INTERMETALLIC COMPOUNDS FOR ENERGY STORAGE

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Abstract

Modern metallurgy has a close collaboration with many other industrial fields and also with gas production industry. Using of hydrogen and nitrogen atmospheres in steel production and rolling show us metallurgy industry in a role of a big consumer of industrial gases. But from other side, metallurgy plants and companies always plays the role of suppliers for gas industry. This type of collaboration is not new, but in last decade's a development of powder metallurgy provides new possibility for two industries connection on the way of creation new types of energy storage systems, based on metal hydrides.

Using of intermetallic compounds for hydrogen storage in solid form with the formation of chemical compounds (metal hydrides) with the possibility of sorption and desorption, provides energy storage systems with hydrogen densities greater than in the liquid and gaseous states.

Hydrogen storage in intermetallic systems can be the most energy efficient and less energy consuming way of hydrogen storing in the near future. In present article the description of real applications and conditions of intermetallic systems, and possibilities to use metal compounds for creation energy storage systems and using that systems in real life is provided.

Keywords: Metallurgy, powder metallurgy, intermetallic compounds, metal hydrides, energy storage

1. HYDROGEN STORAGE

Among all the kinds of fuel, hydrogen has the highest gravimetric and calorific value 120 MJ/kg (33 kWh/kg) which is several times higher than many of liquid hydrocarbons ~ 42 MJ/kg [1].

Hydrogen using as an energy source is not new and comes from 70´s on the background of the oil crisis in 1973. In 90´s with the development of fuel cell technology, transport companies have started work on the creation vehicles that use hydrogen as a fuel.

The most important energetic process is the combustion of hydrogen, which is accompanied by the release of large amounts of energy and water production without any harmful emissions.

The disadvantage of gaseous hydrogen as the energetic carrier, unlike liquid hydrocarbons, is its low density. Hydrogen storage in solid form based on formation of chemical compounds (i.e. metal hydrides), with the possibility of sorption and desorption (reversible manner) and with a big hydrogen storage density. There are several ways how to store hydrogen in its pure form, such as:

1) Storage of gaseous hydrogen under high pressure in pressure vessels, cylinders or containers with pressure up to 45 MPa. In that case is necessary include to the overall energy balance also compression costs - roughly 15 % of the H_2 stored energy).
2) Production and storage of liquid hydrogen, known as cryogenic methods, at temperature close to 20 K, where are costs for liquefaction and thermal losses are estimated around 30 % of the H_2 stored energy).

2. STORAGE SYSTEMS STRUCTURE

Hydrogen can be stored in solids by adsorption or absorption. During adsorption process, hydrogen is attached to the surface of a material either as hydrogen molecules or as hydrogen atoms. In absorption, hydrogen is dissociated into H-atoms, and then the hydrogen atoms will be incorporated to the crystal lattice of metal (**Figure 1**).

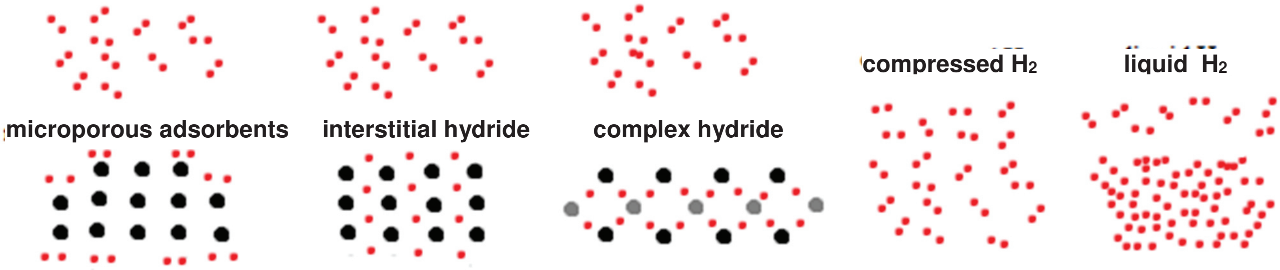

Figure 1 Hydrogen storage systems structure

Reversible formation reaction of metal hydride can be reached by two ways:

Direct interaction hydride-forming metals with gaseous hydrogen: $Me + nH_2 \leftrightarrow MeH_n + Q$

Electrochemically: $Me + nH_2O + e^- \leftrightarrow MeH_n + nOH^-$

Hydrogen storage in intermetallic compounds at working temperatures sharply differing from ambient temperatures, significantly increases the total energy consumption for storage system daily exploitation. Working temperatures depended from properties of using metals and also from reaction kinetics.

