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Hydrogen Storage Technologies for stationary and mobile applications: review, analysis and perspectives

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Abstract

Hydrogen storage systems (HSSs), are the backbone of feasible Hydrogen economy. To provide a reliable renewable energy system, safe, cost effective and compact HSS is due. Physical storage systems involve the compressed gas, liquid and cryo-compressed techniques while material based one involves adsorptive materials, metal hydrides and chemical storage materials. In this paper, the features of a variety of HSSs are impartially discussed. The technical comparative analysis of the different physical and material based types of HSSs illustrates the paradoxical inherent features, including gravimetric and volumetric storage densities and parameters associated with storage and release processes, among these systems. Accordingly, no ideal hydrogen storage technique can be considered the best-fit for all stationary and automotive applications. Therefore, not only a unique HSS solution can properly provide the needs, but a set of complementary HSS solutions which may offer the system designer several options. This set of options can be hardly interpretable in case of the unclear definition of the application needs which may be time variant. Inside this review, the critical insights and recommendations about suitable applications for storage systems are provided. Different standards and codes alongside the corresponding tests are demonstrated for the different storage technologies. Moreover, storage vessels research work is overviewed for the different Hydrogen storage technologies. In addition, the failure behaviour, criteria and prediction models are investigated for composite vessels subjected to high pressures and extreme temperatures degrading their mechanical behaviour and failure resistance.

Keywords: Hydrogen storage technologies, composite pressure vessels, standard and codes, Physical hydrogen storage, material based hydrogen storage, Hydrogen Carrier

Word Count: 33,744

List of Abbreviations

AB	Ammonia borane	LOHCs	Liquid organic Hydrogen carriers
AE	acoustic emission	MAB	metal amidoborane
AMB	amine-metal-borohydride	MAWP	Maximum allowable working pressure
ANR	French national research agency	MEPoPA	Modified Extended-Power Pinch Analysis
API	American Petroleum Institute	MH	metal hydride
APUs	auxiliary power units	MHB	metal hydrazinidoborane
ASME	American Society of Mechanical Engineers	MHHCs	Metal Hydride Hydrogen compressors
BCC	body-centred cubic	MLI	multi-layer insulation materials
BESS	battery energy storage systems	MOFs	metal organic framework
BN	Bayesian Networks	MWCNTs	multi-walled carbon nanotubes

CDM	continuum damage mechanics	NZEB	net zero energy building
CFRP	carbon fibre reinforced polymer	PCA	principal component analysis
CGHS	compressed gas hydrogen storage	PED	Pressure Equipment Directive
COFs	covalent organic framework	PIMs	polymers of intrinsic micro-porosity
EDLC	Electric double layer capacitor	PoPA	Power Pinch Analysis
EIGA	European Industrial Gases Association	PS	Physical storage
EL	electrolyser	PTC	pulse tube cryocooler
EMD	Empirical mode decomposition	QRA	Quantitative risk/reliability Assessment
ESSs	Energy storage systems	SMES	superconducting magnetic energy storage
FC	fuel cell	SMR	Steam methane reforming
FEA	finite element analysis	SOFI	Spray on foam insulation
FW	Flywheel	SRV	safety relief valve
HAZID	hazard identification study	TPRD	thermally activated pressure relief device
HEAs	high entropy alloys	TRACE	Toxic Release Analysis of Chemical Emissions
HEE	Hydrogen environment embrittlement	TRS	thermo-acoustic refrigerator shield
HES	Hydrogen energy storage	UAV	unmanned aerial vehicle
HGMs	hollow glass microspheres	UGS	Underground gas storage
HSSs	Hydrogen storage systems	UN	United Nations
HST	Hydrogen storage technologies	VCS	vapor cooled shield
IEA	International Energy Agency	VDMLI	Variable density multi-layer insulation
LCOE	levelized cost of electricity	ZBO	zero-boil-off
LH2	liquid hydrogen		

1. Introduction

Energy storage systems (ESSs) play a key role in the utilization of the renewable energy resources in overcoming intermittency and fluctuations and increasing their reliability and sustainability [1]–[3]. To overcome energy generation- consumption mismatches, storage systems are proposed for storing the excess generated energy to be reused during peak demand periods. ESSs are classified into chemical, electrical, electrochemical, mechanical and thermal systems [3].

