HYDROGEN STORAGE: RECENT IMPROVEMENTS AND INDUSTRIAL PERSPECTIVES

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ABSTRACT (UP TO 300 WORDS)
Efficient storage of hydrogen is crucial for the success of hydrogen energy markets (early markets as well as transportation market). Hydrogen can be stored either as a compressed gas, a refrigerated liquefied gas, a cryo-compressed gas or in hydrides. This paper gives an overview of hydrogen storage technologies and details the specific issues and constraints related to the materials behavior in hydrogen and conditions representative of hydrogen energy uses. It is indeed essential for the development of applications requiring long-term performance to have good understanding of long-term behavior of the materials of the storage device and its components under operational loads.

1.0 INTRODUCTION

Hydrogen is used worldwide for industrial applications (thermal treatment of metals, glass industry, etc). It is stored and transported in compressed form. More recently, new applications have emerged in the field of energy. The development of hydrogen as a reliable energy vector is strongly connected to the performance and the level of safety of the components of the supply chain. In this respect, achieving an efficient and reliable storage is crucial to address hydrogen energy markets:

- Fuel for transportation: buses, cars, scooters or other vehicles powered with hydrogen and a fuel cell or a combustion engine that requires autonomy, volume savings and lightweight. Fuelling infrastructures requires high pressure buffer driven by pressure cycle lifetime. Depending on footprint constraints, volume savings and lightweight can be a driver.

- Stationary applications: back-up power supply, power supply to off-grid area, power generator for residential. For this application, the cost of hydrogen supply is the main parameter as well as pressure cycle life.

- Portable applications: portable back-up power supply or power generator.

To achieve the required performance (autonomy and weight efficiency), hydrogen can be stored under:

- compressed form at pressures ranging from 20MPa to 100MPa in carbon fibres composite pressure vessels (designated hereafter by COPV) when lightweight/capacity needed or in metal pressure vessels otherwise.

- liquefied cryogenic form at -253°C when large quantity of hydrogen shall be transported and high gravimetric storage performance is sought.

- cryo-compressed form at intermediate low temperature (about 20K) and high pressure (at least 30 MPa) to achieve higher gravimetric and volumetric performance

- solid form in hydrides

The different storage technologies, recent development and perspectives in term of development and research gaps are described hereafter.
2.0 COMPRRESSED HYDROGEN STORAGE

2.1 Overview of compressed hydrogen storage technologies

Hydrogen can be stored in four types of pressure vessels as presented in figure 1. The pressure vessels are generally cylinders but they can also be polymorph or toroid. Metallic pressure vessels are known as type I. Type II pressure vessels consist in a thick metallic liner hoop wrapped on the cylindrical part with a fiber resin composite. The fully composites materials based pressure vessels (designated by COPV) are made of a plastic or metallic liner wrapped with carbon fibres embedded in a polymer matrix (filament winding). When the liner contributes to the mechanical resistance (more than 5%), the COPV is of type III (mostly metal liner). Otherwise, the COPV is of type IV (mainly polymer liner or seldom extremely thin metal liner).

![Figure 1. Representation of type I, II, III and IV COPV [1]](image)

