Metal-hydride reactor for low rate fuel supply with pressure driven adsorption and cooled by natural convection

D V Blinov1,2, V I Borzenko1, A V Bezdudny1, D O Dunikov1,2, A N Kazakov1, I A Romanov1, V N Kuleshov2 and V I Porembsky3

1 Joint Institute of High Temperature, Russia, 111116 Moscow, Krasnokazarmennaya, 17A
2 National Research University "MPEI", Russia, 111250 Moscow, Krasnokazarmennaya, 14
3 National Research Center «Kurchatov Institute» Russia, 123182 Moskow, Akademika Kurchatova pl.1

D.V.Blinov.JIHTTRAS@yandex.ru

Abstract. A metal hydride reactor for hydrogen accumulation RHA-1 containing 18 kg of La0.85Ce0.15Ni5 alloy is created. RHA-1 and has maximum hydrogen capacity of 2.7 st.m3 and nominal capacity of 2 st.m3. Experiments have shown that the reactor could be operated using the pressure difference between an electrolyzer (1 MPa) and a fuel cell (>0.2 MPa) with passive cooling/heating of air in indoor conditions. The equilibrium charge rate is 1 st.L/min, the equilibrium discharge rate is 1.3 st.L. The RHA-1 could be used for long term energy storage and in combination with the 100 W PEM fuel cell is comparable with 12V 210Ah electrochemical batteries. The metal hydride/fuel cell system is lighter and more durable than lead acid batteries and cheaper than Li-ion batteries.

1. Introduction

Energy storage is a key to transformation of energy sector, which enables integration of variable renewables and distributed generation into grids. Few existing technologies are suitable for long term energy storage, including hydro pumped storage, compressed air storage and hydrogen. Conversion of excess energy into hydrogen via electrolysis of water contributes to flexibility and energy security. Accumulation of hydrogen in metal hydrides (MH) is known since the 1960s and is characterized by increased storage safety, comparatively high volumetric density and several other advantages compared to liquid and compressed gas hydrogen storage technologies [1]. Low temperature intermetallic compounds (IMC) of LaNi5 type are perspective materials for hydrogen accumulation, purification and compression [2]. Alloys of this group are highly resistant to gas impurities and cyclic stable [3].

The main limiting factor for hydrogen sorption process is heat transfer inside metal hydride beds [4], because activated intermetallic alloys are powders with particle size of 1-10 μm. These fine dispersed beds have very low thermal conductivity (about 1 W/m K). Moreover, thermal conductivity depends on gas pressure and concentration of absorbed hydrogen [5]. In addition, and the equilibrium pressure of the metal-hydrogen reaction substantially depends on temperature. Thus, insufficient heat transfer significantly reduces hydrogen sorption/desorption rates and causes heat and mass transfer crisis [6]. The focus of metal hydride device development lies in the improvement of thermophysical
properties of IMC by an increase of effective thermal conductivity (mixing and/or sintering with high thermal conductive materials, e.g. copper and aluminium powders, copper foam, etc.) or in the increase of a heat exchange surface between a IMC bed and reactor (finning, spirals, corrugation etc.) [4]. To achieve high flow rates at sorption or desorption intense heat management techniques are needed, with the use of liquid cooling and even steam or electric heating [7]. However, in a case of long term energy storage, the fast charge and discharge of a metal hydride device are not needed. The device could be charged from an electrolyzer powered by a renewable source during hours or even days. In addition, to be competitive with battery storage the discharge times of metal hydride devices should be as long as possible. In this case, the gas flow rates are comparably low (in comparison with nominal hydrogen capacity), and there is no need in the use of liquid cooling or additional electric power input. For relatively low gas flow rates, one can use the gas pressure as the main thermodynamic driving force of sorption/desorption process, utilizing a pressure difference between operational pressures of an electrolyzer and a fuel cell [8]. The goal of the present study is to create an experimental reactor RHA-1 (Reactor for Hydrogen Accumulation), which could realize this strategy. Required charge pressure is around 1 MPa and discharge pressure should be higher than 0.2 MPa. The reactor should be operated indoor with heat exchange to room air by natural convection and with the use of the electrolyzer pressure as driving force for the absorption. The characteristics are determined by parameters of the available electrolyzer and fuel cell.