Suitable energy storage system depends on power and discharge time as shown in Fig. 1. Electric double layer capacitor (EDLC), or the supercapacitor, is an electrochemical capacitor having a large power to weight besides its ability to cover sudden high peak demands. EDLC has little storage time in order of one minute besides its undesired high cost [3]. Therefore, supercapacitor is responsible for peak load intervals as a part of hybrid energy storage systems and not employed individually. In this case, supercapacitor highly reduces the requirements of other storage system components and improves the cost of the whole storage system. In this context, Zhang et al. [4] have proposed a hybrid storage system composed of EDLC, electrolyser (EL), fuel cell (FC) with both metal hydride (MH) and compressed gas hydrogen storage (CGHS) to provide both short and long term energy storage. Various storage technologies have lately aroused such as superconducting magnetic energy storage (SMES) utilizing superconducting coil to form magnetic field and hence to store the energy. However it has very rapid response [3], its high cost restricts its integration in the energy storage fields.

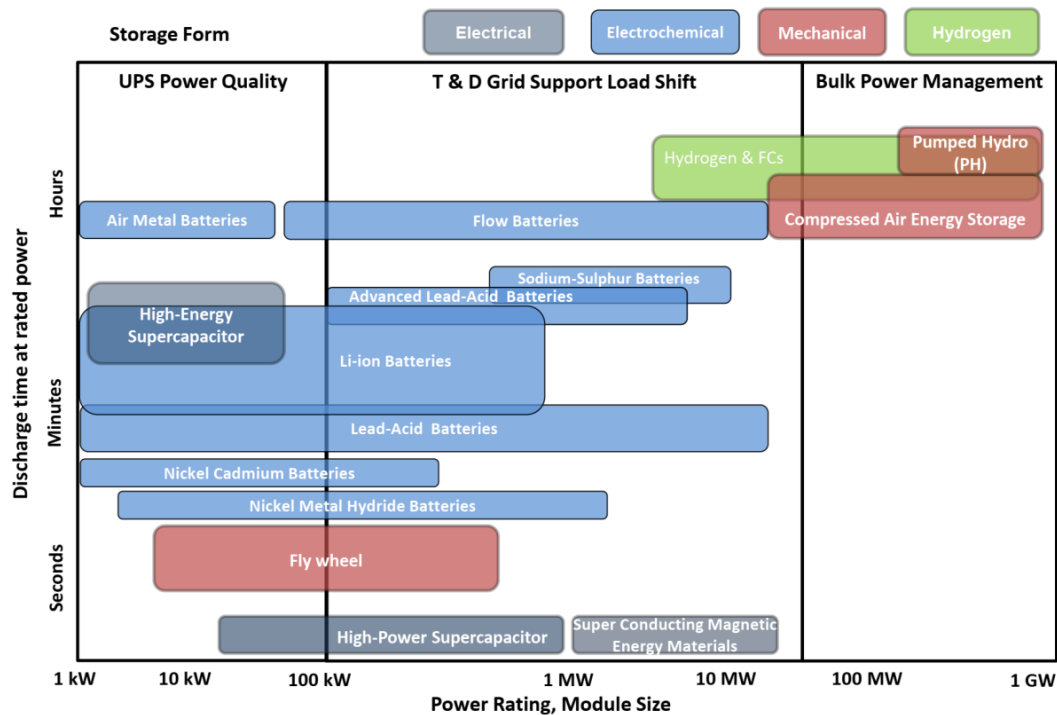


Fig. 1 : Energy storage systems [5].

Flywheel (FW) systems, used as energy storage since antiquity [6], employ electric motors to rotate FWs at high speeds, mostly in high vacuum environment, to store energy. During peak demand, FWs drive generators to supply power. FWs are mainly used to enrich the battery [7]. Recently, it has been used for smoothing the electric power demand or for eliminating electric cuts of weak duration. It is involved in uninterruptible power supplies where the short duration power changes decrease the lifetime of the batteries [6]. Jaafar et al. [6] have studied the hybrid flywheel/battery energy storage system of the hybrid locomotive. That study recommends a certain technique of injecting a part of the low-frequency mission into FWs while keeping priority for their high-frequency mission. That technique decreases the cut-off frequency and consequently decreases the number of battery cells and improving their lifetime. FWs are conveniently employed to transportation and space applications for energy transfer and to stabilize or drive satellites [8], [9]. FWs have high energy storage density, long lifetimes and high efficiency up to 90%. However, their relative small capacity and high power loss, ranging from 3% to 20% per hour are still the main disadvantages. FWs are typically used for storage capacity range of 3-133 kWh [3] for a storage period of several minutes [10].

Batteries, electrochemical devices, are used for storing electrical energy in a chemical form. Despite their fast response while energy absorbance and release, their aging is strongly time- and cycle- dependent [11]. Battery, especially of reasonable prices such as lead acid, is a mature storage technology. Lithium ion and Nickel-Cadmium batteries have relative high cost up to about 2400 \$/kWh [3]. Therefore, intensive work has been considered to reduce their cost. Flow batteries have recently emerged in large-scale grid-connected storage systems. Flow batteries have more long cycle life and high energy efficiencies than conventional ones. The current challenge is to reduce their costs to have commercial penetration [12].