2.2 Some history & key characteristics

The development of metallic pressure vessels was led by industrial needs in the end of the 19th century in particular to store carbon dioxide for beverages. Hydrogen storage at 12 MPa in wrought iron vessels is reported in about 1880 for military use. Pressure vessels made of seamless steels manufactured by drawing and forming of plates (Lane & Taunton British patent) or tubes (Mannesman German Patent) were developed in parallel in late 1880s. Until the 60s, the working pressure was 15 MPa. It was then increased to 20 MPa and then to 30 MPa. High pressure composites pressure vessels were introduced in the 60s in the USA for military and space applications (aluminium or polymer liner with glass fibre wrapping). The first application for the civil market was breathable apparatus for firemen in the 70s. From the 80s these pressure vessels started to be used for diving, fuel storage (compressed natural gas) and leisure applications (paintball) with a more extended material mix. The most common working pressure is ranging from 25 MPa (compressed natural gas) to 30 MPa (oxygen and air for breathing apparatus). More recently (21st century) 35 MPa to 70 MPa COPV were developed and approved for hydrogen energy applications. Moreover regulations, codes and standards have been set up for both industrial gases and fuel gas storages. The market share of composites pressure vessels remains quite small compared to metallic pressure vessels due to their higher cost (about 30 000 000 COPV in the world). The choice of the storage is based on the final application which requires a compromise between technical performance and cost competitiveness. For industrial applications, hydrogen is stored at 20 to 30 MPa in metallic type I cylinders which have poor mass storage efficiency (about 1 wt% of Hydrogen stored), that can be far from targets fixed for Hydrogen Energy applications. As an example, the European target weight efficiency for on-board storage in vehicles is set at 4.8 wt% of hydrogen stored in a system [2]. Such target can be reached by using type III or type IV COPV made of carbon fibre composite with a 70 MPa working pressure (European project Storhy for instance [3]). The table 1 presents the main feature of the different type of pressure vessels.
Table 1. Key characteristics of compressed gas storage pressure vessels

<table>
<thead>
<tr>
<th>Type</th>
<th>Technology maturity</th>
<th>Cost performance</th>
<th>Weight performance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type I</td>
<td>Pressure limited to 50 MPa, ++</td>
<td>++</td>
<td>-</td>
</tr>
<tr>
<td>Type II</td>
<td>Pressure not limited, +</td>
<td>+</td>
<td>0</td>
</tr>
<tr>
<td>Type III</td>
<td>For P \leq 45 MPa (difficulty to pass pressure cycling</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td></td>
<td>requirements for 70 MPa, [4])</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Type IV</td>
<td>For P \leq 100 MPa– First commercial series – liner</td>
<td>-</td>
<td>++</td>
</tr>
<tr>
<td></td>
<td>behaviour in gas to be further studied</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.2 Design & manufacturing

Most common materials are:

- metallic parts: aluminium 6061 or 7060, steel (inox or Chrome Molybdene)
- polymer parts: polyethylene or polyamide based polymers
- composite: glass, aramid or carbon fibre embedded in epoxy resin. The fibre characteristics are given in table 2. Carbon fibres are preferred for 35 MPa and more applications. In the same way, various resins can be used (polyester, epoxy, phenol, etc). Epoxy resins are preferred based on their good mechanical properties, stability and compatibility with filament winding process. Pre-impregnated fibres are commercially available. For cost reasons, fibre impregnation just before the filament winding is most often preferred.

Table 2. Range of fibre mechanical properties.

<table>
<thead>
<tr>
<th>Fibre type</th>
<th>Tensile modulus (GPa)</th>
<th>Tensile Strength (MPa)</th>
<th>Elongation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass</td>
<td>~ 70-90</td>
<td>~ 3300-4800</td>
<td>~ 5</td>
</tr>
<tr>
<td>Aramid</td>
<td>~ 40-200</td>
<td>~ 3500</td>
<td>~ 1-9</td>
</tr>
<tr>
<td>Carbon</td>
<td>~ 230-600</td>
<td>~ 3500-6500</td>
<td>~ 0.7-2.2</td>
</tr>
</tbody>
</table>

For all pressure vessels, the design shall take into account the service, test pressures, the external stresses (like mechanical impacts, chemical, integration, etc), the cycling life, the lifetime and the safety coefficient defined both for static and dynamic conditions. Materials choices shall also take into account failure modes and operating conditions as it will be discussed in next section. For example, figure 2a gives the main stresses considered for metallic cylinders/liners (note that domes are generally overdesigned). The composite wrapping is designed using finite element analysis with respect to static conditions.

Type I pressure vessels and type II and III liners can be manufactured from 3 different processes as shown in figure 2b: from plates by deep-drawing to form the shape, from billets: the billets is first heated to carry out drawing, from tubes. The neck is then formed by hot-spinning. The ports are machined in the excess of metal coming from the spinning step. Heat treatments are then applied to have the desired mechanical properties.
Polymer liners of type IV pressure vessels can be obtained by rotomolding, blow molding or by welding injected domes to an extruded tube of polymer. Metal parts (boss) can be inserted in the domes during the forming process or glued to the liner in a second step.