2. Hydrogen absorbing material
Based on the Vegard’s law, hydrogen equilibrium pressure and thermodynamic functions change monotonously within the single phase of solid solutions. Based on the experimental data from literature the half-empiric model was developed [9]. Perspective alloy compositions for RHA-1 reactor are determined based on La-Ce-Ni ternary system. After preliminary studies, La$_{0.85}$Ce$_{0.15}$Ni$_5$ alloy with suitable performance is chosen for the use in RHA-1. Experimental batch of 18 kg La$_{0.85}$Ce$_{0.15}$Ni$_5$ alloy was prepared by vacuum-induction melting. Desorption isotherms of the alloy were measured by the Sieverts method [10] and presented in figure1, hydrogen storage properties are given in table 1.

![Graph](image)

**Figure 1.** PCT curves of La$_{0.85}$Ce$_{0.15}$Ni$_5$ at 294K, 313K and 333K.

**Table 1.** Thermodynamic characteristics of La$_{0.85}$Ce$_{0.15}$Ni$_5$.

| Composition      | Max. capacity (wt.%) | Reversible capacity (wt.%) | $\Delta H_{\text{des}}$, kJ/mol | $\Delta S_{\text{des}}$, J/mol K |
|------------------|----------------------|-----------------------------|---------------------------------|----------------------------------|
| La$_{0.85}$Ce$_{0.15}$Ni$_5$ | 1.3                  | 1.15                        | 33.2                            | 121.6                            |
3. Metal hydride reactor RHA-1

The RHA-1 reactor (figure 2) consists of four containers (1) made of 3mm thick stainless steel with the diameter of 168 mm. Each container is equipped with the mechanical filter (2) and the ball valve (3). Containers are connected to the common hydrogen collector (4) with the external ball valve (5) and the pressure gauge (6). Each container is filled with 4.5kg of intermetallic alloy La_{0.85}Ce_{0.15}Ni_{5} with overall net weight of 18 kg.

![Figure 2. Metal hydride reactor RHA-1.](image)

The reactor dimensions are 284×423×348 mm. The alloy activation was performed in the reactor fully submerged in a water bath by charge/discharge cycling at hydrogen pressures up to 2.2 MPa and temperatures from 15 to 95°C.

Maximum, hydrogen capacity of the RHA-1 is 2.7 st.m³, nominal capacity is set to be 2 st.m³, to ensure operation at room temperature without additional cooling/heating.

4. Experiment

4.1. Absorption

The scheme of experiments is presented in figure 3. Before the charge the reactor is evacuated with vacuum pump (V_{pump} in figure 3). At absorption, hydrogen from the standard gas cylinder at pressure of 1.08 MPa (P_{in}) is supplied to the reactor at the flow-rate of 100 st.L/h (1.67 st.L/min) via Bronkhorst EL-Flow series flow meter-regulator (FR_{in}). The room temperature, which was around 25°C, no additional cooling was provided.

The absorption experiment was carried out in stages, each stage started from the 100 st.L/h flow rate and was carried out until approx. 400 st.L (by flow counter) was charged into the RHA-1. The first and the second stages are presented in figures 4-7. The results on flow rate show typical critical behaviour: at the beginning the reactor maintains a constant flow rate, due to insufficient cooling by the natural convection the reactor heats up and cannot maintain the constant flow rate. After the crisis the flow rate drops to a value, which corresponds to a balance between thermal power, generated by reaction enthalpy and heat exchange with surrounding air. This flow rate could be called equilibrium flow rate, its value is around 1 st.L/min (60 st.L/h), which corresponds to 33 h charge to nominal capacity. The equilibrium flow rate slightly decreases due to the slope of pressure-composition isotherms (see figure 1) and vanishes when equilibrium pressure becomes equal to inlet pressure.
Figure 3. Scheme of the experimental setup. R – Reducer, FR – Flow meter (regulator), PS – Pressure sensor, V – Valve.

Figure 4. Hydrogen flow rate. Sorption. (First stage).

Figure 5. Hydrogen flow rate. Sorption. (Second stage).

Figure 6. Hydrogen volume. Absorption. (First stage).

Figure 7. Hydrogen volume. Absorption. (Second stage).
4.2. Desorption

At desorption the charged reactor RHA-1 is heated by surrounding air at 25°C and is discharged via ball valve \( V_{\text{out}} \) in figure 3, while outlet flow rate setpoint is 2 st.L/min (120 st.L/h). The hydrogen flow is controlled by the Bronkhorst EL-Flow series regulator \( FR_{\text{out}} \). Desorption is performed in stages, the results of the first and the second are presented in figures 8 and 9.

