0.7 nm.

This was due to an increase in the metal–hydrogen bond energy due to the interaction of hydrogen with opposite pore walls, as well as an increase in the specific surface area (SSA) with a decrease in the pore's diameter. This fact has been experimentally confirmed on various nanostructures [37,38].

For the accumulation of atomic hydrogen in nanostructures, the optimal pore diameter will be 0.3–0.35 nm [16]. Thus, three factors become optimal for the accumulation of atomic hydrogen in nanostructures. Firstly, the size of the metal lattice, which was approximately 0.3–0.35 nm. Secondly, SSA becomes the maximum possible, since, in this case, it was equal to the surface of all layers of the metal lattice. Thirdly, the bond of atomic hydrogen in the metal was many times greater than the bond of adsorbed hydrogen on the pore surface, which was proved in [39–41].

Therefore, studies [36–38] prove that the optimal medium for the accumulation of hydrogen is a finely dispersed metal powder.

It should be noted that the sintered electrodes of nickel–cadmium batteries are exactly sintered fine metal powder.

Fifthly, the positive electrode contains nickel hydroxides. However, it was experimentally proved in [42,43] that nickel oxides (like any transition metal oxides) are catalysts for hydrogen storage.

To study nickel hydroxide as a catalyst for the accumulation of hydrogen in electrodes, we also used a KSL-12 battery. To verify this fact, half of the standard oxide–nickel electrodes in the KSL-12 battery were removed. Then, the metal–ceramic matrices of these electrodes (without nickel hydroxide) were inserted in their place. After a year of battery charging with a current of 1 A, the amount of hydrogen accumulated in the electrodes was determined as usual on the installation (Figure 1).

The metal–ceramic matrix of the electrode has a weight of 14.08 g. It accumulated 20.5 L of hydrogen in this experiment. Therefore, the experimental result showed that the gravimetric capacitances of empty metal–ceramic nickel matrices and metal–ceramic nickel matrices of the oxide–nickel electrode were 13 wt% and  $20.2 \pm 0.1$  wt%, respectively.

Thus, nickel hydroxide is a good catalyst for hydrogen accumulation in metal–ceramic electrodes.

Lastly, using an electrochemical method, hydrogen accumulated in the electrodes of the batteries over several years. In the frame of the thermo-chemical standard method (1), the process of the hydrides' obtainment lasts from some minutes up to several hours. However, for many accumulation processes of one substance in another, the duration of the process is of great importance. It is especially so if the accumulation process is very slow and difficult, as it was in our case.

Most probably, it is exactly the favorable combination of all of the above-mentioned factors in alkaline batteries that allows the accumulation of hydrogen in their electrodes in these huge amounts (Tables 1 and 2).

On the basis of the conducted experimental studies, the following conclusions can be drawn:



Firstly, if nickel–cadmium batteries are continuously charged with a current of about  $0.1 C_n$  ( $C_n$ -nominal capacity) for a year, then the maximum possible amount of hydrogen will accumulate in the electrodes of these batteries (Tables 1 and 2).

Secondly, when batteries are charged, in the case of dense packing of electrodes, hydrogen accumulates in both positive and negative electrodes. However, in general, the gravimetric capacity of the sintered oxide–nickel electrode  $(3.22/24) \times 100 = 13.4 \text{ wt\%}$  (Table 3) is greater than the gravimetric capacity (10.6 wt%) of the plastic-bonded cadmium electrode. Therefore, if a hydrogen storage system is created based on a nickel–cadmium battery, it is advantageous to replace the cadmium electrodes with oxide–nickel electrodes. In this case, the capacity of the entire battery as HSS should increase by about 10%, which was confirmed by our direct experimental studies.

Thirdly, our preliminary experimental studies have shown that the accumulation time of the maximum amount of hydrogen (in the proposed HSS) can be significantly reduced to several months or even days. To do this, it was necessary to optimize the structure of the electrodes, use optimal hydrogen accumulation catalysts (instead of nickel hydroxide), and use an asymmetric alternating current in order to accumulate hydrogen in the electrodes.