For composites pressure vessels, the composite is obtained by filament winding of the fiber embedded in the resin (either by wet winding or by using pre-impregnated fibers). The composite is wrapped using a circumferential angle (hoop) for type II pressure vessels and a combination of circumferential, helical and polar angles for type III and IV pressure vessels as illustrated in figure 3. The curing of the resin of the composite is finally carried out by UV exposure and more typically by curing in an oven.

For each technology, quality controls of the materials and of manufacturing steps are performed and monitored. The pressure vessel final control is a proof test, typically at 1.5 times the working pressure. Development of non destructive testing technique would bring additional information.

2.3 Materials issues & R&D challenges

The compatibility of the gas with the materials chosen and the impact of operating conditions on the materials and the structure have to be assessed. The whole lifecycle of the pressure has to be considered: storage, transportation, use (emptying, handling, etc), filling steps including gas quality management, periodic inspection and maintenance. The objective is to prevent the risk of failure by burst or leak in service and guaranty the performance.
- **Metallic parts (pressure vessel, liner and boss)**

In general, metallic materials and in particular steel, in contact with hydrogen are affected by hydrogen embrittlement (HE), with consequent degradation of mechanical properties and premature crack. It results from H atom dissolution and trap (stress corrosion cracking). Major efforts have been performed by the industry and academia in mitigating this problem through a better understanding of the HE mechanisms, the improvement of alloys manufacturing, components assembling, and appropriated mechanical testing [3] [5]. Regarding to the latter issue, different testing methods exist to assess fracture toughness properties of metallic materials in gaseous hydrogen ($K_{IEAC}$): ASTM 1681 [6], ASTM 1820 [7] and methods B and C of ISO 11114-4 [8] and ANSI/CSA [9]. An experimental study is on going to assess the different methods and evaluate the need for harmonization of testing methods [5] [10].

Premature failure in fatigue for metal liner of COPV can occur at high pressure, Fuelling stations buffers are subjected to extensive pressure cycles with reduced pressure amplitudes,

- **Polymer parts (liner of type IV pressure vessels)**

A high purity of hydrogen is required to guarantee performance and reliability of fuel cells. The draft standard ISO 14687-2 set these hydrogen specifications in terms of maximum quantity of impurities admitted (see Table 3). So far, among the species listed in Table 3, water has been identified as the main compound that could degas from a polymer liner. The content of water in a polymer depends on its chemical nature. Thermal gravimetric analysis have evidenced that polyethylene water uptake can be neglected while the water uptake of polyamide is of several weight percent (the weight percent depends on the polyamide grade). Such water content in the polymer liner could lead to the implementation of additional drying steps of COPV prior to gas filling to respect the 5 ppm specification.

<table>
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<tbody>
<tr>
<td>Component</td>
</tr>
<tr>
<td>Inert gases (Nitrogen + Argon)</td>
</tr>
<tr>
<td>Oxygen</td>
</tr>
<tr>
<td>Carbon dioxide</td>
</tr>
<tr>
<td>Carbon monoxide</td>
</tr>
<tr>
<td>Total hydrocarbons</td>
</tr>
<tr>
<td>Water</td>
</tr>
</tbody>
</table>

The permeation of gases is an inherent phenomenon for all gases in contact with polymers. It is the result of gas molecules dissolution and diffusion in the polymer matrix [12]. Because hydrogen is a small molecule, the permeability is enhanced. For safety reasons, permeation maximum allowable rates are defined in standards and regulations.