The results are similar to absorption, the subcritical stage of desorption is characterized by the constant flow rate. After the crisis, the flow rate steadily decreases to the equilibrium value of 1.2-1.3 st.L/min. Thus, the RHA-1 could supply hydrogen to operate a 100 W fuel cell during approx. 25 h.

![Figure 8. Hydrogen flow rate. Desorption (First stage).](image)

![Figure 9. Hydrogen flow rate. Desorption (Second stage).](image)

The energy capacity of the RHA-1 could be estimated as 2.5 kWh, and with the 12 V fuel cell stack it could replace a 210 Ah battery. Prices for LaN5 type alloys are about 20-30 USD/kg, thus, the metal hydride energy storage on the base of RHA-1 is quite cheap and costs of an energy storage is almost determined by a fuel cell price. Comparison of metal hydride/fuel cell energy storage with batteries is presented in table 2. Li-ion batteries and MH/FC systems are lighter and offer more charge/discharge cycles, while lead-acid batteries are much cheaper.

| 12V-210 Ah energy storage                      | Dimensions, mm | Weight, kg | Price, USD | Cyclic life |
|-----------------------------------------------|----------------|------------|------------|-------------|
| Metal hydride/Fuel cell system, incl.          | 400 × 500 × 450 | 30         | 2100       |             |
| RHA-1 metal hydride storage                   | 284 × 423 × 348 | 28         | 600        | >1000*      |
| 100 W fuel cell (Horizon H-100 PEM)           | 118 × 104 × 94  | 2          | 1500       |             |
| Lead-acid deep cycle AGM battery (FULLRIVER 12V - DC210-12) | 239 × 209 × 530 | 60.5       | 800        | 800@80%DOD  |
| Li-ion battery (WhisperPower WP-ION PowerPlus 12V LiFePo4) | 313 × 414 × 225 | 27         | 3800       | 5000        |

* depends on quality of hydrogen, could be regenerated

5. Conclusion

The modular metal hydride reactor for hydrogen accumulation RHA-1 is created. The reactor contains 18 kg of La0.85Ce0.15Ni5 alloy and has maximum hydrogen capacity of 2.7 st.m³ and nominal capacity of 2 st.m³. Experiments have shown that the reactor could be operated using the pressure difference between an electrolyzer (1 MPa) and a fuel cell (>0.2 MPa) with passive cooling/heating of air in
indoor conditions. The equilibrium charge rate is 1 st.L/min, the equilibrium discharge rate is 1.3 st.L. The RHA-1 could be used for long term energy storage and in combination with the 100 W PEM fuel cell is comparable with 12V 210Ah electrochemical batteries. The metal hydride/fuel cell system is lighter and more durable than lead acid batteries and cheaper than Li-ion batteries.

Acknowledgments
Authors from JIHT RAS thank the Russian Ministry of Science and Higher Education for support of investigations on hydrogen for energy storage (subsidy 05.607.21.0313 RFMEFI60719X0313).

6. References
[1] Sandrock G and Bowman R C 2003 *J. Alloy. Compd.* **356-357** 794-9
[2] Lototskyy M V, Yartys V A, Pollet B G and Bowman Jr R C 2014 *Int. J. Hydrogen Energ.* **39** 5818-51
[3] Hirscher M et al. 2020 *J. Alloy. Compd.* **827** 153548
[4] Afzal M, Mane R and Sharma P 2017 *Int. J. Hydrogen Energ.* **42** 30661-82
[5] Hahne E and Kallweit J 1998 *Int. J. Hydrogen Energ.* **23** 107-14
[6] Borzenko V, Dunikov D and Malyschenko S 2011 *High Temperature* **49** 249-56
[7] Tarasov B P, Bocharnikov M S, Yanenko Y B, Fursikov P V and Lototskyy M V 2018 *Int. J. Hydrogen Energ.* **43** 4415-27
[8] Dunikov D O and Blinov D V 2019 *Int. J. Hydrogen Energ.* **44** 7422-7
[9] Mitrokhin S, Zotov T, Movlaev E and Verbetsky V 2013 *J. Alloy. Compd.* **580** S90-S3
[10] Malyschenko S P, Mitrokhin S V and Romanov I A 2015 *J. Alloy. Compd.* **645** S84-S8