STORAGE OF HYDROGEN

G. Spazzafumo
Department of Industrial Engineering, University of Cassino, Italy

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Contents

Summary

The hydrogen storage systems currently used or under development have been classified and described with reference to process, energy density, safety and other relevant aspects. Taking into account the hydrogen application fields as an energy carrier and taking into account various parameters which are significant in relation to the applications, a comparison among the hydrogen storage system has been carried out. Different systems are suitable for different applications and therefore could be developed as commercial systems in the future. The most recent storage system, graphite nanofibers, if experimental data will be confirmed, seems the unique one to be suitable for almost all applications.

1. Introduction

Hydrogen is an energy carrier, probably the main energy carrier of the future. This is due to its extreme versatility: on the one hand it can replace the traditional fuels; on the other hand it is easily convertible into electrical energy through fuel cells with high efficiencies even by means of small plants. Until a few years ago the need for an energy carrier like this was due to the efforts towards substitution of the traditional sources of energy with renewable sources (including the nuclear fusion) and was therefore futuristic. Now the development of the fuel cells for transport and a greater awareness for pollution problems in the urban environment are opening up these prospects for the use of hydrogen.

An energy carrier must, of course, be stored and distributed. These operations may be performed according to different processes. Each method of storage has particular features which make it come out more or less suitable for the use in a particular field and which may influence the choice in an even more decisive way than cost considerations. For example, essentially important aspects are safety, especially when people are exposed to hazard, or the weight and the overall dimensions, for movable applications.

The main forms of hydrogen storage may be pure or combined, and in the latter case there can be a chemical bond or a physical bond. Table 1 shows a classification of the different options.

Pure	Combined
Gaseous in cylinders	Metal hydrides
Gaseous in microspheres	Liquid hydrides
Liquid	Carbon nanotubes
Slush	Graphite nanofibers

Table 1: Hydrogen storage systems

2. Gaseous Hydrogen

Gaseous hydrogen is the simplest form for storage; in fact molecular hydrogen is found in nature in that state. Usually gaseous hydrogen is stored in pressurised tanks or in cylinders with pressure of 20 MPa. There are no particular problems with the gas compression and with the subsequent reuse. The idea of recovering part of the energy used for compression can be exploited with the steady applications, while it must be rejected for movable applications because the resulting advantage is insignificant, when compared with the problems arising out of the system dimensions and weight.

The need to reach such high storage pressures is justified because of the gas low density. So it is necessary that the containers are made with materials and dimensions such as to endure higher pressures. The use of composite materials make possible to construct tanks that are light and suitable for very high pressures, up to 69 MPa. They can be used for hydrogen transport because they allow us to multiply the transport capacity by a factor 1.5 and this can balance the high cost of such tanks.

However, as the pressure increases, there is an advantage as regards the dimensions which decrease progressively, while the weight decreases only at the beginning, when the variation is caused by the diameter decrease, and then it increases, when the thickness increase prevails (Figure 1). The energy density of a gaseous hydrogen tank is in the range 1-2.5 MJ/l when storage pressure varies between 20 and 70 MPa. Variation in weight also depends strongly on the materials: energy density is in the range 2-10 MJ/kg.

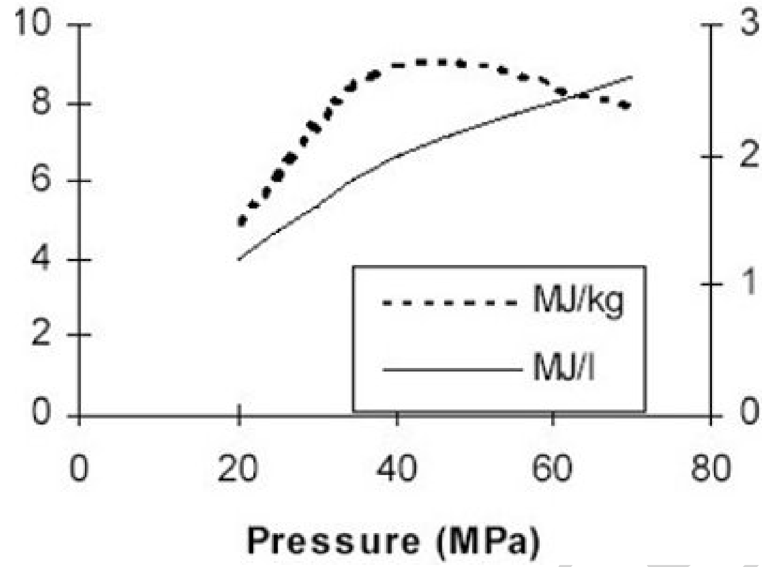

Figure 1: Energy density for gaseous hydrogen in cylinders

By cooling compressed hydrogen down to 80 K, which is the liquefaction temperature for nitrogen, it is possible to increase density by a factor of 3.5. This requires materials suitable for very low temperature and also requires technological development especially for composite materials.