3. PROPERTIES OF DIFFERENT STORAGE SYSTEMS

Palladium (Pd) and its alloys is one of the best metals for hydrogen storage [3], but the price of this material does not allow its use widely [4]. Complex hydrides have the biggest storage hydrogen density in comparison with other types of hydrides, but the most of them are not relevant for reversible hydrogen storage systems. In the **Table 1** are shown the characteristics of different hydrides which are usually used for hydrogen storage.

The micro porous adsorbents and interstitial hydrides have a same density and volumetric capacity but the second one could work at an ambient temperature.

Table 1 Basic types of hydrogen storage systems and their properties [2]

Hydrogen storage type		**Gravimetric capacity (wt.%)**	**Volumetr. capacity (kg/m^3)**	**Working temp. (K)**
Compressed (70 MPa)	CGH_2	100	39	ambient
Liquid	LGH_2	100	70.8	20
Microporous adsorbents	Zeolite- based	≤ 7.5	≤ 48	77
Interstitial hydrides	$LaNi_5$	1.49	87	~ ambient
Complex hydrides	Mg_2NiH_4	3.6	98.8	373-473

Anyway, all discussion and searching for new or best material for energy storage leads to compromise between system cost and weight capacity. System cost consists mainly from price of using storage material or alloy and operation costs, that include energy losses for heat transfer during sorption and desorption cycles. It means in ideal case it must be system based on cheap and wide spread materials, with a big store weight capacity, which can provide stable exploitation characteristics at temperatures close to ambient, during big amount of charging - discharging cycles.

4. APPLICATION OF STORAGE SYSTEMS

4.1. Stand-alone power systems

Private houses and industrial facilities, which identify completely independent of any vendor and an external source, always attracted people in the whole world. The main task is an integration of all presented technologies into a single power system adapted for home and industrial applications. Solar and wind power systems and autonomous backup power supply as well as fuel cells are widely used in industry, vehicles, etc. and also used for household needs. There are also ready-made solutions for the integration of photovoltaic power systems and hydrogen. Such hybrid power systems were also examined and tested by the authors in other studies [5, 6, 7].

For the widespread implementation of solar-hydrogen systems, there are several obstacles, one of which is the high investments costs of systems components and the general safety risks related to storing of hydrogen. Hydrogen is the lightest gas; it is lighter than air, extremely volatile and flammable. Furthermore, when gaseous hydrogen is stored under high pressure, hydrogen can penetrate through the wall of the tank or vessel and diffuse to the surroundings. For solving problem of safety and reliability of hydrogen storage, metal hydrides (i.e. hydrogen in bonded form) have been proposed to use in these systems.

4.2. Description of demonstration system

Experimental independent stand-alone energetic system with implemented hydrogen technologies was developed and realized in Laboratory of Fuel cells Application at VSB-Technical University of Ostrava where is in operation from fall 2010. This independent energy system basically consists from solar panels, several power inverters, as well as of accumulator batteries - the standard set of equipment for energy production and independent power supply systems (**Figure 2**).

