

The Possibilities of Obtaining Hydrogen from Renewable Energy Sources and its Subsequent Storage

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Abstract— The article analyzes the possibilities of hydrogen producing by electrolysis of water using electricity derived from renewable energy sources and its storage. Possibilities of usage of hydrogen compared to other energy sources seem to be mainly favourable because of the high conversion efficiency hydrogen to electricity and minimal environmental impact. If hydrogen is produced from renewable sources and used in fuel cells, and the resulting product is only heat and water, therefore it can be concluded that hydrogen is an environmentally clean fuel.

Keywords— Hydrogen, renewable energy, electrolysis, storage, adsorption, metal hydride

I. INTRODUCTION

Price fluctuations in markets for fossil fuels, their limited stocks, geopolitical pressures and growth of energy consumption are currently defining the important position of RES. The area of RES is, for understandable reasons, among the priorities of both European and national energy policy. At present, attention is also directed on the area of hydrogen production from RES.

Since electric energy production using photovoltaic panels or wind is marked by inequalities caused by unstable natural conditions, these sources represent a significant burden for the power transmission and distribution system.

In order to overcome the variability of output powers of photovoltaic and wind power plants, there is an option of storing the produced energy in addition to the energy transfer. Electric energy can be stored only if converted into another form of energy. Just hydrogen technologies are used for storage of the energy produced from RES at volatile performance right at the production site. The hydrogen thus produced can then be used either as a fuel for transporting or re-producing electric energy by using fuel cells.

The principal advantage of hydrogen as opposed to electric energy is the possibility of its storage. When considering more advanced hydrogen production technologies, such as high-temperature electrolysis, it is possible (at least partially) to also use thermal energy, which positively affects the overall conversion efficiency. It should be noted that before hydrogen acquires economic importance when utilizing its energy potential, there must be easy access to its sufficient quantity; it must be cheap, safe and efficient.

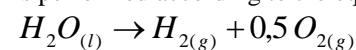
Research in the area of the element and its use for the production of electric energy is at a high level and continues at

a breakneck tempo. Interest in hydrogen as an energy source of the future, mainly because it is clean and the richest energy source per unit of weight. For its efficient use, it is necessary to comprehensively address the problems resulting from its production, storage and transport.

II. THE POSSIBILITIES OF OBTAINING HYDROGEN

Hydrogen is a lightweight and virtually ubiquitous gas, able to issue its energy not only through combustion after a single transmission and distribution through pipeline, as well as in its liquid state, but also through direct conversion into electric energy in the fuel cells. It is not toxic and only water or water vapour is the waste product of its combustion.

Hydrogen is mainly spread in the form of the most known molecule – water. Its re-acquisition is subject to chemical decomposition, called water electrolysis. Water decomposition is performed according to the equation [2]:



$$\Delta H_{298}^{\circ} = 286,25 \text{ kJ}$$

$$\Delta G_{298}^{\circ} = 237,36 \text{ kJ}$$

(1)

Sustainable hydrogen production is the decisive factor for the development of the entire hydrogen economy. Hydrogen can be produced in several ways, which are currently dominated by the steam reforming of natural gas, followed by coal gasification, i.e. fossil fuels (90% of the production). Fossil fuel hydrogen produces increased greenhouse gas emissions, negating the benefits of hydrogen.

For this reason, it is necessary to search for suitable alternative sources of energy for the production of hydrogen in water electrolyzers. There is a possibility of producing the hydrogen from so-called “green energy” through electrolysis, high temperature water decomposition, gasification, biomass pyrolysis. The economic potential of renewable energy sources restricts the low energy density associated with low efficiency and the large differences between installed add-ins and the actual performance caused by discontinuous energy currents (e.g. wind or solar energy). The space to increase the usable capacity of RES is also an increase in the efficiency of electrolyzers. This will achieve higher conversion efficiency. Significant progress has been made in this direction through electrolyzers using a PEM (Proton Exchange Membrane). The

principle of function of the PEM electrolyser is illustrated in Fig. 1.