If hydrogen is produced through electrolytic cells at a pressure of 4 MPa and a temperature of 300 K, to compress it until the pressure of 20 MPa is reached, with compression efficiency of 87%, it is necessary to supply a work of compression of 2.99 MJ/kg, that is to say equivalent to 2% of the higher heating value of hydrogen.

Regarding safety the best solution would be to make a tank with spherical shape, because there would be a uniform stress on the material. On the other hand, this shape is undoubtedly the least convenient from the point of view of the disposition inside the system, especially if it is on board. Again regarding safety it is also important to consider the possible pressurisation due to the heating and therefore the arrangement of appropriate safety valves.

Otherwise gaseous hydrogen could be stored in hollow glass microspheres, with a diameter between 50 and 100 nm. This method is based on the dependence of permeability to hydrogen on temperature of glass. Hydrogen is put inside the microspheres at a pressure of 40-50 MPa and at temperature of 300-400 °C. After the cooling at ambient temperature, the hydrogen diffusion through the glass walls decreases so that, even if the outside pressure decreases to the atmospheric value, inside the microspheres hydrogen remains at high pressure. Actually, at ambient temperature as well there is a slight loss of hydrogen, because the glass at that temperature is not quite impermeable. The phenomenon, often unwelcome, is influenced by the characteristics of the glass used to make the microspheres, as well as, of course, by the pressure and temperature values. As the molar percentage of forms of glass without reticulated structure increases, the losses of hydrogen decrease, but it has negative consequences when it is necessary to store hydrogen because of the decreased permeability.

During the filling procedures, to limit the number of microspheres which break, to the minimum values, it is important to handle them taking particular precautions. First of all it is necessary to make the sample of microspheres reach the chosen filling temperature, usually 350°C. Then we must raise gradually the pressure, so that the difference of pressure between the microspheres outside and inside is not too high, usually 20 MPa. Amid one increase and the other of the pressure, it is necessary to allow hydrogen to pass through the glass walls, keeping a constant pressure for a sufficiently long time. Finally, the temperature will be brought back to the ambient value.

To obtain the release of stored hydrogen, it is necessary to make the microspheres reach a temperature which must increase at the increasing of the desired outflow speed.

The maximum working pressure of the microspheres is limited by the glass mechanical resistance and by the dimensions of the microspheres. The quantity of hydrogen which can permeate the microspheres walls, during the filling and emptying procedures, depends fundamentally upon the balls dimensions, upon the composition of the glass, upon the gradient of pressure through the walls and upon the temperature.

In the ideal case of microspheres which are exactly alike and packed in a compact way, and ignoring the thickness as regards the diameter, the available volume is about the 74% of the total space, so hydrogen is stored with a size reduction of 150-200 times (storage energy density 1.8-2.4 MJ/l)

From a gravimetric point of view the mass of hydrogen that can be stored per unit mass of the sample is about 0.04 (storage energy density 5.6 MJ/kg).

If Q is the volume of hydrogen per unit mass of the sample passing through the microspheres walls with a difference of pressure ΔP, we have:

$$Q = k \cdot \frac{S}{s} \cdot \Delta P$$

where k is the permeability of the microspheres with respect to hydrogen, S is the medium surface per unit mass and s is the microspheres medium thickness.

If T is the absolute temperature and M the molar percentage of forms of glass without reticulated structure, then we have:

$$k = 2.21 \cdot 10^{-19} \cdot \left(3.4 + 8 \cdot 10^{-4} \cdot M^3\right) \cdot T \cdot e^{\left(-\frac{3600+165 \cdot M}{T}\right)}$$

and if d is the medium diameter and ρ_m is the microspheres density and ρ_v is the glass density, then:

$$S = \frac{6}{d \cdot \rho_m} \text{ and } s = \frac{d}{2} \cdot \left(1 - \sqrt[3]{1 - \frac{\rho_m}{\rho_v}} \right).$$

3. Liquid Hydrogen

In order to increase further the volumetric density of hydrogen storage it is possible to resort to liquefaction and storage in cryogenic containers. Liquid hydrogen has, in fact, a density which is about 800 times higher than gaseous hydrogen at atmospheric pressure.

