Metal hydride hydrogen storage and purification technologies

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Abstract. The results of the development of metal hydride (MH) reactors for the storage and purification of hydrogen of various types are presented. Two methods of metal hydride purification of hydrogen are presented. The use of the MH method of flow-through purification of hydrogen has high hydrogen recovery rates at high volume contents of hydrogen in the mixture (≥10% vol.), while the method of periodic evacuation of accumulated impurities is most effective at low hydrogen contents in the mixture (<10% vol.).

1. Introduction
Growing industrialization and increasing of world energy carrier consumption dynamics inevitably enlarges the influence on the global ecosystem and pushes the humankind to research for new approaches to increase energy generation and consumption effectiveness. Interest in hydrogen as an alternative type of fuel had existed for years. Above all, it is connected with high prices for traditional types of energy resources, political characteristics of forming the energy market along with many different ecological aspects of utilizing traditional fuel [1].

Transition to truly ecologically pure hydrogen production is possible only with the use of renewable energy sources (RES). Utilization of locally available RES (including the biohydrogen ones) combined with storing energy in hydrogen with its subsequent use in fuel cell could be the way to a development of complex energy generation and utilization systems of relatively small power scale (below 20 kWt).

Hydrides of intermetallic compounds (IMCs), liable to selective hydrogen absorption, are to be perspective materials for the development and construction of hydrogen storage and high purity fuel supply systems for FC. Stationary autonomous energy systems are mainly focused on compactness, operational safety and productivity rather than on weight characteristics. That is why the MH storage and purification systems coupled with RES could be perspective for the development of such systems. MH device could be a thermal energy storage system at the same time, due to the existence of high thermal reaction of hydrogen sorption-desorption processes (25-70 kJ/mol H\textsubscript{2}), thus consumer heat supply could be rationally organized [2,3].

Main scientific and technical problems of development and constructing highly efficient MH hydrogen storage devices are connected with a managing of thermal and mass transfer inside the MH filling volume. Finely dispersed powder of IMC in the MH reactor has a size of 1-10 μm and possess relatively low thermal conductivity (0.1-1 W/m·K), which depends on free hydrogen pressure and absorbed hydrogen concentration) [4]. Ineffective way of organization of heat input-output inside the
IMC filling with a high thermal effect of reaction leads to emerging of crisis events characterized by rapid decreasing of reaction dynamics [5]. Gaseous admixtures are also make great impact on the hydrogen sorption kinetics. Even the presence of inert gases in the main volume of hydrogen leads to blocking of access for hydrogen to the IMC surface, thus forcing one to exploit the techniques of removing accumulated admixtures in the MH devices [6].

Another existing type of scientific-technical problems bound to the development of effective technologies of MH storage and purification devices integration with FC-based energy systems, hydrogen sources (electrolyzer, bioreactor) and the source of initial energy (wind, solar systems). Model integrated energy supply systems are to become crucial for the solving of these problems with fine-tuning of all the possible work modes, especially the emergency ones for all components of the energy system [7,8].

2. Materials and metal hydride reactors
Operational characteristics of developing MH devices, as part of integrated energy systems, should be consistent with the requirements of FC and electrolyzer (operation pressure, hydrogen purity, hydrogen flow rate). Tweaking an IMC composition allows one to make an alloy of needed sorption/desorption pressure in a temperature working range of 0 to 100°C to meet the requirements for hydrogen storing and cleansing. AB5-type hydrides can achieve needed for the development of hydrogen storing systems parameters. As for AB5-type alloys – it allows us to provide hydrogen desorption processes with a use of FC/electrolyzer waste heat.

Melting of IMC samples for our research work was undertaken in electric arc furnace in the argon atmosphere. PCT-isotherms of sorption and desorption processes were obtained via Siverts method (figure 1) [9].

![Figure 1. PCT curves of the AB5 alloys used at a temperature of 25 °C (50 cycles).](image-url)

Experimental research of thermal processes in the MH hydrogen accumulation and purification systems were conducted employing experimental rig 12-04 of JIHT RAS in the laboratory of hydrogen energy technologies. Complex experimental rig is designed to:

• Experimental research thermal and mass exchange processes in the porous bed of IMC during the sorption of pure and polluted hydrogen.
• Utilize gathered data to verify mathematical models of thermal and mass transfer inside the MH hydrogen accumulation and purification devices.
• Experimental research different modes of operation of developed MH devices several types and several IMC loads.
• Research sorbing and thermophysical properties of different IMCs.
• Research problems of integration of hydrogen production sources, purification and accumulation systems and FCs.
• Refinement of automation and operation of energy systems with MH hydrogen accumulation and purification subsystems.