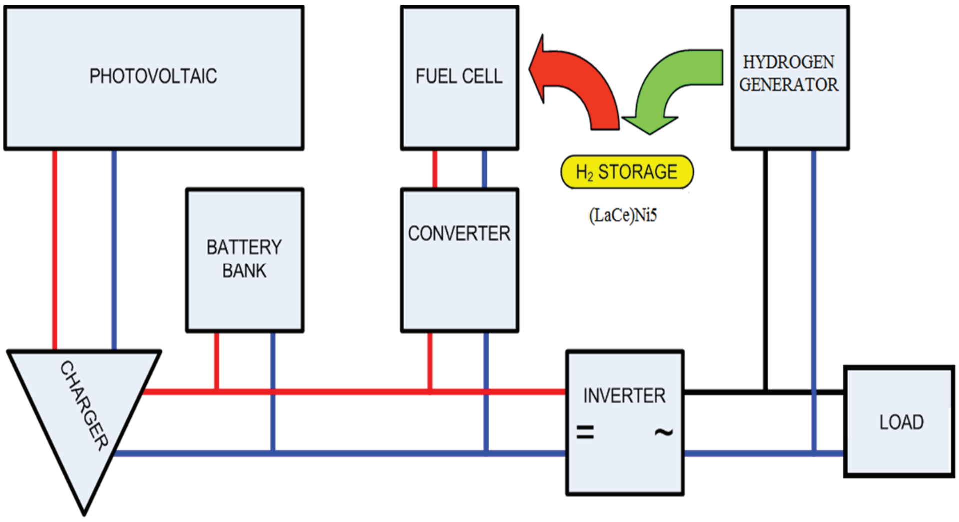

Figure 2 Basic scheme of the system

The circuit of power supply, looks like a standard scheme - solar panels produce electricity, which is partly used for the current supply, partially stored in batteries. The primary energy resource installed within the power system is, therefore, represented by an array of photovoltaic panels located on the laboratory roof. The photovoltaic system (PVS) is made of 12 pieces photovoltaic panels with the total installed power of 1.98 kWp. The direct-current (DC) power is fed into the DC/DC converter (charger) and subsequently forwarded to the direct-current bus with nominal voltage of 48 V defined by the auxiliary accumulator storage bank linked with the bus. The nominal capacity of power storage bank that consist from four accumulators in series connection is 75 Ah, which defines its total power capacity of 3.6 kWh.

The main function of the accumulator storage bank in the energetic system is accumulation of electrical energy produced by photovoltaic panels that does not directly cover consumption of a load. Another function of the accumulator power storage is the functionality as power “buffer” from which electrolyzers consumption is covered under a defined temporal constraints of the photovoltaic system that are caused by immediate worsening of local meteorological situation. The remaining energy is stored in batteries, the capacity of which is sufficient for equipment work. With good weather, solar panels by solar energy produced needed amount of energy that can be used for the second part of the energy supply system - electrolyzers.

The said direct-current bus is also provided with a stabilizing DC/DC converter for connection of one of the essential hydrogen technologies - a Polymer Electrolyte Membrane (PEM) type fuel cell. As the specific fuel cell was after several necessary adjustments its electronic systems used the Ballard’s NexaTM Power Module readily available on the market. Production of hydrogen in the system is handled by an electrolyzer, which operated during the period of power surplus from photovoltaic source to store the power in hydrogen.

The electrolyzer available for production of hydrogen was the laboratory unit low temperature PEM type Hogen GC600 connected to the system via an alternating-current (AC) bus. The electrolyzer is able to supply approximately 0.6 NL per minute of gaseous H_2 at the pressure up to 1.38 MPa.

Table 2 Power system characteristics for of inconvenient solar period

Energy (kWh) amount of H_2 [NL]	**Supplied**	**Drawn**
Energy supplied from PVS	10.008	-
Energy at charger output	9.756	-
Energy at inverter input	24.139	-
Energy drawn from the system	-	19.596
Energy drawn by load	-	18.021
Amount of hydrogen produced	-	100.53
Equivalent amount of energy in H_2	-	0.296
Energy drawn by electrolyzer	-	1.575
Amount of hydrogen consumed	12 631.0	-
Equivalent amount of energy in H_2	37.173	-
Energy supplied by fuel cell	14.138	-
Energy supplied from PVS	25.267	-
Energy at charger output	24.605	-
Energy at inverter input	34.081	-
Energy drawn from the system	-	30.564
Energy drawn by load	-	23.506
Amount of hydrogen produced	-	465.12
Equivalent amount of energy in H_2	-	1.369
Energy drawn by electrolyzer	-	7.058
Amount of hydrogen consumed	8 138.8	-
Equivalent amount of energy in H_2	23.952	-
Energy supplied by fuel cell	8.911	-

The produced gaseous hydrogen can be stored by standard way - in 3 standard pressure vessels with water volume of 50 L. The total capacity of stored H_2 equals to water volume of 150 L, which corresponds to approximately 2 Nm^3 (normal cubic meters; gas volume related to normal pressure 100 kPa and temperature 20 °C) of hydrogen gas in a bundle, i.e. which is approx. 650 NL (normal liters) per one pressure vessel at the maximum pressure in electrolyzer.