The evaporation of liquid hydrogen inside the tanks must be very limited, because the consequent pressurisation of the tank could become a danger. So, the storage temperature being very low, it is necessary to have very efficient tank insulation systems, so as to reduce to minimum the heat exchange with the environment. The contemporary necessity for a good insulation and of a high resistance, also at low temperatures, implies a rise in weight and dimensions and therefore a great decrease in energy density: the weight of hydrogen stored is about 18% of the weight of the cryogenic tank and the volume available for hydrogen is 50% of the total of the tank.

There are different cycles for the liquefaction of hydrogen. The simplest is the Linde cycle, which is schematically shown in Figure 2 with the schematic of a plant in Figure 3. This cycle is suitable for liquefaction of gases with an inversion temperature (that is the one at which the Joule-Thomson coefficient changes its sign) lower than the ambient temperature: for hydrogen this temperature is 205 K.

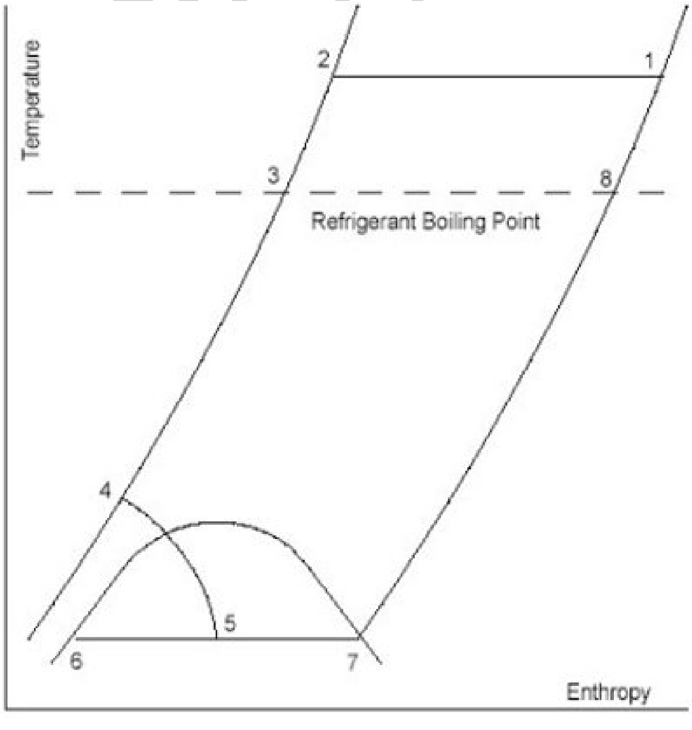

Figure 2: Linde cycle for hydrogen liquefaction.

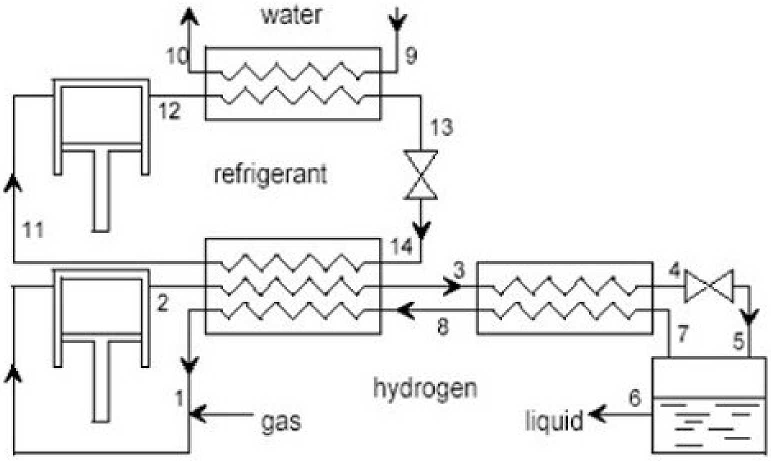

Figure 3: Schematic of a Linde plant for hydrogen liquefaction

Liquefaction is done by a sequential process of compression-cooling-expansion. Because of the very low liquefaction temperature of hydrogen (20.3 K at atmospheric pressure) it is necessary to use a primary coolant, water, and a secondary coolant with an intermediate liquefaction temperature. This secondary coolant is liquefied with procedures similar to the ones for hydrogen and then it is made to evaporate again taking heat from hydrogen. Usually nitrogen is used as secondary coolant.

Making an energy balance of the hydrogen circuit, we have:

$$\dot{m}\cdot h_2+\dot{m}_r\cdot h_{14}=\dot{m}\cdot h_1+\dot{m}_r\cdot h_{11}+\dot{m}_l\cdot\left(h_6-h_1\right)$$

where $\dot{m}$ is the total mass flow (that is to the compressor) of hydrogen, $\dot{m}_l$ is the mass flow of liquefied hydrogen, $\dot{m}_r$ is the mass flow of the coolant, *h* is the enthalpy.