Thus, using the electrochemical method of hydrogen accumulation, it was possible to obtain metal hydrides with specific capacities four times higher than the criteria established by the US DOE [16] for onboard hydrogen storage systems, as well as previously obtained results for any reversible materials used in hydrogen storage systems.

#### 4.2. Dehydrogenation of Metal Hydrides

The use of the generally accepted thermo-chemical method (1) for hydrogen desorption from the obtained metal hydrides is extremely inefficient. Firstly, this requires a temperature of about  $800 \text{ }^\circ\text{C}$  (Section 3.1). Maintaining this temperature requires a lot of energy. In addition, this temperature significantly exceeds the thermodynamic criteria set by the US DOE ( $85 \text{ }^\circ\text{C}$ ) [16] for onboard HSS. Secondly, even at such a high temperature, the rate of hydrogen evolution from metal hydrides is about a hundred times less [24] than the required minimum rate established by the US DOE [16]. Thirdly, this method is inertial, since heating and cooling of hydrides requires a significant amount of time and additional energy costs.

It should also be noted that hydrides that meet all US DOE requirements have not yet been found [16].

In our previous paper [24], it was proved that thermal runaway can be used very effectively for the desorption of hydrogen from metal hydrides (instead of the traditional thermo-chemical method (1)).

In the case of thermal runaway, desorption of hydrogen from the oxide–nickel and cadmium electrodes occurs in about 4 min [24]. Such a rate of hydrogen desorption cannot be achieved using the conventional thermo-chemical method of hydrogen desorption (1). This desorption rate value is about 20,000 times [24] higher than the kinetic criteria set by US DOE [16]. Moreover, in this case, the rate of hydrogen desorption from the electrodes can be controlled by electrical engineering methods [24].

In addition, when using thermal runaway, the thermodynamic criteria established by the US DOE are not relevant, since the thermal runaway process can occur at any temperature and pressure. While in the thermo-chemical method (1), pressure and temperature are the main factors providing both the desorption process and the absorption process of hydrogen in metals.

Thus, theoretically using the electrochemical method of hydrogen accumulation and the thermal runaway process, one can not only achieve all the criteria established by the US DOE for metal hydrides [16] but also significantly exceed them.

It should be noted that when using these two methods, the process of sorption and desorption of hydrogen from metal–ceramic matrices is reversible since we used the same electrodes in many cycles of sorption and desorption of hydrogen.

In conclusion, I would like to note that although there are quite a lot of works on the study of thermal runaway these works mainly investigate thermal runaway in lithium-ion batteries. There are very few works on the study of thermal runaway in lead–acid and nickel–metal hydride batteries. In 30 years of research on thermal runaway in batteries, we found only one paper [44] on the study of thermal runaway in nickel–cadmium batteries. This is an unreasonably low interest in the study of such a dangerous phenomenon as thermal runaway in nickel–cadmium batteries. After all, nickel–cadmium batteries are used in high-risk vehicles, such as airplanes.

## 5. Conclusions

The conducted experimental studies define a promising direction for the development of fundamentally new hydrogen storage systems with highly specific parameters.

However, it should be noted that none of the hydrogen storage systems that exist today meet the requirements of the US DOE in all criteria. It is the lack of reliable hydrogen storage systems that can compete with the fuel tanks of cars containing gasoline that is the main obstacle to the widespread use of hydrogen energy.

In this manuscript, it is strictly experimentally proven that, by using the electrochemical method of accumulation of hydrogen and thermal runaway to desorb hydrogen from metal hydrides, it is possible to create a hydrogen storage system that exceeds all US DOE criteria by several times.

Difficulties in this direction are also noted in the manuscript, the solution of which requires additional studies. Firstly, these are studies to reduce the time of hydrogen accumulation. Our preliminary studies have shown that the time of hydrogen accumulation can be significantly reduced. Secondly, it is necessary to study the thermal runaway in more detail.