Hydrogen is considered as an important clean energy source owing to its capability to produce energy without any harmful effects to the environment [13]–[16]. It is utilized either in fuel cells to produce electricity or to be burnt to generate thermal energy. Water is produced in the two scenarios. One of the crucial parameters for hydrogen is its production technology which could have slightly harmful effects to environment if produced from fossil fuels. It could have green effect if produced from renewable energy and hence it becomes highly renewable and sustainable. When Hydrogen is utilized as energy storage, it is produced through electricity conversion into Hydrogen which is known as electrolysis. Stored Hydrogen could be easily re-electrified in FCs with round trip efficiency up to 50% or to be burnt in gas power cycles with 60 % efficiency [11], [17]. Correspondingly, Hydrogen has relatively low efficiency for electricity storage. Therefore, direct Hydrogen use

is recommended in fields such as chemical and petrochemical industries or blending with natural gas in natural gas pipelines [17].

Integration, or even replacement, of Hydrogen storage systems in battery energy storage systems (BESS) has been deeply investigated. This hybridization would achieve reasonable costs with attractive performance especially for seasonal energy storage. According to Douglas [18], hybrid battery/HSS has overcome the single battery-use constraints such as cost, charge/discharge capacity and environmental issues. Therefore, more compatibility with large scale PV systems can be realized. Jafari et al. [19] have analysed HSSs used for stand-alone solar energy systems. The study has concluded that HSS was the most economical option for 8 days autonomies. Nevertheless, battery bank involvement has been more convenient for short-term storage to improve the system performance and reliability. Furat et al. [20] have investigated three different scenarios for 100% renewable energy for stand-alone microgrid (SAM); BEES, HSS and hybrid battery/hydrogen as a storage system. The proposed scenarios have been compared with the conventional DG-based SAM system. Hybrid battery/Hydrogen system has shown the least NPC and COE for the project lifetime. Colbertaldo et al. [21] have assessed HSS against BESS for 100% renewable sustainable energy system in California. The complete elimination of fossil fuels from power systems in California would require 30 TWh battery capacity which costs 20 times the proposed HSS composed of Electrolyser and FC. Groppi et al. [22] have investigated the integration of HSS into BESS in a small island in order to increase RES dependency and consequently the system sustainability. According to [22], both systems might reach the same levelized cost of electricity (LCOE) of 0.257 €/kWh. BESS/HSS may reduce carbon dioxide by 10.87% instead of 10.72% for only BESS scenario. Hybrid BESS/HSS system has extremely managed the surplus electricity contrary to BESS as well as increasing the system sustainability. Moreover, sensitivity analysis has shown the economic advantages of the proposed hybrid. Hybrid Battery/Hydrogen systems have been utilized to provide more reliable and cost effective off-grid hybrid renewable energy system [23]. Optimal energy management strategies such as FC environmental performance evaluation [24], monitoring hybrid systems and home energy management [25] have been investigated. Several studies have dealt with the optimisation techniques both to minimize the energy loss, generation cost and GHG emissions and to optimize the time allocation of domestic loads [26]–[28].

Optimal size of the components of Hydrogen energy storage systems such as Hydrogen tank, electrolyzer and fuel cell is the most important step in storage system design process. In this context, Bandyopadhyay [29] has proposed the power pinch analysis (PoPA) due to its more simplicity than mathematical modeling besides adequate insights by graphical tools. Hereafter, Esfahani [30] has suggested the extended and modified extended power pinch analysis, EPoPA and MEPoPA for the same purpose. According to [30], MEPoPA involvement, considering power losses in storage system components, has reduced the capacity of Hydrogen tank, electrolyser and fuel cell by 51.53%, 44.9%, and 25.43% lower than that designed by EPoPA respectively. Mehrjerdi et al. [31] have proposed the solar/hydro model with HSS for net zero energy building (NZEB). Optimal power of solar, hydro, EL and FC systems and Hydrogen tank capacity have been determined through GAMS software. The return on invested capital for the proposed system, if RES is utilized, might be 4 years. Olateju et al. [32] have provided the integrated wind-hydrogen 'FUNNEL-COST-H2-WIND model' for optimal EL/battery sizing for energy storage to minimize hydrogen production cost. Electrolysers decrease hydrogen cost as hydrogen flow rate increases for the same EL while optimal battery capacity has been the same for a specific flow rate range. According to [32], published in 2016, the best production cost of Hydrogen has been \$9.00/kg H₂.