If $x=\dot{m}_r/\dot{m}$ and $y=\dot{m}_l/\dot{m}$ we have $y=\left[\left(h_1-h_2\right)+x\cdot\left(h_{11}-h_{14}\right)\right]/\left(h_1-h_6\right)$ and the maximum fraction of liquefied hydrogen is $y_{max}=\left(h_8-h_3\right)/\left(h_8-h_6\right)$ where h_3 and h_8 are bound to the evaporation temperature of the secondary coolant.

The minimum specific energy necessary to isobarically liquefy hydrogen from ambient temperature and atmospheric pressure is $w_{min}=T_1\cdot\left(s_1-s_6\right)-\left(h_1-h_6\right)=14.2\text{ MJ/kg}$ where *T* is the temperature and *s* the specific entropy and the subscripts 1 and 6 represent the initial and final conditions respectively. Actually the necessary energy is much higher and this is really one of the more critical aspects of the use on large scale of this form of storage.

The Linde cycle underwent in time some changes directed to reduce the compression work and to increase the fraction of liquefied hydrogen. Besides, it is necessary to consider that the molecule of hydrogen can be found in two different energetic states, the ortho-hydrogen form and the para-hydrogen form, depending on the configuration of the nuclear spins. At ambient temperature hydrogen is formed by a mixture defined normal-hydrogen and composed of 25% of para-hydrogen and 75% of ortho-hydrogen. For higher temperatures this mixture remains unchanged, while as the temperature decreases the para-hydrogen percentage increases progressively (Table 2). The energetic level of the para-hydrogen form is lower than that of the ortho-hydrogen form, so the isothermal change ortho-para-hydrogen is exothermic. Without the use of the catalysts this change occurs spontaneously and proceeds very slowly: then liquefaction of normal-hydrogen takes place and the subsequent heat transfer connected to the above mentioned change causes partial evaporation of hydrogen. To prevent this from occurring, it is necessary to use suitable catalysts and remove during the liquefaction phase the heat connected to the ortho-para-hydrogen change.

K	10	20	30	40	50	100	200	300	500
%	100.00	99.82	97.02	88.73	77.05	38.62	25.97	25.07	25.00
J/mol	1417	1417	1417	1417	1416	1295	440	74	0

Table 2: Para-hydrogen contents and conversion heat at equilibrium conditions

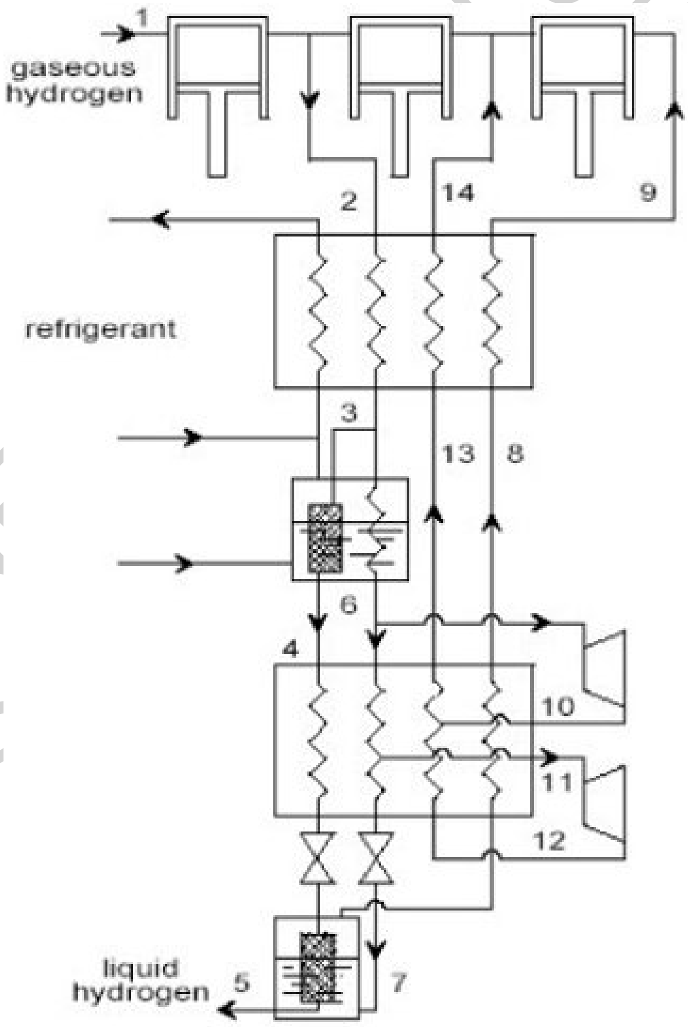

Figure 4: Schematic of a plant for hydrogen liquefaction

It follows that the plants used for the liquefaction of large quantities of hydrogen employ cycles much more complicated than the above seen one. One example is schematically shown in Figure 4.