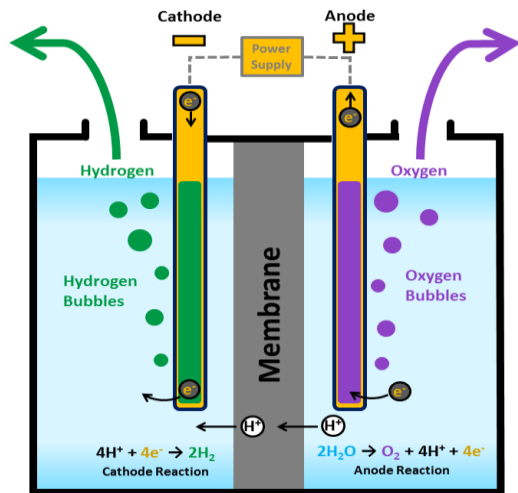


Fig. 1. Production of hydrogen through water electrolysis.

Water molecules decompose on the anodes through the catalytic effect of platinum on the oxygen, electrons and hydrogen nuclei (protons) that pass through the PEM. Nuclei are coupled with electrons to form hydrogen molecules on the cathode. The minimum theoretical amount of energy needed to produce 1 m^3 is 2.94 kWh.

III. POSSIBILITIES FOR HYDROGEN STORAGE

Hydrogen storage is considered to be one of the most critical issues, making it necessary to address for the implementation of economic and viable hydrogen-energy systems. Without efficient storage systems, it will be very difficult to achieve favourable values for the hydrogen economy. Physical limits for hydrogen storage are the density of compressed and liquid hydrogen. The hydrogen storage specifications arising from its physical and chemical properties are shown in table I.

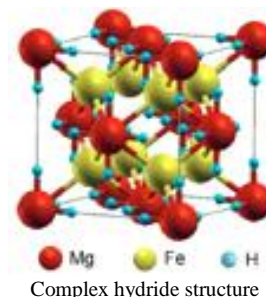
TABLE I. Physical and chemical properties of hydrogen compared to commonly used fossil fuels.

Fuel	Temperature (°C)	Density (kg·m ⁻³)	Specific Volume (SV) (l·kg ⁻¹)	Multiple SV with regard to petrol	Calorific Value (MJ·kg ⁻¹)	Energy density (ED) (MJ·l ⁻¹)	Multiple ED with regard to petrol
Hydrogen 1 bar	20.00	0.084	11,939.00	8,354.70	119.00	0.01	0.0003
Hydrogen 250 bar	20.00	17.00	58.80	41.15	119.00	2.02	0.0650
Hydrogen 350 bar	20.00	22.20	45.20	31.60	119.00	2.64	0.0850
Hydrogen 700 bar	20.00	39.00	25.90	18.14	119.00	4.60	0.1500
Liquid hydrogen	- 253.00	71.08	14.10	9.85	119.00	8.46	0.2700
Liquid propane	20.00	498.00	2.00	1.40	46.30	23.08	0.7400
Liquid petrol	20.00	700.00	1.43	1.00	44.50	31.15	1.000

Source: The Czech Hydrogen Technology Platform

There are currently three types of hydrogen storage technologies:

- 1.) *Hydrogen (gas phase)* – in high-pressure storage vessels, this method is uneconomic because the storage of hydrogen gas is limited by its volume due to low density, thus increasing the cost of storage vessel materials.
- 2.) *Hydrogen (liquid phase)* – condensation requires energy, an environment with high volatility, and a cryogenic temperature in a perfectly insulated tank.
- 3.) *Metal Hydrides* – Hydrogen storage, compact and secure at an ambient temperature.