Quick emptying of COPV may in some cases lead to a deformation of the liner when pressure is released, as depicted in Figure 4. Though the mechanism is not fully understood, it can be attributed to the diffusion of hydrogen through materials and accumulation at the interfaces, voids and in materials (solubility). The occurrence of the deformation depends on the maximum pressure in the cylinder and on the pressure maintained in the cylinder at the end of emptying. Residual pressure valves use thus appears mandatory. Emptying speed also seems to have an effect that must be further analyzed. Further tests are needed to propose recommendations on operating conditions and assess the effect of liner
deformation on cylinder lifetime (does it lead to an increase risk of leakage?). Such question tackles multidisciplinary fields by coupling diffusion mechanisms to mechanics.

Figure 4. X-Ray tomography of a polymer liner COPV with permanent deformation after an emptying

During filling and emptying, the structure and in particular the polymer liner and the boss liner junction are subjected respectively to high (65 or 85°C, depending on standards) and low temperatures (-40 to -60°C, depending on standards). Materials have to be chosen accordingly to avoid materials degradation and thus leak risk.

- **Composite parts (types II, III and IV)**

Regarding the composite wrapping, damage accumulation can result from pressure loads & environment impact in operation [13] and accidental mechanical impacts. In the scope of hydrogen energy markets, COPV can be subjected to a broad range of impacts either usual or accidental (car accident, fall or impact during handling and transportation of transportable COPV). Damage mechanisms occurring in such composites are fibre breaks, delamination and matrix cracking.

Damage resulting from a mechanical impact or a fall, its evolution under typical in-service loadings (monotonic pressurization, filling/emptying cycles,...) and the corresponding loss of performance are not well described for COPV as only a few studies tackle the consequence of impact on the residual life time of composite materials obtained by filament winding [14][15][16][17]. It is thus important to continue the effort on the development of knowledge on the effect on mechanical impact on pressure vessels performance. In addition, it is observed that a surface impact creates damage in the thickness of the composite as illustrated in figure 5 [17] and can even damage the liner as illustrated in figure 6 for type III COPV.

Figure 5. (a) illustration of the external surface composite damage and (b) in the thickness of the composite by XRay CT Scan for a mechanical impact with angular impactor [17].
Periodic inspection of COPV is required by regulations. Currently, periodic inspection consists of a visual inspection (internal and external) and a hydraulic proof test. As an alternative to hydraulic proof test which gives poor information on the real damage level in COPV (as illustrated in figures 5 and 6), non destructive techniques (NDT) providing more information on damage level are under development. Acoustic emission is for instance studied [10] [18] and a proposal of standard is under construction (ISO 19016).

Bonfire tests were carried out on different COPV, mostly with a polymer liner. Time to burst and pressure at time to burst have been evaluated. At time to burst, the pressure in COPV increases by less than 10% [19]. The increase of pressure is thus not responsible for the burst of COPV, as observed in metallic pressure vessels. The knowledge of the degradation of the composite materials in fire is thus important to predict the behaviour of COPV in fire. Further research is needed on that topic.

3 CRYOGENIC STORAGE

3.1 History & key characteristics

Cryogenic vessels are commonly used for more than 40 years for the storage and transportation of industrial and medical gases. Hydrogen needs to be liquefied at -253°C, the process is both time consuming and energy intensive. Up to 40% of the energy content can be lost (in comparison with 10% energy loss with compressed hydrogen). On the other hand, the main advantage associated to cryogenic storage is the density of liquid and thus storage efficiency (see figure 7). It explains why liquid hydrogen is used in space programmes. Liquid hydrogen is difficult to store over a long period because of product loss by evaporation. As a consequence, it is not a preferred solution for on-board storage in vehicles but more used for gas delivery using trucks which can exceed a capacity of 60 000L. Stationary vessels can be used at customer sites for storage. The intercontinental transport of hydrogen will probably be carried out in liquid form using dedicated ships.
In order to manage storage at -253°C, high efficiency (vacuum) insulated vessels. Such vessels are composed of an inner pressure vessel and an external protective jacket (see figure 8). To reduce the thermal conductivity of the space between the inner vessel and the outer jacket, perlite (powder structure) or super insulation (wrapping with layers of aluminium films) are used.

