Pocket Electrodes as Hydrogen Storage Units of High-Capacity

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In this study, it has been experimentally proven that the pocket electrodes of the Ni-Fe batteries in the process of their operation absorb hydrogen in large quantities. There is no hydrogen inside the electrodes of new batteries, but after 6 years of service life the electrodes reach their maximum hydrogen capacity. The active mass capacity of an oxide-nickel electrode as a hydrogen absorber was quantified as 22 wt% and 444 kg·m⁻³. These values exceed 3 times the earlier obtained results (using traditional methods) for hydrogen absorption by carbon nanomaterials or any other carbon materials.

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Hydrogen storage is one of the most challenging technical barriers on the way of energy-engineering development based on the hydrogen. The safest and most effective method to store hydrogen is use of solid media, such as sorbent materials and hydrides. However, the specific capacity indexes for reversible hydrogen storages are not yet sufficient for practical use of the existing hydrogen storage units. Today many publications are devoted to ways of solving this problem.

The criteria for an onboard hydrogen storage system have been defined by the US Department of Energy (DOE) in close collaboration with the automotive industry. The most frequently quoted 2015 target is a gravimetric system storage capacity exceeding 5.5 wt%. Moreover, it should be capable of releasing hydrogen at ambient conditions. In addition to a high gravimetric capacity, the 2015 requirements also include a volumetric capacity of at least 40 kg·m⁻³.

Nevertheless, till now in spite of the extensive investigations, materials have not been found yet capable to meet all the DOE requirements.

During the past decade, nanostructured carbon materials and light-element complex hydrides were the focus of intense interest. A rule, the obtained in various researches average gravimetric capacity of hydrogen storage in the nanostructured carbon materials was equal to 3–7 wt%.

In our earlier study, it was demonstrated that as a result of the thermal runaway of nickel–cadmium batteries, large amounts of hydrogen are released. The thermal decomposition of electrodes demonstrated that hydrogen accumulates in the electrodes of Ni-Cd batteries in the process of their operation. So KSX-25 battery with the service period of over five years contains approximately 800 liters of hydrogen.

According to the operation manual of the KSX-25 battery, it is charged in two stages: firstly by a current of 10A over a period of 3 h, and secondly by a current of 5A over a period of 2 h. Consequently, these batteries overcharge by a factor of 1.6 as compared to their nominal capacity. Overcharge is required for complete charging of the batteries. Thus, in the course of charging, almost 15 Ah are used for electrolyte decomposition with the evolution of hydrogen and oxygen.

\[ 2e^- + 2H_2O \rightarrow H_2 \uparrow + 2OH^- \] (cathode) \[ 2OH^- \rightarrow 1/2O_2 \uparrow + H_2O + 2e^- \] (anode)

Consequently, one charging of a KSX-25 battery produces 6 L of hydrogen and 3 L of oxygen. The hydrogen is characterized by very high diffusion permeability. The diffusion coefficient of hydrogen atoms is 10¹⁰ times higher than a diffusivity of oxygen. Therefore, upon dissociation of an electrolyte into hydrogen and oxygen in a battery, oxygen escapes from a battery, while hydrogen escapes from a battery partially and another part of it is accumulated in electrodes. Thus, the discovered 800 liters of hydrogen may have been accumulated during 134 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 accumulate the discovered amount of hydrogen.

The capacity of an oxide-nickel sintered electrode as a hydrogen absorber was quantified as 13.4 wt% and 400 kg·m⁻³. The capacity of the sintered nickel matrix of the oxide-nickel electrode as a hydrogen absorber was quantified as 20.1 wt% and 400 kg·m⁻³.

The obtained result exceeds the earlier obtained results for any reversible metal hydrides, including magnesium hydride or complex hydrides 3 times. In investigation by experiments, it was proved that the thermal runaway can be used as a new high-performance method of desorption of hydrogen from metal-hydrides. On its kinetic and thermodynamic parameters, this method is considerably superior to requirements established by US Department of Energy for onboard hydrogen storage systems. For its processing, the thermal runaway does not require any certain temperature or pressure.