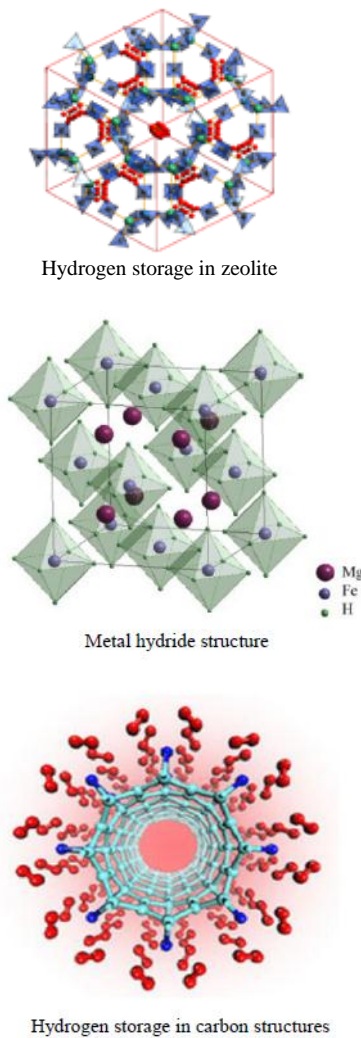


Fig. 2. Possibilities for hydrogen storage.

A. Storage of Hydrogen in Pressure Vessels

The amount of hydrogen that can be stored in pressure vessels is mainly influenced by the amount of used absolute pressure. We use state equations of real gas to describe the amount of stored gas. The deviation from ideal gas expresses the compressibility factor. This can be calculated from Noble-Abel's state equation for real gas, representing the simplified form of the Van der Waals state equation by neglecting the correction for the mutual attraction of molecules [3]:

$$Z_{vyp} = 1 + \frac{b \cdot p}{R \cdot T} \tag{2}$$

where Z_{vyp} is the compressibility factor computed from the Noble Abel equation, b - correction to its own molecule volume. For hydrogen: $b = 15.84 \cdot 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$, R universal gas constant, $R = 8.31447 \text{ Jmol}^{-1} \cdot \text{K}^{-1}$.

By substituting the compressibility factor into the real gas state equation:

$$p \cdot v = Z_{vyp} \cdot r \cdot T \tag{3}$$

where v is the specific volume of hydrogen ($\text{m}^3 \cdot \text{kg}^{-1}$).

We achieve the following relationship from the gas density equation (2):

$$\rho = \frac{p}{\left(1 + \frac{b \cdot p}{R \cdot T}\right) \cdot r \cdot T} \tag{4}$$

Where ρ is the density of hydrogen ($\text{kg} \cdot \text{m}^{-3}$), p - absolute pressure (Pa), r - the specific gas constant of hydrogen $r = 4124.65 \text{ J kg}^{-1} \cdot \text{K}^{-1}$, T - thermodynamic temperature (K).

With respect to the correction to the molecules' own volume, b is the amount of hydrogen that can be stored through compression as expressed by the given density shown in Fig. 3. The resulting density of hydrogen, thus the amount of hydrogen that can be stored at a given pressure and temperature in a container at a volume of 1 m^3 , also depends on the operating temperature. With a standard storage pressure of 70 MPa, 37 to 43 $\text{kg} \cdot \text{m}^{-3}$ may be stored at a temperature range of 20 to 40 °C.

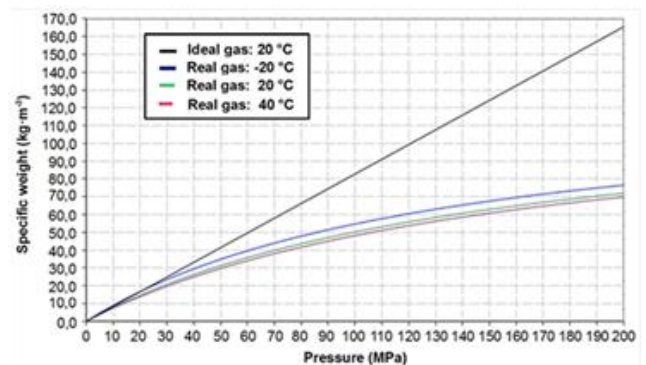


Fig. 3. Specific weight (density) of hydrogen at various pressures and operating temperatures.