3.2 Materials & design

To form the inner pressure vessel, cold stretching of stainless steel can be used to allow reducing the wall thickness and the cost. It is used in particular in Europe. Design methods are described on ISO 21009-1 – cryogenic vessels – static vacuum insulated vessels, part 1: design, fabrication, inspection and test, ISO 21009-2, cryogenic vessels, static vacuum insulated vessels – part 2 operational requirements.

Hydrogen embrittlement effect is usually observed at ambient temperatures and can often be neglected above +100°C. In the case of unstable austenitic stainless steels often used for cryogenic vessels, the maximum effect is reached at -100°C but can be neglected for temperatures below -150°C as displayed on figure 9.
At low temperature, change of mechanical characteristics, expansion and contractions phenomena and more importantly brittleness have to be considered. In general, for metallic materials, ductility and toughness decrease and the yield strength, hardness and modulus increase with the decrease of temperature. In the case of ferritic or martensitic steels, toughness drops rather suddenly in a relatively narrow temperature range leading to a transition from a ductile failure to a brittle failure. It is important to consider relative contractions at low temperature, especially for assemblies made of different materials. As an example, it can be seen that the main stainless steels used contracts in appreciably the same way. To avoid cold embrittlement of brittle parts through the thermal conduction, proper insulation has to be used. In conclusion, stabilized austenitic stainless steels and aluminium alloys are the main metallic materials used at low temperatures in hydrogen environment (note that nickel ferritic steels can be used above -200°C).

4 CRYO-COMPRESSED STORAGE

Cryo-compressed storage combines properties of both compressed gaseous hydrogen and liquefied hydrogen storage systems. It is developed to minimize the boil-off loss (dormancy) from liquefied hydrogen storage while retaining a higher system energy density. Hydrogen is stored in an insulated tank that can accept cryogenic temperatures (20K) and high pressure (at least 30 MPa) at ambient temperature. The fact that the tank is able to withstand high pressures allows greater pressure increases before hydrogen has to be boiled off. Such cryogenic pressure vessels significantly extend the time before starting evaporative losses when they are in operation and thus increase storage autonomy.

As an example, the BMW Group has started validation of cryo-compressed hydrogen storage for hydrogen vehicles with high energy and long range requirements [20, 21]. The diagram depicted in figure 7 reported by BMW [20] shows that cryo-compressed H2 enables high storage density (80 g/l). The cryogenic gas is denser than liquid hydrogen.

The tank consists of a type III composite pressure vessel with a metallic liner that is encapsulated in a secondary insulated jacket, whose role is to limit heat transfer between the hydrogen and the environment. More details on the cryo-compressed storage tank design can be found in [22]. Experiments have also been performed to evaluate the effect of combined pressure and cryogenic temperature cycling on the composite material properties of tanks [20].

Cryo-compressed storage tanks can be filled with hydrogen at any state between 20K liquid H2 and ambient temperature gaseous H2. Filling the tank with compressed gas instead of liquefied hydrogen is expected to be more economical. In terms of infrastructure, cryo-compressed tanks offer refuelling flexibility as they are compatible for gaseous and liquid.
5 HYDRIDES STORAGE

Storage of hydrogen in solids offers some advantages compared to storage under pressure or in liquid state in terms of volumetric density. Hydrogen can be absorbed reversibly by solid compounds under temperature and pressure conditions. It can also be generated in situ irreversibly by hydrolysing some compounds (for example, alkali metal borohydrides such as LiBH4 or NaBH4 having high theoretical gravimetric capacities of 18.4 wt% and 10.6 wt%, respectively). The disadvantage with this method is the need to regenerate the by-product by chemical treatment on a suitable site. We will focus here on hydride materials capable of storing hydrogen reversibly.

The formation of hydrides results of dissociative chemisorption. The hydrogen molecule is first dissociated on the surface of the solid and then its atoms diffuse into the metal host. Depending on the bonding mechanism between the hydrogen and the host material, different families of hydrides exist: ionic hydrides (ionic bonding), covalent hydrides (covalent bonding) and interstitial metal hydrides (metallic bonding). Ionic and covalent hydrides are also called complex metal hydrides.

