Metal hydride technologies for renewable energy

Alexey Kazakov¹, Dmitry Blinov¹,², Ivan Romanov¹, Dmitry Dunikov¹,² and Vasily Borzenko¹

¹Joint institute for high temperatures RAS, Krasnokazarmennaya str. 17a, Moscow, Russia
²National Research University "Moscow Power Engineering Institute" Krasnokazarmennaya str. 14, Russia

Abstract. Significant progress in the installation of renewable energy requires the improvement of energy production and storage technologies. Hydrogen energy storage systems based on reversible metal hydride materials can be used as an energy backup system. Metal hydride hydrogen storage systems are distinguished by a high degree of safety of their use, since hydrogen is stored in a solid phase, a high volumetric density of stored hydrogen, and the possibility of long-term storage without losses. A distinctive feature of metal hydride materials is the reversible and selective absorption and release of high-purity hydrogen. This paper presents experimental studies of LaNi5-based metal hydride materials with a useful hydrogen capacity of 1.0–1.3 wt.% H₂ with equilibrium pressures of 0.025 - 0.05 MPa and 0.1 - 1.2 MPa at moderate temperatures of 295 - 353 K for the hydrogen purification systems and hydrogen long-term storage systems, respectively. The applicability of metal hydride technologies for renewable energy sources as energy storage systems in the form of hydrogen is also shown.

1 Introduction

In recent years, there is a steady increase of installed capacity based on renewable energy resources. Renewable power accounted for 70% of net additions to global power generating capacity in 2017, the largest increase in renewable power capacity in modern history. The average growth rate of modern renewable energy technologies in the last decade has reached 5.4%. Solar PV additions were up to 29% relative to 2016, to 98 GW. More solar PV generating capacity was added to the electricity system than net capacity additions of coal, natural gas and nuclear power combined. Wind power also drove the uptake of renewables with 52 GW added globally [1]. A reduction of traditional hydrocarbon energy carriers’ consumption, development and installation of energy-saving technologies, increase of electricity production based on renewable energy sources contributes to improving the environmental situation in the world, rational use of energy resources and decentralization of energy supply.

The Russia’s long-term energy strategy provide for the development of new renewable energy technologies, as well as bioenergy technologies [2]. Renewable energy sector is an important part of sustainable energy development of Russia, since about 2/3 of the Russia's territory with population about 20 million is not covered by Unified Energy System [3]. The use of expensive imported fossil fuels in power plants with internal combustion engines is characterized by low efficiency and causes significant harm to the environment. Distributed renewable energy solutions, such as photovoltaic plants, small wind farms, biomass plants and micro hydropower plants, can provide electricity to remote areas or suffer from unstable power supply. Research and development of efficient autonomous power supply systems using locally available renewable energy sources is highly relevant. In addition, combination of such systems with energy storage in hydrogen - a universal and environmentally friendly secondary energy carrier, can improve overall system efficiency.

One of the main obstacles for the development of renewable based autonomous power plants for remote regions is the inconsistency of energy supply and consumption schedules. The uneven nature of operation modes for wind and solar power plants requires the creation of an energy storage system that will satisfy the needs of the consumer according to the load schedule he needs. Hydrogen energy storage systems can be a promising solution [4-7]. According to power plants based on wind or sun renewable energy sources, energy transformation can be shown as hydrogen production by electrolysis from renewable energy, hydrogen storage in a compressed or solid-state form and power generation by fuel cells or hydrogen combustion plants (including internal combustion engines) [4, 8]. Another promising solution is biological hydrogen production from local biomass, its purification and end-use in fuel cell to produce energy [9-11].

Among different technologies of hydrogen purification and storage, those ones based on metal hydride hydrogen storage systems, utilizing selective and reversible hydrogen uptake and release, can become economically feasible [12, 13]. In this case, hydrogen stored in solid state inside the metal hydride bed, what provides enhanced safety during operation. Present work is related to experimental investigations of several metal
Hydride materials and their implementation to hydrogen purification and storage systems.

2 Metal hydride technologies

Hydrogen storage by metal hydrides comprises an intermetallic alloy phase that has the capability to absorb and store atomic hydrogen in interstitial sites of metal lattice. Metal hydrides represent an exciting process of hydrogen storage, which is inherently safer than the compressed gas or liquid hydrogen storage. The typical interaction of metal hydrides with hydrogen can be expressed by following equation:

\[
M + \frac{x}{2} H_2 \leftrightarrow MH_x + \Delta H
\]

where M is metal/intermetallic alloy, H is hydrogen.

The interaction of metal and hydrogen can be divided into three regions [14]: a dissolution of hydrogen in the metal matrix forming solid solution (α phase); a coexistence of the hydrogen solid solution and hydride (α + β phase); hydrogen dissolution in hydride (β-phase) (Fig. 1).