Second way - is to store hydrogen in form of metal hydride. Produced by electrolysis, hydrogen is supplied to the storage system - steel cylinders filled by metal alloy based on the intermetallic compound AB_5 type, with capacity from 1.5 up to 10 Nm^3 of H_2 for each storage vessel. For energizing of the private sector and small production areas the pressure of hydrogen production and storage must be not very high for safety reasons and regulation. With metal hydride storage tanks that pressure could be not more than 1.0-1.5 MPa. Low storage pressure with big amount of stored hydrogen together with a small physical volume of storage vessels provides a big advantage for final user of that system.

Finally hydrogen is supplied to the fuel cells. In the fuel cell hydrogen recombined with atmospheric oxygen to produce electricity and steam formation (**Figure 3**).

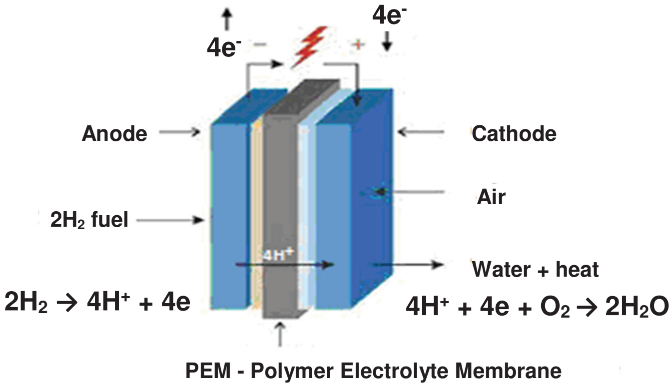

Figure 3 Fuel cell basic work princip

4.3. Hydrogen production and storage system characteristics

The pressure of H_2 production and storage depends on the needs of a particular project, and for large or industrial facilities can be up to 3 MPa, without additional compressor installation (**Table 3**).

Table 3 Range of system characteristics depending on the specific needs

System characteristics	**Range**	**Unit**
Storage or charging H_2 pressure	0.2-3	MPa
H_2 system performance (for 1 electrolyzer)	1.5-100	Nm^3 / h
H2 storage capacity metal hydrides based (for 1 storage tank)	1.5-10	Nm^3
Power consumption (for 1 electrolyzer)	10.5-490	kWh
	7- 4.9	kWh/Nm^3
Power supply for electrolysis	380	V
	50/60	Hz
Electrolyzer unit weight	270-15000	kg
Electrolyzer unit dimensions, L,P,H	940x540x1500 - 9700x2500x2700	mm

In laboratory installation was used metal hydride storage system, based on lanthanum, cerium and nickel. At the same time researching goes to the way of alloy modification for increasing H_2 storage capacity. In general view hydrogen storage systems looks like a stainless steel cylinders filed by alloy and internal cooling system placed around active zone of sorption (**Figure 4**).

Figure 4 General wiev of H_2 storage tank based on (LaCe)Ni_5 alloy, 1500 L and 10 000 L of H_2

(LaCe)Ni_5 - the alloy, which used in experimental works, has following characteristics (**Table 4**).

Table 4 Parameters of metall hydride hydrogen storage system

System characteristics	**Range**	**Unit**
Nominal system capacity of H_2	1500	NL
Weight of system	12	kg
Weight of active material (alloy)	9	kg
Water volume (based on real dimension)	4.1	L
Maximal pressure	2.5	MPa
Charging pressure	1.5	MPa
Charging temperature	25	°C
Charging time	~60(with cooling)	min
Discharging pressure	0.2 -0.7	MPa
Discharging temperature	25 - 45	°C

5. THE MEASUREMENTS AND TEST RESULTS

In experimental work were studied properties of hydrogen storage system in a real work conditions, and the effect of such parameters as a hydrogen flow, pressure and sorption and desorption temperatures.

5.1. Charging

Charging took place at ambient temperature and for sorption was used a cooling system, because reaction of metal hydride formation is exothermic reaction and heat must be remove from the system during charging. The cooling system was feed by chilled water with ice inside of the water tank. Temperature of water like a cooling agent was ~10 °C. This not so critical temperature change in comparison with tap water temperature (~15 °C) provided the significant change of adsorption speed and fuller filling of storage tank by hydrogen. The difference in hydrogen capacity between two charging's ~233 NL of storing hydrogen after 60 minutes of charging, which means more than 15% difference from maximum storage capacity.