The most relevant parameters used to determine a good storage material are related to the absorption thermodynamic properties, defined by measuring under equilibrium conditions the hydrogen pressure-composition characteristics at a given temperature. In addition to the thermodynamic characteristics, the kinetics also plays an important role. Absorption of hydrogen is an exothermic process while its desorption or release is an endothermic process. Therefore, good management of heat transfers with the exterior is required, with the possible association of a heating system for desorption and a cooling system for absorption, to avoid penalising the kinetics.

Ionic hydrides are salts like NaH, LiH … with a high degree of ionic character. Typical binary ionic hydrides tend to be quite thermally stable toward releasing hydrogen with the exception of magnesium. In fact, magnesium hydride is not a true ionic hydride as the interaction between hydrogen and magnesium is partly ionic and partly covalent. Ionic hydrides are difficult to use ince their reversibility conditions are very high in terms of pressure and temperature. However, given their high gravimetric capacity, their hydrolysis reaction can be exploited for in situ hydrogen production, with the drawback of by product formation.

In interstitial metal hydrides, there is no discrete formation of compound. Hydrogen atoms fill determined interstitial sites in the metallic structure and solid solution formation is common. Their reversibility conditions are close to normal temperature and pressure conditions. Numerous compounds known for their absorption properties are listed in the hydride database US Department of Energy (DOE) Hydrogen Storage Materials Database http://hydrogenmaterialssearch.govtools.us/. Interstitial hydrides by their nature are composed of high atomic number transition metals, and therefore contain a low mass fraction of hydrogen. To date, most of the known compounds have a reversible storage capacity less than 3 wt% of hydrogen as shown in Figure 10. Despite a highly interesting volumetric density, their low gravimetric storage capacity is not suitable for many applications.
Covalent hydrides encompass compounds such as MgH2, AlH3, the boranes and borohydrides and related derivatives such as amines … where the bonding is highly localized between the hydrogen and the central element. Many of these materials are known to release hydrogen at temperatures above room temperature and up to several hundred °C, and can release more than 9 wt % hydrogen. There is an intensive effort of research worldwide in this field. An overview of the storage materials developed through the Centers of Excellence of the US Department of Energy H2 storage program is presented in Figure 11.

A very promising hydride material is MgH2. It was proposed 40 years ago for H2 storage [25]. It is attractive for its low raw material cost and high gravimetric capacity of 7.6 wt%. Initial hydrogenation is difficult and the resulting hydride is therefore expensive. It is why nanostructuring, with or without catalyst addition, was used to improve the initial reactivity to hydrogen [26] but the synthesis employs sophisticated techniques that are difficult to scale up. Recently Dahle and Nogita [27] synthesized a hypoeutectic Mg-Ni alloy by casting, a low-cost method more suitable to large-scale industrial production. This technology is currently developed by the Australian company Hydrexia.
An example of the Hydrexia alloys produced using conventional casting equipment is shown on Figure 12.

Figure 12: Hydrexia’s magnesium alloy [29]

The ISO standard 16111 is referenced in the UN regulation for dangerous good transportation. The scope of the standard covers small cartridge (< 120 ml) to 150L pressure vessels. The standard is under revision to update it for large capacity and may extend the water capacity of the vessels to volume up to 450L for hydrogen bulk transportation applications.

6 CONCLUSION

In order to store hydrogen, cryogenic and compressed storage are the most mature technology. Hydrogen energy applications have triggered the development of high pressure compressed storage in composites pressure vessels and new solutions like cryo-compressed and hydrides. The feasibility of those last technologies has been demonstrated and the standardization and regulation framework is under construction. Magnesium hydride is one of the most promising candidates for solid-state hydrogen storage. Regarding composites pressure vessels, challenges remain to improve the durability and reliability of while still ensuring the safety of cylinders in service over periods of 20 years and more for high pressure storage (up to 70 MPa). In particular, the impact of operating conditions on the materials and on the structure has to be assessed to refine the choice of materials, qualification tests and operating conditions when necessary. Periodic inspection tools also have to be developed to evaluate if the COPV still fits for service.

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