[Image 57x416 to 286x517]

Fig.1. a) Sorption-desorption isotherm with plateau slope and hysteresis; b) idealized PCT diagram of «metal – hydrogen» system, adapted from [15].

During the formation of the metal hydride, hydrogen molecules are dissociated into hydrogen atoms on the metal surface, which insert themselves into interstitial spaces inside the lattice of intermetallic compounds and/or alloys. The effect is reversible and the direction is determined by the pressure (and temperature) of the hydrogen gas. If the pressure is above a certain level (the equilibrium pressure), the effect proceeds to the right to form hydride, whereas below the equilibrium pressure, hydrogen is liberated and the intermetallic matrix returns to its original state. The equilibrium pressure, itself, depends upon temperature. It increases due to expansion with an increment in temperature (and vice versa) [16].

The volume expansion between the coexisting α- and the β-phase corresponds in many cases 10–20% of the metal lattice. Therefore, at the phase boundary, large stresses are created that frequently lead to a decrепitation of brittle host metals including intermetallic compounds, resulting in a final hydride powder with a representative particle size of 1–10 μm.

The equilibrium pressure as a function of temperature is related to the changes of enthalpy ΔH and entropy ΔS by the Van’t Hoff equation:

\[
\ln \frac{P(H_2)}{P^0} = \frac{\Delta H}{RT} - \frac{\Delta S}{R}
\]

where \(P(H_2)\) is the hydrogen equilibrium pressure at α to β hydride phase conversion; \(P^0\) is the standard pressure (Pa), R is the ideal gas constant, and T is the absolute temperature (K).

The reversible hydrides of intermetallic compounds are primarily considered as promising materials for the hydrogen storage and purification. The intermetallic compounds can be represented by the general formula \(A_nB_nH_{x}\), where A is a hydride forming metal (La, Ce, Mn, Ti, Zr, V, Mg), and metal B does not interact with hydrogen under normal conditions (Ni, Co, Fe, Mn, Cr, Al and others). Depending on the metal A to metal B ratio, the IMCs can be classified in several basic types: AB, AB₂, AB₃, AB₅, AB, A₂B, Ti, V-based solid solutions. These materials have a remarkable combination of properties, including selective hydrogen absorption from gaseous mixtures, reversibility of interaction with hydrogen, mild operating conditions, high volumetric density of hydrogen in the solid state. Main disadvantage is low gravimetric density, which does not exceed 1 - 2 %wt., but it is not a significant limitation for stationary applications [12, 17]. To date, there are a number of practical application of metal hydrides in hydrogen storage systems [18-21], hydrogen compression [22-28], hydrogen purification [29-31].

Major advantages of the AB₅ type intermetallic compounds are the possibility of fine tuning of their operating conditions within moderate conditions at temperatures 273 – 373 K and pressures 0 – 1.0 MPa with a mixture of a compound composition. AB₅ intermetallic compounds can be easily activated, do not form protective oxide films, which is an advantage that gives AB₅ alloys an unusual resistance to small amounts of O₂ and H₂O in H₂. These impurities do not poison AB₅ alloys, only slightly lower the capacity. CO, H₂S are a strong poisonous gases, but the recovery of the initial properties of the alloy can be achieved by heating (100 °C) and passing pure H₂ through the alloy [17]. According to hydrogen production from renewables (wind, solar and biomass) most important properties for metal hydride storage system are low plateau pressure at near ambient conditions, cyclic stability and gas impurity resistance.

3 Experimental investigations of AB₅ intermetallic compounds

Two series of AB₅ alloys with low equilibrium pressures (LP alloys): LaNi₅₋ₓFeₓₐₓMnₓ₀,₃, LaNi₅₋ₓAlₓₐₓMnₓ₀,₂, LaNi₅₋ₓAlₓ₀,₃Mnₓ₀,₂ and high equilibrium pressures (HP alloys): La₅₋ₓₐ₋ₓₐ₀,₃Niₓ₀,₃, La₁₀₋ₓₐ₋ₓₐ₀,₇Niₓ₀,₃, MnNiₓ₋₀ₓₐ₋₁₈Feₓ₀,₈ₐ for different purposes were prepared by argon arc melting [32]. Low-pressure alloys are suitable for hydrogen purification from biologically produced gas. In addition, high-pressure alloys are perspective for long-term hydrogen storage produced from renewables by electrolysis.