The present paper is devoted to examination of hydrogen storage in pocket electrodes of nickel-iron batteries. During more than a decade, we investigated the process of hydrogen storage in electrodes of nickel-iron batteries of various capacities in various discharge modes. There was determined that the gravimetric storage capacity of hydrogen in the nickel-iron batteries depends neither on battery capacity nor on its discharge mode. That is why in this article, the investigations results are represented that were obtained by us by the example of the batteries FL-250.

Experimental

For estimation of the hydrogen volume stored in electrodes of the batteries FL-250, they were exposed to thermal decomposition in a thermal chamber.

For studying the electrodes, the installation from the article was used. The installation represents a metal thermal chamber in the form of a tube with the length of 1.8 m and diameter of 2 cm. The sealed end of the tube was placed into a muffle furnace, while a rubber plug with a tube for gas extraction was inserted into the other end of the same tube. During the experiment, the one pocket of the oxide-nickel electrode was placed in ceramic crucible, which then was placed into the working thermal chamber. To decrease the heat exchange inside the thermal chamber, a round porous ceramic plug with the length of 20 cm was inserted above the crucible (Fig. 1). Heating the electrode in the thermal chamber resulted in a release of gas from it. This gas was partially cooled by passage through the standard coil (9) meter to entry into the gas intake chamber (2). As the gas entered the chamber, the pressure above the water increased, and this was registered by the manometer. To balance the internal pressure in the intake chamber and...
atmospheric pressure, part of the water was removed from the intake chamber (via tap (5)) into the retort (4). The water level in the retort gave an indication of the amount of gas that had entered the intake chamber during the period studied within the accuracy of 10 ml.

In each experiment one pocket from an electrode was exposed to the thermal decomposition. This was determined by the thermal chamber size. Each electrode was decomposed at 600°C. The reasons for choosing this temperature were as follows. In preliminary experiments, it was determined that visible release of gas starts at about 200°C. Big release of the gas starts at temperatures in excess of 600°C for both the oxide–nickel and iron electrodes. Thus, the temperature of 600°C was chosen as an optimum value for thermal decomposition of both the iron and oxide-nickel electrodes.

For the experiments in a random way, five batteries FL-250 were selected with different service lives. All the batteries were operated under the same conditions. In each battery to the thermal decomposition, three pockets were exposed of both oxide-nickel and iron electrodes. The thermal decomposition of each pocket lasted in average 9 to 12 days, 11 to 13 hours per day. In the experiments beginning within a day from a pocket, hydrogen released in average volume of 3 L from an iron electrode and 4.5 L from oxide-nickel one respectively. The thermal decomposition process stopped when the day hydrogen release left to be as little as less than 80 ml. The experimental results are represented in the Table I. In the table, there are shown the average values of the gas released for the three pockets from each battery.

Analysis of the released gas in the experiment using VOG-2M gas-analyzer showed that it consisted only of hydrogen. The absolute error in the percentage concentrations is 0.3–0.5.

Table I. Hydrogen content in pockets of the oxide-nickel and iron electrodes (batteries FL-250) with different service life.*

| No. of the battery | 1 | 2 | 3 | 4 | 5 |
|--------------------|---|---|---|---|---|
| Period of operation (years) | new | 3.2 | 4.5 | 6 | 10.6 |
| Type of electrode | Ni | Fe | Ni | Fe | Ni | Fe | Ni | Fe |
| Amount of gas released, liters | 0 | 0 | 33.4 | 11.6 | 50.2 | 25.8 | 54.0 | 33.1 |
| Ni | Fe | Ni | Fe |

*The relative error in the data in Table I is 3–5%.