However, at present, only in this direction, it is possible not only to achieve all of the US DOE criteria but also significantly exceed them.

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## References

1. Michaelides, E.E. *Energy, the Environment, and Sustainability*; CRC Press: Boca Raton, FL, USA, 2018.
2. Argyrou, M.C.; Christodoulides, P.; Kalogirou, S.A. ES for electricity generation and related processes: Technologies appraisal and grid scale applications. *Renew. Sustain. Energy Rev.* **2018**, *94*, 804–821. [[CrossRef](#)]
3. International Energy Agency. *CO<sub>2</sub> Emissions from Fuel Combustion—Overview*; IEA-Chirat: Paris, France, 2019.
4. International Energy Agency. *Key World Statistics*; IEA-Chirat: Paris, France, 2020.
5. Michaelides, E.E. Thermodynamics, Energy Dissipation, and Figures of Merit of Energy Storage Systems—A Critical Review. *Energies* **2021**, *14*, 6121. [[CrossRef](#)]
6. Mahlia, T.M.I.; Saktisahdan, T.J.; Jannifar, A.; Hasan, M.H.; Matseelar, H.S.C. A review of available methods and development on ES; Technology update. *Renew. Sustain. Energy Rev.* **2014**, *33*, 532–545. [[CrossRef](#)]
7. Michaelides, E.E. Transition to Renewable Energy for Communities: Energy Storage Requirements and Dissipation. *Energies* **2022**, *15*, 5896. [[CrossRef](#)]
8. Nikkhah, S.; Allahham, A.; Bialek, J.W.; Walker, S.L.; Giaouris, D.; Papadopoulou, S. Active Participation of Buildings in the Energy Networks: Dynamic/Operational Models and Control Challenges. *Energies* **2021**, *14*, 7220. [[CrossRef](#)]
9. He, W.; Mo, O.; Remøy, A.; Valøen, L.O.; Sätendal, H.; Howie, A.; Vie, P.J.S. Accelerating Efficient Installation and Optimization of Battery Energy Storage System Operations Onboard Vessels. *Energies* **2022**, *15*, 4908. [[CrossRef](#)]
10. Broom, D.P. *Hydrogen Storage Materials: The Characterisation of Their Storage Properties*; Springer: London, UK, 2011.
11. Abe, J.O.; Popoola, A.P.I.; Ajenifuja, E.; Popoola, O.M. Hydrogen energy, economy and storage: Review and recommendation. *Int. J. Hydrog. Energy* **2019**, *44*, 15072–15086. [[CrossRef](#)]