Increasing the storage pressure is problematic in terms of the strength of the pressure vessels, while the calculated wall thickness increases with pressure, increasing the total weight of the device. This is reduced by the use of pressure vessels with an internal insulating container (Al, steel, plastic) coated on the outside with a composite material. One disadvantage is also the high hydrogen diffusivity of metals at high pressures, causing mass losses mainly in the contact surface areas of the reduction valves and other accessories.

By increasing pressure in pressure vessels, the change of hydrogen density at high pressures is small, while the cost of compression along with investments in pressure vessels increases.

B. Storage of Hydrogen in a Liquid State

By reducing the temperature below the boiling point of 20.39 K (-252.76 °C) and removing the condensation heat, its state changes to liquid. In a liquid state, hydrogen can be stored at a density of $70.79 \text{ kg} \cdot \text{m}^{-3}$ at normal pressure. The problem is low temperature when during its increase it may return to evaporation and thus specially isolated cryogenic vessels must be used.

Also despite the sufficient insulating ability of cryogenic vessels, evaporation losses occur due to the receipt of

evaporation heat from the surroundings. Due to the existing heat flow from the surroundings into the interior of the vessel, hydrogen evaporates inside the vessel, resulting in the gradual increase of pressure. Upon reaching the maximum operating pressure (approximately 450 kPa), a safety valve is opened, which releases the evaporated hydrogen into the atmosphere, lowering the pressure in the vessel. The amount of released hydrogen is called evaporation loss.

Isolation does not only reduce the heat flow from the surroundings but it also protects against contact with the surroundings. Upon the access of air, there is the condensation of water vapour contained in the air and its subsequent freezing. In addition, atmospheric oxygen condenses below 90 K and freezes at 50 K. Nitrogen condenses at 77 K and freezes at 63 K. The knowledge of these temperatures indicates that exposure to atmospheric gases will arise in contact with such low temperatures.

C. The Adsorption of Hydrogen to Carbon Materials

When storing 4.1 kg of hydrogen in a pressure vessel with a volume of 0.1 m³, there is required pressure at 75 MPa at a temperature of 298 K but only 15 MPa pressure at a temperature of 77 K. Pressure can be reduced to 6 MPa if activated AX-21 [4], [5] coal pellets are added to the vessel. The adsorption of gases on the surface of the activated carbon is dependent on the contents of the material's surface. Micropores with a diameter of (1-2)·10⁻⁹ m have the greatest impact on the ability to store hydrogen. Macropores with a diameter of (100-200)·10⁻⁹ m have no impact on adsorption. With commercially available Busofit activated carbon, the specific surface area is 1140 m²·g⁻¹ to 1570 m²·g⁻¹, g l g⁻¹, with a mostly microporous material with a macroporous surface of 0.5-2.0 m²·g⁻¹. The main disadvantage of using activated carbon is the used temperature in the area of liquid nitrogen (77 K), at which the desired storage volume is reached. 0.0223 kg of hydrogen per 1 kg of fibre (2.23% by weight %) is stored at the temperature of the Busofit-M8 fibre. Also, despite the relatively low temperature, it is possible to reduce costs compared to the use of liquid hydrogen, since nitrogen cooling is cheaper, more energy-efficient and more affordable. The storage of hydrogen gas at a temperature of 77 K is about 20% cheaper than storage in liquid form.

The ability to store hydrogen depends on the surface size of the adsorbents, whereby larger surfaces are obtained with the adsorbents in powder form. Fig. 4 shows the weight percent of hydrogen stored at a temperature of 77 K and various pressures in powder form and pellets. The advantage of carbon materials is mainly their low density, large porous structure and chemical stability. The adsorption and desorption of hydrogen in carbon nanoparticles, nanoporous materials and activated carbon show little or no hysteresis (Fig. 5) and have relatively rapid kinetics at a temperature of 77 K [4-6].