Results and Discussion

Table I (batteries No. 4, 5) demonstrates that the electrodes of the FL-250 batteries with long service life contain a huge amount of hydrogen. The data of the Table I refer to one pocket of an electrode. In the battery FL-250, there are 11 iron and 10 oxide-nickel electrodes. Notably, an oxide-nickel electrode consists of 16 pockets, while iron one of 13 pockets. So in one battery FL-250 there are approximately 13373 L hydrogen, where there are 8640 L in oxide-nickel electrodes and 4733 L in iron electrodes.

The batteries FL-250 are charged with the current 65 A during 7 hours. Consequently, these batteries are overcharged by a factor of 1.8 as compared to their nominal capacity. The overcharge is required for complete charging of the batteries. Direct experimental measuring showed that at charging, the battery FL-250 produces in average 80 L hydrogen and 40 L oxygen. Thus, the discovered 13373 L of hydrogen may have been accumulated during 168 charging-discharging cycles. But by the end of its life span, a FL-250 battery is likely to have gone through a number of charging-discharging cycles ten times more. Therefore, it can – in principle – accumulate the found amount of hydrogen.

Hydrogen is absent in the electrodes of new nickel-iron batteries, but during its service life, the amount of hydrogen inside the electrodes increases (Table I, batteries No. 1–5). Our many-year experimental researches showed that a hydrogen volume absorbed by electrodes stops increasing after 5 or 6 years of their service lives in dependence on intensity of the batteries operation (Table I).

Now let us evaluate the specific parameters of an oxide-nickel electrode as a hydrogen absorber. An oxide-nickel pocket accumulates about 54 L hydrogen during a long service life of the battery FL-250 (Table I, batteries No. 4, 5). The active mass weight of a pocket before hydrogen desorption makes 22 gram. So the gravimetric capacity of the active mass of the oxide-nickel electrode as a hydrogen absorber is equal to 22.0 wt%. The active mass of the oxide-nickel electrode consists of nickel hydroxide and graphite. The obtained result exceeds the earlier obtained results for graphite (using traditional methods) five times21 and the best results obtained for nanostructured carbon 2 times.12–15

Considering that the physical dimensions of an oxide-nickel pocket of a FL-250 battery are equal to 14.9 × 1.3 × 0.55 cm, we obtain that the volumetric capacity of active mass of an oxide-nickel electrode as a hydrogen absorber is equal to 444 kg m⁻³. This result significantly exceeds the earlier obtained results for nanostructured carbon.124

Also with due consideration that the weight of the active mass of the iron electrode is equal to 17.49 g and its sizes are 14.9 × 1.69 × 0.29 cm, we obtain that the gravimetric and volumetric capacities of the iron electrode active mass are equal to 16.9 wt% and 406 kg m⁻³ respectively. These values are close to the values obtained by us earlier for a sintered oxide-nickel electrode.21

Now let us give consideration to reasons of such high specific capacities of hydrogen storage in active mass of oxide-nickel electrode. First of all, it must be noted that in an oxide-nickel electrode there are all factors, which contribute to hydrogen accumulation. At present, these factors are under intensive research.