12. Ellabban, O.; Abu-Rub, H.; Blaabjerg, F. Renewable energy resources: Current status, future prospects and their enabling technology. *Renew. Sustain. Energy Rev.* **2014**, *39*, 748–764. [[CrossRef](#)]
13. Andreasen, K.P.; Sovacool, B.K. Energy sustainability, stakeholder conflicts, and the future of hydrogen in Denmark. *Renew. Sustain. Energy Rev.* **2014**, *39*, 891–897. [[CrossRef](#)]
14. Mathiesen, B.V.; Lund, H.; Connolly, D.; Wenzel, H.; Østergaard, P.A.; Möller, B.; Nielsen, S.; Ridjan, I.; Karnøe, P.; Sperling, K.; et al. Smart Energy Systems for coherent 100% renewable energy and transport solutions. *Appl. Energy* **2015**, *145*, 139–154. [[CrossRef](#)]
15. Zhang, F.; Zhao, P.; Niu, M.; Maddy, J. The Survey of Key Technologies in Hydrogen Energy Storage. *Int. J. Hydrog. Energy* **2016**, *41*, 14535–14552. [[CrossRef](#)]
16. Hydrogen, Fuel Cells & Infrastructure Technologies Program. Multi-year research, development and demonstration plan. In *Planned Program Activities for 2005–2015*; U.S. Department of Energy, Energy Efficiency and Renewable Energy: New York, NY, USA, 2009.
17. Alefeld, G.; Volkl, J. (Eds.) *Hydrogen in Metals: Basic Properties*; Springer: Berlin, Germany, 1978; Volume 1.
18. Galushkin, N.E.; Yazvinskaya, N.N.; Galushkin, D.N. Study of thermal runaway electrochemical reactions in alkaline batteries. *J. Electrochem. Soc.* **2015**, *162*, A2044–A2050. [[CrossRef](#)]
19. Galushkin, D.N.; Yazvinskaya, N.N.; Galushkin, N.E. Investigation of the process of thermal runaway in nickel-cadmium accumulators. *J. Power Sources* **2008**, *177*, 610–616. [[CrossRef](#)]
20. Galushkin, N.E.; Yazvinskaya, N.N.; Galushkin, D.N. Thermal Runaway in Sealed Alkaline Batteries. *Int. J. Electrochem. Sci.* **2014**, *9*, 3022–3028.
21. Galushkin, N.E.; Yazvinskaya, N.N.; Galushkin, D.N.; Galushkina, I.A. Causes analysis of thermal runaway in nickel-cadmium accumulators. *J. Electrochem. Soc.* **2014**, *161*, A1360–A1363. [[CrossRef](#)]
22. Galushkin, N.E.; Yazvinskaya, N.N.; Galushkin, D.N. The mechanism of thermal runaway in alkaline batteries. *J. Electrochem. Soc.* **2015**, *162*, A749–A753. [[CrossRef](#)]
23. Yazvinskaya, N.N.; Lipkin, M.S.; Galushkin, N.E.; Galushkin, D.N. Research of Nanomaterials as Electrodes for Electrochemical Energy Storage. *Molecules* **2022**, *27*, 837. [[CrossRef](#)]
24. Galushkin, N.E.; Yazvinskaya, N.N.; Galushkin, D.N. Thermal runaway as a new high-performance method of desorption of hydrogen from hydrides. *Int. J. Hydrog. Energy* **2016**, *41*, 14813–14819. [[CrossRef](#)]
25. Galushkin, N.E.; Yazvinskaya, N.N.; Galushkin, D.N. Analytical model of thermal runaway in alkaline batteries. *Int. J. Electrochem. Sci.* **2018**, *13*, 1275–1282. [[CrossRef](#)]
26. Galushkin, N.E.; Yazvinskaya, N.N.; Galushkin, D.N. Nickel-cadmium batteries with pocket electrodes as hydrogen energy storage units of high-capacity. *J. Energy Storage* **2021**, *39*, 102597. [[CrossRef](#)]
27. Galushkin, N.E.; Yazvinskaya, N.N.; Galushkin, D.N.; Galushkina, I.A. Analysis of thermal runaway aftereffects in nickel-cadmium batteries. *Int. J. Electrochem. Sci.* **2016**, *11*, 10287–10295.
28. Guo, Y. Thermal runaway. In *Encyclopedia of Electrochemical Power Sources*; Garche, J., Ed.; Elsevier: Amsterdam, The Netherlands, 2009; Volume 4, p. 241.