X-ray diffraction measurements of AB₅ alloys have shown high homogeneity of the samples. XRD diagrams confirm that the structure of the samples belong to CaCu₅ type. PCT curves are measured in 295 – 333 K temperature range for all samples. PCT curves of both low-pressure and high-pressure alloys at 295 K are shown in Fig. 2, 3.
Partial substitution of Ni by Al, Mn, Fe significantly reduce hydrogen equilibrium pressure in comparison with original LaNi₅. Bigger atoms of Al, Mn, Fe enlarge crystal unit cell parameters leading to increase of interstitial holes in crystal structure. Highest reversible capacity is measured 1.2% wt. for LaNi₄.₈Al₀.₂, but hydrogen equilibrium pressure is too high for use in biohydrogen purification. LaNi₄.₈Fe₀.₃Mn₀.₁ alloy shows appropriate properties at near ambient conditions.

On the other hand, partial substitution of La by Ce or use of mixture of rare earth metals named as “mishmetal” Mn increases hydrogen equilibrium pressure. This effect appears because of decrease of crystal unit cell for Ce-substituted alloys. The particular behavior of Ce-substituted alloys has been attributed to the intermediate valence state of Ce (Ce⁴⁺, Ce²⁺) [33]. Two alloys La₀.₉Ce₀.₁Ni₅ and La₀.₉Ce₀.₁Ni₃ have suitable equilibrium pressures and hydrogen capacities for long-term hydrogen storage application.

Results of the thermodynamic measurements are listed in Table 1. Low pressure intermetallic compounds tend to form more stable hydrides than high pressure ones. On the other hand, high pressure intermetallic compounds have larger reversible hydrogen capacity at the same conditions.

Table 1 Thermodynamic parameters of AB₅ type intermetallic compounds

| MH alloy          | Pₜₐₓ  | Cₑₑₑ | ΔHₑₑₑ  | ΔSₑₑₑ  |
|-------------------|-------|------|--------|--------|
|                   | 295 MPa | wt.% | kJ/mol | kJ/mol |
| Low pressure alloys |       |      |        |        |
| LaNi₄.₈Fe₀.₃Mn₀.₁ | 0.049  | 1.0  | -36.8  | 119.7  |
| LaNi₄.₈Al₀.₂Mn₀.₂ | 0.033  | 0.9  | -35.0  | 107.2  |
| LaNi₄.₈Al₀.₂      | 0.074  | 1.2  | -35.5  | 116.9  |
| High pressure alloys |      |      |        |        |
| La₀.₉Ce₀.₁Ni₅     | 0.19   | 1.1  | -31.2  | 112.1  |
| La₀.₉Ce₀.₁Ni₅     | 0.36   | 1.3  | -33.1  | 123.0  |
| La₀.₃₆Ce₀.₆₄Ni₄.₁₅Fe₀.₈₅ | 1.18 | 1.1  | -28.3  | 115.₈  |

4 Metal hydride system for hydrogen purification

The separation and purification of hydrogen using metal hydrides is based on the selective hydrogen absorption by hydrogen storage materials. Metal hydride hydrogen separation system can be a promising solution for small-scale power generating devices based on biologically produced hydrogen. Hydrogen extraction from liquid phase during anaerobic fermentation by different types of metal hydrides is investigated in [34]. Miura et al. [35-37] presented 100Nl/h lab scale and 3 Nm³/h bench scale systems based on metal hydrides for hydrogen extraction from reforming gas. Surface modification (fluorination, electroless deposition, etc.) of metal hydrides was applied to improve poisoning tolerance against CO and CO₂ [30, 31, 38-40]. Our research team [41] showed practical applicability of metal hydride technology for biohydrogen separation from different gas compositions. Separation of hydrogen by flow-through technique was applied in tubular metal hydride reactor with external and internal heat exchangers. LP alloy LaNi₄.₈Fe₀.₃Mn₀.₁ and HP alloy La₀.₉Ce₀.₁Ni₅ are experimentally investigated in tubular metal hydride reactor RSP-8 (Fig.4) with external and internal heat exchangers for continuous hydrogen purification and storage. Metal hydride powder is in the annular gap as a thin layer between two heat exchangers to enhance thermal conductivity and increase overall purification efficiency. For LP alloy the purification rate of 81 st.L/h from a mixture containing 59 vol.% of hydrogen with recovery 94% was achieved. HP alloy shows lower purification efficiency compared with LP alloy because of a small pressure gap between inlet hydrogen pressure and equilibrium pressure of the alloy. On the other hand, HP alloy can release hydrogen for fuel cell supply without any additional heating.

Two reactors RSP -8 are integrated to lab scale power generation system “H2Biopower” as hydrogen purification and storage unit. HP alloy La₀.₉Ce₀.₁Ni₅ is used to supply PEM fuel cell at required pressure.
The “H2Biopower” system includes the following main parts (Fig.5):
1. Tank of modelled biohydrogen (gas mixture of hydrogen 50 % vol. and carbon dioxide 50 % vol.);
2. Metal hydride hydrogen purification and storage system based on two reactors RSP-8 developed by JIHT RAS (working hydrogen capacity of each metal hydride reactor is 110 Nl H₂);
3. Power plant based on fuel cell Hoppecke-E-200, power 200 W;
4. Automated Data Acquisition System based on NI PXI.