Firstly, in the paper22 there was shown that in a case of pure carbon nanostructures, it is impossible to reach a high gravimetric capacity of hydrogen storage. An increase of the gravimetric capacity of hydrogen storage is possible only by way of doping of carbon nanostructures22 or by changing of their structure, particularly by
decreasing of their pores size.\textsuperscript{27,28} In the paper\textsuperscript{27} based on quantum-thermodynamic model, there was demonstrated theoretically that with decreasing the pores size, the gravimetric capacity of carbon nanostructures grows. Notably, the pores optimal diameter was found to be approximately equal to 0.7 \textnormal{nm}. The gravimetric capacity growth along with pores size decrease is explained by growth of two factors values. The first factor is growth of hydrogen binding energy since the overlap of the interaction potential fields from the interior pore surface will enhance the carbon–hydrogen interaction. Secondly, smaller pores have higher specific surface area (SSA) for a given pore volume. These theoretical conclusions were confirmed experimentally on a great deal of carbon nanostructures.\textsuperscript{26,27} Now, if to perform the same calculations as in the paper\textsuperscript{27} (keeping in mind that supposedly it is not hydrogen molecules that penetrate but instead hydrogen atoms do), then for pores optimal size we will obtain the diameter of 0.3-0.35 \textnormal{nm}. This size is equal to interplanar distance in the graphite crystal lattice. So for atomic hydrogen, an optimal condition is invasion into the graphite interplanar space, and the graphite powder is the optimal medium for the atomic hydrogen storage. Besides, an impact of the highlighted above two factors (promoting increase of material gravimetric capacity) grow drastically in a case of the atomic hydrogen penetration into the graphite. Firstly, the hydrogen binding energy increases tens times as compared to the hydrogen binding energy on the graphite surface (or any other carbon nanostructure, even with taking doping by metal atoms into consideration), which is shown directly in experiments in the papers.\textsuperscript{31-33} Secondly, for the hydrogen atoms being inside of graphite, a specific surface area (SSA) will be equal to surface of all carbon layers in the graphite, and herewith this SSA exceeds SSA of any other carbon nanostructure many times. So if to aim at obtaining an atomic hydrogen absorption, then based on all the performed both theoretical and experimental researches,\textsuperscript{27-29} one can affirm that an optimal medium for atomic hydrogen penetration is the graphite powder (or any other carbon nanostructure with the same density of carbonic layers). Moreover, in the case of atomic hydrogen penetration inside of the graphite, the gravimetric capacity of hydrogen storage must grow many times, which is namely what is seen in our experiments.

Secondly, in a great number of works there was shown that doping of carbon nanostructures with alkaline or transition metals leads to considerable growth of their gravimetric capacity.\textsuperscript{26,34,35} This phenomenon is connected anyhow both with general energy increase of binding between hydrogen and carbon nanostructures and with hydrogen molecules dissociation on metal surface and their further penetration (already in atomic form) into the carbon nanostructures,\textsuperscript{26,27} and this is especially important for the graphite powder. It should be noted that in the oxide-nickel electrode of the battery FL-250, the graphite powder is just doped with nickel.

Thirdly, in the case of metal hydrides and graphite, a considerable growth of the gravimetric capacity is obtained in a case of use of finely dispersed powders (they can be prepared by milling in ball mills).\textsuperscript{36-38} Any imperfections of crystalline structure (particularly dislocations) are traps for hydrogen, as they decrease the energy of hydrogen atoms as compared to their location in normal interstice. Besides they are the centers of hydrogen absorption, and also contribute to hydrogen penetration into the graphite depth. Hence, imperfections of the graphite crystalline structure cause sharp rise of hydrogen miscibility in it.

Besides, in micro-defects of graphite, there can be developed a very high capillary pressure of hydrogen,\textsuperscript{39,40} which also will promote hydrogen diffusion into graphite. It should be noted that as for the oxide-nickel electrode of the battery FL-250, namely the finely dispersed powder graphite is used.

Fourthly, after six-year-operation, electrodes in batteries FL-250 are very densely stacked. Thus, hydrogen evolved at the iron electrode during charging of the battery may penetrate into the pores of both oxide-nickel, and iron electrodes. Hence, in all probability, the oxide-nickel electrode accumulates hydrogen not electrochemically, but due to the high capillary pressure. It was shown in paper,\textsuperscript{41} that capillary pressure in battery’s electrodes can reach 100 MPa and more.

Fifthly, for increasing gravimetric capacity of carbon nanostructures, various catalytic agents are used, in particular KOH.\textsuperscript{38,39} In the paper,\textsuperscript{38} it is shown that via KOH activation, hydrogen capacity of mesoporous carbon is enhanced one and half times. It should be noted that in the battery FL-250 the KOH solution is used as an electrolyte.