In such a plant the hydrogen to be liquefied is divided into a primary flow and a secondary flow. The first one is converted from ortho-hydrogen to para-hydrogen in two different stages: the former one (3-4) at the nitrogen boiling point and the second one (5-6) at the hydrogen boiling point.

The secondary flow is partially liquefied (6-7) without conversion and is used in the second stage for primary flow conversion. The secondary flow is also used for energy recovery by means of two turbines which produce mechanical energy and at the same time provide for gas cooling.

The work of liquefaction increases therefore at the increasing of the final concentration of para-hydrogen: to liquefy 1 kg of hydrogen with a final concentration of para-hydrogen equal to 95% it is necessary to supply about 35 MJ, corresponding to about 2.5 times the minimum value and also to about the 25% of the energetic content of hydrogen itself.

It is however necessary to notice that, because of the slowness of the spontaneous conversion process, the optimum concentration of para-hydrogen depends on the storage time.

4. Slush Hydrogen

Slush hydrogen is a mixture composed of 50% of liquid hydrogen and 50% of solid hydrogen at the temperature and at the pressure of the triple point (table 3).

The slush presents a fluid-dynamic behavior similar to the liquid hydrogen one and can be distributed exploiting the same infrastructures, besides it has a higher density (+15%) presenting less leaks for evaporation.

	liquid (NLC)	liquid (TP)	slush (TP)	solid (TP)
Temperature (K)	20.39	13.96	13.96	13.96
Pressure (kPa)	101.33	7.20	7.20	7.20
Density (kg/m^3)	70.77	77.22	81.50	86.50
Enthalpy (kJ/kg)	271.0	212.8	183.7	154.6

Table 3: Hydrogen characteristics at Normal Liquefaction Condition and at Triple Point

To produce the slush the method of scraping is used. This method utilizes liquid helium to produce solid hydrogen on the surface of a heat exchanger.

The solid hydrogen produced is then scraped with a sort of auger and mixed with the residual liquid hydrogen, while gaseous helium is recycled to be liquefied again.

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Bibliography

It is not useful to report a traditional bibliography because we can divide the hydrogen storage systems in two groups:

- established technologies, like gaseous hydrogen stored in cylinders or liquid hydrogen stored in cryogenic tanks: most of data are probably available in every energy related handbook;
- technologies under development, which require a further division:
    - ∗ metal hydrides: it is possible to write some volumes only reporting the titles of articles written about them and most of the articles concern only one or few specific hydrides so that it is not useful at this concern;
    - ∗ carbon structures: there are not many articles, but they are not easy to find; moreover, when this article will be published there will be other article more updated because this field is under continuos development.

Interesting and updated articles can be found on:

- International Journal of Hydrogen Energy;
- Proceedings of World Hydrogen Energy Conference;
- Proceedings of HYPOTHESIS (Hydrogen Power Theoretical and Engineering Solutions International Symposium).

A good suggestion is also to check on some relevant web sites. There are a lot of them more or less related to hydrogen; here are some of them:

- http://www.eren.doe.gov/hydrogen/
- http://www.HyWeb.de/gazette-e
- http://www.hfcletter.com/
- http://www.ttcorp.com/nha/
- http://www.rebresearch.com/H2links.html

Biographical Sketch

Giuseppe Spazzafumo was born in Carrara (Italy), 29 Dec. 1959. Graduated (Mechanical Engineering, thesis on plants of biophotoproduction of hydrogen) in 1984 from University of Pisa. PhD (Energetics, thesis on use of MCFC in powerplants) in 1988 at University of Pisa. He works at University of Cassino since 1989: Lecturer, 1989-1991, Assistant Professor, 1992-2002, and Associate Professor since 2002. Reviewer of International Journal of Hydrogen Energy since 1989. Coordinator of HYPOTHESIS (HYdrogen POwer THeoretical and Engineering Solution International Simposium) series. Secretary of Italian Hydrogen Association (Forum Italiano dell'Idrogeno) since its creation.

Member of IAHE Board of Directors since 1999.

Prof. Spazzafumo was engaged in researches in Hydrogen Energy Fields since 1984. He is author of more than 50 scientific papers related to hydrogen energy systems or fuel cell systems. His work concerns theoretical studies and simulations of hydrogen energy systems, from hydrogen production to hydrogen final use.