Experimental rig (figure 2) consists of gas ramp, solid-polymer electrolyte electrolyser of 10 st.l H₂/min gas flow, MH block of fine purification, made of 3 reactors RSP-3, MH hydrogen accumulation system RS-1 to provide 5 kWt FC with fuel, flow-through purification reactors RSP-8, gas analyzer (GA), gas flow regulators (FR) and gas flow meters (FM), electromagnetic valves (EV), pressure sensors (PS) and vents. Block of fine purification, RSP-8 reactors and RS-1 systems are in the metallic box equipped with air exhaust vent with air exchange multiplicity from 12 to 15. The placement and the box are equipped with sensors of dangerous accumulation, paired with emergency exhaust vent to turn it on if the hydrogen concentration in the room reaches 1%. Measuring equipment and gas flow regulators are operated via PC block based on LabView system.

![Figure 2. Schematic diagram of the experimental rig 12-04 of the JIHT RAS.](image)

Several different types of reactors, varied by their thermal exchanger design, were created for the fine purification block subsystem (figure 3). Mathematical models of thermal and mass exchange processes during pure and polluted hydrogen sorption in the MH bed were used for the development of inner and outer thermal exchange patterns [10,11].
Figure 3. Hydrogen storage and purification reactors: 1 – Type 1 (cartridge) [12]; 2-Type 2 (pipe board); 3-Type 3 (RSP-3 reactor) (pipe board) [13]; 4-Type 4 (bellows); 5-Type 5 (RSP-8 flow-through purification reactor) [14].

3. Results and discussions

Analysis of performance of MH hydrogen accumulation systems is usually focused on its practical side – integral dynamics of hydrogen sorption, change in number of absorbed hydrogen with respect to time. Efficiency of different types of MH reactors was evaluated by conducting a series of experiments of sorption process for the pure hydrogen with the flow restriction maxed at 120 st.l./min. Reactor types represented on figure 3 were used. The experimental data obtained (figure 4) revealed, that the most effective, in terms of inner thermal exchange optimization, method is an application of thin (less than 10mm) MH layer and introduction of channels for the heat carrier inside the filament.

Figure 4. Hydrogen sorption for five types of reactors.

To solve the target of extracting the hydrogen from the gas mixture 2 purification methods were used: recurrent evacuation method utilizing MH reactors type 3 (RSP-3) and flow-through method utilizing MH reactor type 5 (RSP-8). Research of hydrogen purification experimental processes were conducted by the use of inert gases as admixtures (N$_2$ and CO$_2$).

Hydrogen purification technique via RSP-3 reactors consisted in recurrent evacuation of accumulated in the reactor free volume mixture. The evacuation could conducted in different operating modes, depending on the specific goal of optimization: constant evacuation time interval, constant target pressure after which the evacuation starts or constant volume of evacuated gas. For the further
development of the purification subsystem the “constant target pressure (atmospheric)” mode was chosen. (figure 5 and Table 1).

![Figure 5](image-url)

**Figure 5.** Hydrogen purification using the RSP-3: hydrogen with an impurity (3% vol. N₂), evacuation to atmospheric pressure. Black – gas injection, red - evacuation an impurity.

| Impurity, % vol. | Losses, % |
|-----------------|-----------|
| 0               | 0         |
| 3               | 17        |
| 10              | 22        |
| 25              | 33        |

**Table 1.** Hydrogen losses during purification by the RSP-3 reactor.

Flow-through metod utilizing MH reactor type purification technique is basically a flushing the mixture of hydrogen and other gases through the porous filament of IMC. Experiments were conducted by means of RSP-8 reactor (figure 3). Hydrogen is recurrently pushed from the top of RSP-8 to its bottom part through the bed, while the most part of existing hydrogen is being absorbed in the IMC and the rest of it is exhausted from the bottom of the reactor along with non-absorbable admixtures. figure 6 represents integral coefficient of hydrogen extraction during the continuous-flow purification.

![Figure 6](image-url)

**Figure 6.** The change in the Recovery ratio of hydrogen depending on the degree of charging of the RSP-8 reactor and the restriction of the flow rate of the H₂/CO₂ mixture (50/50% vol.): 1 -20 st.l / min; 2 -3 st.l / min; 3-10 st.l / min: 4 -3 st.l / min without reactor cooling.
Utilizing the continuous-flow purification with RSP-8 reactors demonstrates high rates of hydrogen extraction (the efficiency reaches 85% along with relatively high current reactor capacity ≤ 80% (figure 6)).

4. Conclusions

Hydrogen stores in the MH accumulation and purification systems in a bound solid-state in a hydrides of metals and alloys with a high volumetric density and relatively low pressure (below tens of atm.) which proves to be convenient and safe to use it in the autonomous systems of energy provision.

IMCs used in the MH systems possess peculiarity to separately absorb hydrogen, allowing them to be used in the development of hydrogen extraction systems and combined MH accumulation and purification systems. MH continuous-flow purification technique has high hydrogen extraction rate while the portions of hydrogen in mixture is relatively high (≥10% vol.) and it allows to subsequent utilization of purified hydrogen in a FC fuel supply system. On the other hand, the periodic evacuation technique is most effective while the portions of hydrogen in mixture does not exceed 10% vol.

External cooling of MH reactors proved to be ineffective. Intensification of processes inside the MH filament should be carried out via adjusting the powder layer thickness (less than 10mm) and utilizing thermal exchangers of “tube bundle” and “tube in tube” types.

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