29. Galushkin, N.E.; Yazvinskaya, N.N.; Galushkin, D.N. Ni-Cd batteries as hydrogen storage units of high-capacity. *ECS Electrochem. Lett.* **2013**, *2*, A1–A2. [[CrossRef](#)]
30. Galushkin, N.E.; Yazvinskaya, N.N.; Galushkin, D.N.; Galushkina, I.A. Oxide-nickel electrodes as hydrogen storage units of high-capacity. *Int. J. Hydrog. Energy* **2014**, *39*, 18962–18965. [[CrossRef](#)]
31. Galushkin, N.E.; Yazvinskaya, N.N.; Galushkin, D.N. Pocket electrodes as hydrogen storage units of high-capacity. *J. Electrochem. Soc.* **2017**, *164*, A2555–A2558. [[CrossRef](#)]
32. Kojima, Y.; Kawai, Y.; Haga, T. Magnesium-based nanocomposite materials for hydrogen storage. *J. Alloys Compd.* **2006**, *424*, 294–298. [[CrossRef](#)]
33. Shang, C.X.; Bououdina, M.; Song, Y.; Guo, Z.X. Mechanical alloying and electronic simulations of (MgH<sub>2</sub>+ M) systems (M= Al, Ti, Fe, Ni, Cu and Nb) for hydrogen storage. *Int. J. Hydrogen Energy* **2004**, *29*, 73–80. [[CrossRef](#)]
34. Borgschulte, A.; Lohstroh, W.; Westerwaal, R.J.; Schreuders, H.; Rector, J.H.; Dam, B.; Griessen, R. Combinatorial method for the development of a catalyst promoting hydrogen uptake. *J. Alloys Compd.* **2005**, *404–406*, 699–705. [[CrossRef](#)]
35. Veziroglu, T.N.; Yajie, Z.; Deyou, B. (Eds.) *Hydrogen Systems*; Pergamon Press: Oxford, UK, 1986; Volume 1, pp. 550–553.
36. Cabria, I.; Lopez, M.J.; Alonso, J.A. Simulation of the hydrogen storage in nanoporous carbons with different pore shapes. *Int. J. Hydrog. Energy* **2011**, *36*, 10748–10759. [[CrossRef](#)]
37. Gogotsi, Y.; Portet, C.; Osswald, S.; Simmons, J.M.; Yildirim, T.; Laudisio, G.; Fischer, J.E. Importance of pore size in high-pressure hydrogen storage by porous carbons. *Int. J. Hydrog. Energy* **2009**, *34*, 6314–6319. [[CrossRef](#)]
38. de la Casa-Lillo, M.A.; Lamari-Darkrim, F.; Cazorla-Amoro's, D.; Linares-Solano, A. Hydrogen storage in activated carbons and activated carbon fibers. *J. Phys. Chem. B* **2002**, *106*, 10930–10934. [[CrossRef](#)]
39. Denisov, E.A.; Kompaniets, T.N. Interaction of graphite with atomic hydrogen. *Tech. Phys.* **2001**, *46*, 240–244. [[CrossRef](#)]
40. Tazhibaeva, I.L.; Klepikov, A.K.; Shestakov, V.P.; Romanenko, O.G.; Chikhay, E.V.; Kenzhin, E.A.; Cherepnin, Y.S.; Tikhomirov, L.N.; Zverev, V.A. Hydrogen release of reactor irradiated RGT-graphite. *J. Nucl. Mater.* **1996**, *233–237*, 1198–1201. [[CrossRef](#)]
41. Kanashenko, S.L.; Gorodetsky, A.E.; Chernikov, V.N.; Markin, A.V.; Zakharov, A.P.; Doyle, B.L.; Wampler, W.R. Hydrogen adsorption on and solubility in graphites. *J. Nucl. Mater.* **1996**, *233–237*, 1207–1212. [[CrossRef](#)]

42. Oelerich, W.; Klassen, T.; Bormann, R. Metal oxides as catalysts for improved hydrogen sorption in nanocrystalline Mg-based materials. *J. Alloys Compd.* **2001**, *315*, 237–242. [[CrossRef](#)]
43. Polanski, M.; Bystrzycki, J. Comparative studies of the influence of different nano-sized metal oxides on the hydrogen sorption properties of magnesium hydride. *J. Alloys Compd.* **2009**, *486*, 697–701. [[CrossRef](#)]
44. Alvin, J.S.; Joseph, C.D. The thermal runaway condition in nickel-cadmium cells and performance characteristics of sealed light weight cells. *J. Electrochem. Soc.* **1962**, *109*, 360–364.