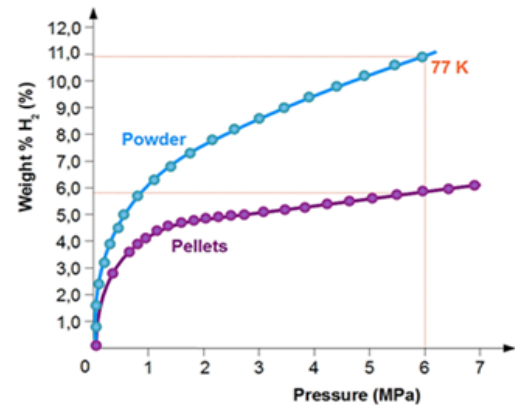


Fig. 4. The weight percentage of hydrogen storage in activated AX-21 carbon at a temperature of 77 K.

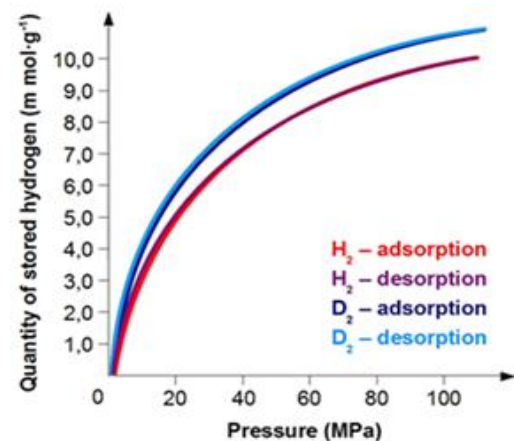
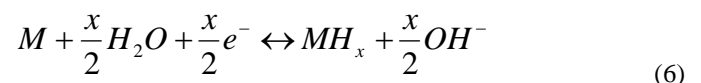


Fig. 5. Adsorption and desorption of hydrogen and deuterium to activated carbon at a temperature of 77 K.

IV. STORAGE OF HYDROGEN IN THE FORM OF METAL HYDRIDES

Hydrogen creates metal hydrides with some metals and alloys, which in some cases have a higher storage density than storage in pressure and cryogenic vessels. Storage in metal hydrides is a safer and more volume-efficient form of storage. We recognize two possible paths in the hydration of metals, through direct chemical sorption and the electrochemical cleavage of water according to reactions [7], [8]:



The metal hydride is comprised of a host metal lattice and hydrogen atoms.

Metal and hydrogen comprise two different types of hydrides, the phase when only part of the hydrogen is absorbed and the phase when the metal is fully saturated with hydrogen. Interesting choices for use are Li, Be, Na, Mg, B and Al, mainly because of their low weight and their ability to create compounds with a high content of hydrogen.

A. Compounds Based on Magnesium

Magnesium-based metal hydrides are continuous subjects of research due to their low cost, refractoriness, vibration resistance, reversibility and cyclic stability. Magnesium hydride MgH_2 has the highest energy density ($9 MJ \cdot kg^{-1}$) of all reversible hydrides. This compound combines the advantages of high hydrogen weight content (7.66 wt % H_2), low

magnesium prices and its reversibility. The disadvantage is a high desorption temperature, slow desorption kinetics and its high reactivity with oxygen. A critical factor for the use of metals for the creation of metal hydrides is their surface, which must allow the dissociation of the hydrogen nuclei and their subsequent diffusion into the metal. In Tab. 2 there are some types of magnesium hydrides along with their properties.

TABLE II. Properties of selected magnesium hydrides.

Material	Temperature (°C)	Pressure (bar)	Kinetics (min)	Cyclic stability	Hm.% H_2
$MgCoH_5$	$T_{abs} = 450 - 550$	$p_{abs} = 17 - 25$	Without data	1000 cycles	4.48
MgH_2 -5 wt% V	$T_{ats} = T_{des} = 300$	$p_{abs} = p_{des} = 1-3$	$t_{abs} = 2$ $t_{des} = 10$	2000 cycles	5.00
Mg/MgH_2 -5wt% Ni	$T_{abs} = 230 - 370$	$p_{abs} \text{ a } p_{des} = 4.0 - 1.4$	$t_{abs} = 90$	800 cycles	6.00
MgH_2 -0,2mol% Cr_2O_3	$T_{ats} = T_{des} = 300$	$p_{abs} \text{ a } p_{des} = 1 - 2$	$t_{abs} = 6$	1000 cycles	6.40