5.2. Discharging

For discharging of storage system tank was used a fuel cell type "Nexa Ballard System" like a real device of useful, safety and stable hydrogen consumption. Stable hydrogen consumption or constant hydrogen flow is a most important parameter for user or hydrogen consumer (in that case consumer is a fuel cell) and thanks to integrated in a fuel cell mass flow meter was possible to control and regulate the discharge flow. In other way free discharge flow without regulation provide very sharp temperature decreasing on a hydride side.

Presence of fuel cell together with the hydrogen storage can be used like the energy storage system and gives possibility to use hydrogen like a source of electrical energy. The connection of fuel cell to the electric load instead of the any grid could provide the effective regulation of discharging flow depends on the fuel cell consumption profile - the regulation of thermal impact during both reactions cycles

Desorption is an endothermic reaction and tank temperature must be keep in range 25-45 °C. Measured parameters during cycle of desorption with stable hydrogen consumption shows in **Figure 5**.

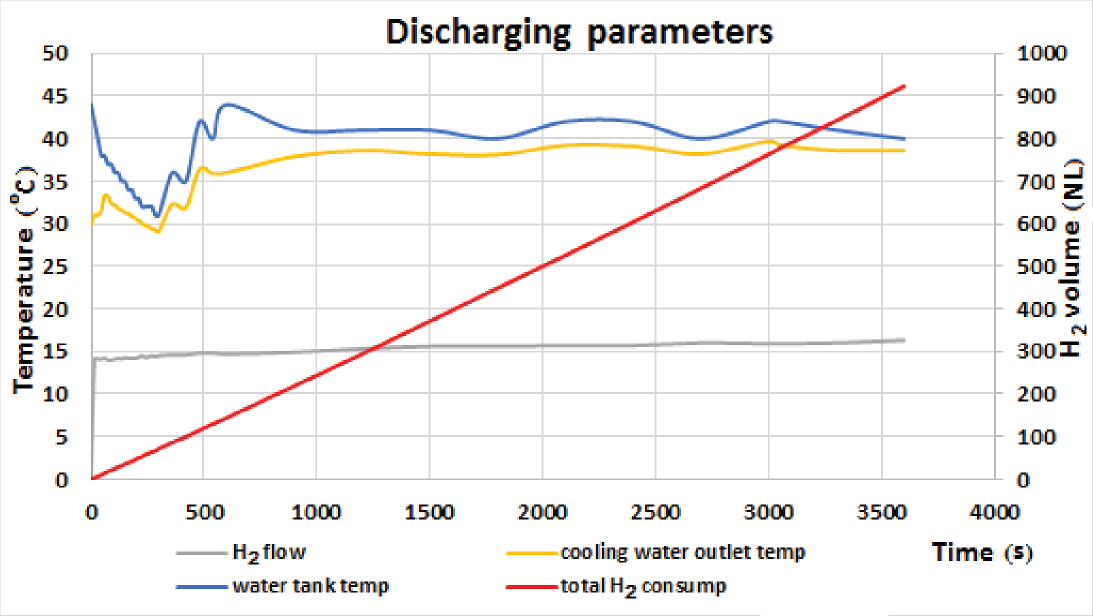

Figure 5 System parameters during discharging

From the hydrogen consumer side it will be interesting only amount of hydrogen which system could give during the discharging, and only discharging process could give a real information about system capacity.

6. CONCLUSION

Studies of properties, kinetics of different alloys based on metals like La, Ce, Ni or another metals together with polymers, modification of traditional alloys and creation of totally new artificial materials will provide a development of new energy area - hydrogen energetics and hydrogen mobility. Low storage pressure with big amount of stored hydrogen together with a small physical volume of storage vessels provides a big advantage for final user of that system in comparison with classic hydrogen storage methods.

That amount of hydrogen (~1500 L) could be stored at electrolyzer output pressure 1.38 MPa:

- in 2 standard hydrogen 50 L gas cylinders with capacity 13.8 NL of H_2 / 1 L of tank water volume,
- in the compact and safety metal hydride tank at ambient temperature, with capacity 365.8 NL of H_2 / 1 L of tank water volume,
- full hydride tank (1500 NL) could provide 100 minutes of continues fuel cell work with constant hydrogen flow 15 NL/min.

Next researching and modifications of LaCe and other alloys could provide increasing of hydrogen storage capacity and material costs decreasing, that allows to use these storage systems not only in laboratory scale.

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