Sixthly, it is a well known fact that oxides of transition metals act as catalysts of hydrogen accumulation in metals.\textsuperscript{40,41} As for carbon nanostructures, this question has been studied not enough till now. We believe that the transition metals oxides promote hydrogen molecules dissociation releasing atoms. This is very important for hydrogen atoms diffusion into metals and graphite but it is not important for superficial adsorption of hydrogen molecules. We believe that namely that is why this question has been investigated not enough till now. So we conducted a number of single experiments for studying catalytic characteristics of nickel hydroxide used in the oxide-nickel electrodes of batteries FL-250. With this purpose in mind in our first experiment, we charged a new oxide-nickel electrode (free of hydrogen) of batteries FL-250 in dense stacking condition with two iron electrodes during 750 hours with current density 16 mA \textnormal{cm}^{-2}. This current density corresponds to the common current density, which the battery FL-250 charges with. The long-time recharge is needed for electrolyte decomposition into hydrogen and oxygen and for hydrogen storage in electrodes. The result was that the measured gravimetric capacity of active mass of oxide-nickel electrode made 0.5 wt\%. In the second experiment the active mass of oxide-nickel electrode was replaced with the graphite powder used in this electrode as a filler. Charging of this electrode was made in the same conditions that in the first experiment. The result was that the measured gravimetric capacity of the graphite powder made only 0.03 wt\%. It means that the nickel hydroxide used in the oxide-nickel electrode of the battery FL-250 possesses a very powerful catalytic action for the process of hydrogen penetration into graphite powder.

Lastly, the process of hydrogen accumulation in the batteries’ electrodes takes place all through their service life. This is more than six years in the present study. During charging process of the battery FL-250, its electrolyte decomposes into hydrogen and oxygen. Hydrogen is characterized by a very high diffusion permeability. For example, at the temperature 20°C the diffusivity of hydrogen in nickel is approximately 10\textsuperscript{10} times higher than diffusivity of nitrogen or oxygen.\textsuperscript{3} These features explain why upon dissociation of an electrolyte into hydrogen and oxygen in a battery, only hydrogen accumulates in the electrodes, while oxygen escapes to the atmosphere.

In the modern methods of hydrogenation, the hydrogen accumulation process in carbon materials can take from several minutes to several hours. Conducted for the last 20 years analysis of research scientific works on hydrogen accumulation in carbon materials showed that most probably there were no experiments on hydrogen accumulation in carbon materials under high external hydrogen pressures (which can exist at graphite micropores) during a long enough period of time (several years). However, the impact of the external pressure as well as the duration of the process are the important factors in any processes of penetration of one substance into another. It is especially so, when the penetration process is as extremely slow and difficult as in our case.

That was namely the favorable combination of all these factors, in all probability, that allowed storing such great amount of hydrogen in the electrodes of the batteries FL-250.

**Conclusions**

It must be noted, that an oxide-nickel pocket electrode by its specific parameters of hydrogen accumulation exceeds the requirements of the US Department of Energy.\textsuperscript{16} However, due to the high temperature of hydrogen desorption and the low speed of absorption/desorption the given materials cannot be used as hydrogen batteries for future hydrogen-fueled vehicles. Nevertheless, their use in stationary devices cannot be excluded.

We would like also to highlight that the phenomenon of the hydrogen large volumes storage in the electrodes of Ni-Cd and Ni-Fe...
batteries in the course of their operation was found just recently. A complicated and poorly studied phenomenon requires further researches use of traditional methods. Undoubtedly, investigation of this phenomenon is quite unusual one. It allows accumulating hydrogen in metal hydrides and carbon materials in volumes considerably exceeding hydrogen volumes in all known materials obtained with use of traditional methods. Undoubtedly, investigation of this complicated and poorly studied phenomenon requires further researches conduction, both theoretical and experimental ones.

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