The high desorption temperatures from Mg and the slow kinetics of the process do not allow for practical use and thus catalysts such as Pd, Ni, Ge, Ti and various oxides of V, Cr, Fe and titanium are added to magnesium. Palladium has a favourable effect on the desorption of hydrogen, and in the case of accidental oxygen access, palladium oxides are created which, during a temperature increase in the hydrogen desorption process, regenerate back to Pd. Its disadvantage is a very high cost. Hydrogen has a high affinity for nickel and already with a 1% magnesium addition, the storage capacity is 50%, reducing the absorption temperature from 275 °C to 175 °C, decreasing the desorption temperature from 350 °C to 275 °C. Ti and V additives reduce surface oxidation and therefore favourably affect cyclic life. $Mg_{1,9}Ti_{0,1}Ni$ nanocrystalline demonstrates good absorption kinetics even at room temperature. V_2O_5 and Cr_2O_3 3 oxides favourably affect

powdered magnesium, in which they cause significant defects. This enables better diffusivity in the magnesium lattice.

B. Complex Hydrides

Complex hydrides are another class of storage materials for solid hydrogen storage, creating elements in contact with water. Sodium, lithium and beryllium are the only elements capable of creating hydrides with a greater weight percentage of hydrogen than magnesium. The hydrogen content of $LiBH_4$ is up to 18% by weight. The disadvantage of complex hydrides is their relatively poor kinetics and desorption thermodynamics. At first, there was assumed the inability to use these compounds to store hydrogen due to the inability of the reversibility of the complex hydrides. Acceptable results of improved desorption properties have been achieved after the addition of catalysts (especially Ti).

TABLE III. Properties of selected magnesium hydrides.

Material	Temperature (°C)	Pressure (bar)	Kinetics (min)	Cyclic stability	Hm.% H_2
$NaAlH_4$ -2 mol% Ti	$T_{des} = 25-160$	$p_{abs} = 20-120$	$t_{abs} = 300, t_{des} = 40$	Without data	3.80
$NaAlH_4$ -2 mol% $Zr(OPr)_4$	$T_{des} = 200$	$p_{des} = 1$	Without data	3 cycles	4.00

V. CONCLUSION

The expansion of hydrogen technologies encounters three major technical and economic challenges: efficient hydrogen economy, efficient fuel cells, and the design of safe tanks for hydrogen storage, production and distribution.

The fundamental change must be in the supply offer (hydrogen-producing technologies and sources) as well as on the demand side (hydrogen conversion technologies) fundamentally affecting hydrogen infrastructure. Research and

development, which can affect the costs of the entire chain and enhance the technology, is very important for the successful functioning of hydrogen technologies.

A fundamental measure is to create public awareness and encourage consumers to accept hydrogen as an alternative fuel or energy carrier. This measure also implies the development of a national regulatory environment on the side of individual states for the promotion and expansion of hydrogen technologies. An important aspect would be international

cooperation for the creation of cross-border hydrogen infrastructure.

Within the Technical University of Košice, the Department of Power Engineering workplace (Faculty of Mechanical Engineering) has been addressing the production, storage and energy use of hydrogen since 2006. In the years 2010 to 2013, the VUKONZE project (Research and Development Operational Project from EU structural funds) has built a new "Hydrogen Technologies" laboratory.

The VUKONZE Project (Research on the Efficiency of the Integration of Combined Renewable Energy Sources) is aimed at making research and development in renewable energy sources (RES) more efficient at the Technical University in Košice (TUKE) by building a common experimental and presentation space. Within the project, an information and knowledge portal for the comprehensive support of the management and safety of the VUKONZE Centre quality system was established, guaranteeing comprehensive support in the following areas:

- operation management and cooperation with social and economic practices,
- monitoring and management of real and virtual experiment technologies in the centre's laboratories,
- comprehensive knowledge support for the presentation, publicity and usage of research and development results.

Creating an open network-conceived research space creating prerequisites for the integration of scientific and research capacities have been created not only within the region but also across all Slovakia [9], [10].

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