For continuous operation, a battery is provided that is connected to fuel cell in parallel. At the beginning of fuel cell operation, the battery is charged from the fuel cell. Then the required electric power is delivered to the consumer. Fuel cell operates at a load of 163 W for 23 minutes and at a load of 181 W and 18 min.

The demonstration lab scale power generation system “H2Biopower” shows practical applicability to integrate different pathways for hydrogen production such as dark fermentation through its purification and storage by metal hydrides and end-use in fuel cells. However, metal hydrides with low equilibrium pressures are necessary for direct hydrogen extraction because hydrogen partial pressure does not exceed 0.04-0.06 MPa in produced
5 Metal hydride system for stationary hydrogen storage

Metal hydrides are known as a potential efficient, low-risk high-density hydrogen storage materials since the late 1970s [17, 44-46]. The use of metal hydride materials is characterized by compactness, safety, simplicity and flexibility. Application of metal hydrides can provide high volumetric hydrogen storage capacity, safety and reliability, high purity of the supplied H2. Lower pressure of stored hydrogen and limited rate of hydrogen release improves operational safety in the case of accidental leaks or even rupture of the hydrogen storage containment.

In order to achieve a good performance, the metal hydride reactor must be properly designed. However, the coupling process of porous flow, heat and mass transfer, and reaction kinetics in the reactor are highly transient and complicated, and many issues have to be taken into account in a realistic reactor scheme [47].

Several types of reactor design are proposed by laboratory of hydrogen energy technologies [41, 48, 49]. The design of the metal hydride reactor RS-1 is most suitable for long term stationary hydrogen storage. The reactor is stainless steel tube type heat exchanger with inner channels for liquid heating and metal hydride placed in the annular gap between the channel for liquid and the outer wall of each tube (Fig. 8). The reactor consists of 49 tubes with length of 65 cm united by common hydrogen collector. Each tube has stainless steel mesh filter at the inlet to retain metal hydride inside the tube. Total weight of La0.4Ce0.1Ni1.6 metal hydride is 81 kg at 70% fill of each tube.

Maximum capacity of RS-1 reactor is 12 Nm³ H2, which indicates full charge of metal hydride powder bed. Nominal capacity is 10 Nm³ H2. Ce-substituted La0.4Ce0.1Ni1.6 intermetallic compound is used as hydrogen storage material. Solid state hydrogen storage system in an explosion proof design for backup power supply is developed based on RS-1 metal hydride reactors (Fig.9). Technical characteristics are presented in Table 2.

![Fig. 8. Metal hydride hydrogen storage reactor RS-1: general view and frontal section.](image)

![Fig. 9. Long-term stationary metal hydride hydrogen storage system for backup power supply.](image)

| Technical characteristics |  |
|---------------------------|---|
| Hydrogen flow rate, Nm³/h | 10 |
| Hydrogen purity at inlet, %vol. | 99.95 |
| Hydrogen capacity, Nm³ | 20 |
| Hydrogen purity at outlet, %vol. | 99.9995 |
| Working hydrogen pressure, MPa | 0.4 |
| Heat transfer fluid temperature, ºC | 0–95 |
| Heat transfer fluid flow rate, Nm³/h | 0.8±2 |
| Power consumption, kW | 0.3 |
| Thermal energy consumption rate at reactor charge, kW | 6 |

6 Conclusions

Hydrogen energy storage systems based on reversible metal hydride materials show their perspectives in implementation with rapidly growing renewable energy production technologies. AB₅ type intermetallic compounds have many advantages such as easy activation, impurity tolerance, mild operating conditions, high volumetric density of hydrogen in the solid state and variety of compositions to meet the requirements for practical application in different fields.

LaNi₅ based intermetallic compounds substituted by Ce, Al, Mn, Fe are prepared and investigated for different purposes. Reversible hydrogen capacities reach 1.1 – 1.3%wt. and hydrogen equilibrium pressures are in a wide range from 0.033 to 1.18 MPa for investigated alloys.

The demonstration lab scale power generation system “H2Biopower” is developed including two RSP-8 metal hydride reactors as a hydrogen separation system. One fully charged RSP-8 metal hydride reactor is able to supply fuel cell during 45 minutes to produce electric...
energy. Practical applicability to integrate different pathways for hydrogen production such as dark fermentation through its purification and storage by metal hydrides and end-use in fuel cells is shown.

Long-term hydrogen storage system with capacity 20 Nm³ H₂ based on RS-1 metal hydride reactor filled with La₅(Ce₀.₁₅Nd₀.₈₅)N₃ intermetallic compound for backup power supply is presented.

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