Certain energy storage systems such as pumped hydro, thermal and gas storage systems could employ underground cavities and/or tanks which are settled above ground. Underground gas storage (UGS) could utilize porous media such as saline aquifers and depleted hydrocarbon reservoirs or engineered cavities having high construction cost [10]. In UGS, stored gas is divided into working gas, available to withdrawal, and cushion gas which rests on the cavity. Working gas could represent 70-80 % in salt caverns while only 20 % in aquifers [10]. Matos et al. [10] have listed the criteria and requirements for site selection as an underground storage system including host rocks reservoirs, solution-mined salt caverns and porous rock reservoirs.

Klumpp [33] has performed economic analysis for PH, CAES and HSS for short, medium and long term storage with respect to 2016 and 2030 prices. According to [33], PH has been considered suitable for short/medium

storage. However, CAES has been recommended for long term storage. For PH, CAES and HS, LCOE have reached (77/89 €/MWh), (106/107 €/MWh) and (272/273 €/MWh). LOCE for short/medium storage respectively. For long term storage, the LOCE have increased to about 326, 235 and 280 €/MWh for PH, CAES and HS respectively. In 2030, HS in caverns may be the most favourable system for long-term storage with 84 versus 288 and 184 €/MWh for PH and CAES respectively. It is forecasted that HS will significantly reduce the gap to the cheapest PH technology in short and medium-term storage. Karellas and Tzouganatos [34] have analysed four micro-CAES arrangement and Hydrogen for energy storage in the island of Karpathos. The single-stage system with air preheating has possessed the most energetic and exergetic efficiencies. However, it has drawbacks associated with cost and environment. The two-stage arrangement without air preheating has been slightly more efficient than HS. CAES systems have more capital expenditure. However, the HSS's O&M costs were higher.

Energy market has three main purposes for hydrogen involvement being stationary, transportation and portable applications [35]. Transportation applications require high gravimetric and volumetric capacities, moderate working pressure and temperature, fast kinetics, less heat during uptake and release, multi cycle reversibility, high safety and less infrastructure expenditure for recharge and recycling [36]–[43]. Automotive industry is one of the main fields which benefit from Hydrogen technology and associated storage methods [44], [45]. High-pressure composite vessels are economically important in order to provide suitable hydrogen storage for that field [46]. Composite pressure vessels with metal (Type III) and non-metal (Type IV) liners are commonly employed in automotive sector [47]. Unlike transportation market, stationary applications greatly focus on adequate material for storage tanks than capacities, kinetics or even working conditions [36], [39], [48].

In this research, authors investigate the different ESSs. Hereafter, Hydrogen based energy storage systems are discussed both individually or combined as a hybrid solution. Study focuses on Hydrogen storage technologies (HST) involving physical and material based storage systems. Different HSTs are overviewed according to their operating principles, storage density, cost and suitable applications. Throughout this study, utilized vessels for hydrogen storage are deeply studied including optimal design, failure analysis, safety and the corresponding codes, standards. Hydrogen production, transportation and storage technologies are briefly introduced in Section 2. In Section 3, physical storage technologies are intensively discussed. The research work related to physical storage vessels is deeply investigated in Section 4. Material based Hydrogen storage technologies are analysed in Sections 5. Research work related to material based Hydrogen storage containers are overviewed in Section 6. Finally, different codes and standards are demonstrated for different hydrogen storage technologies in Section 7.

2. Hydrogen Storage Technologies

Hydrogen energy is an effective solution to the pollution and energy crisis due to its cleanliness and cyclic utilization [49]. It is the most abundant, lightest, sustainable, nontoxic element. It represents an eco-friendly energy source and fuel as an alternative to conventional fuel [50], [51] which could only supply petroleum, natural gas and coal for a maximum of about 40 years, 60 years and 156 years respectively [15]. Hydrogen could be produced using both renewable and non-renewable energy resources. Its sustainability increases when produced using renewable energy resources. Besides, it is beneficial to water and food supply for third world countries [35]. Methanol production from H₂ and CO₂ and polymers fabrication from water and CO₂ [52], [53] could extensively help the Hydrogen economy achievement.

The achievement of more efficient, economic, safe and affordable techniques for HS and its transportation will positively lead to more feasible Hydrogen economy [49], [54]. Furat et al. [55] have introduced the relationship and interdependency of corners of Hydrogen square: production, storage, safety and utilization for each hydrogen energy storage systems. In 2019, Kayfeci et al [56] have listed the hydrogen production cost with renewable and non-renewable production methods as shown in Fig. 2. Ocean energy involves three major types: tidal, wave and ocean thermal energy conversion (OTEC). Although the current research projects employ ocean systems for Hydrogen production, still the hydrogen production cost of this innovative

technology is not precisely mentioned. To estimate the corresponding costs for the different ocean energy systems, levelized cost of electricity (LCOE) [57]–[61] and electrolysis cost for hydrogen production process are considered. Table 6 represents hydrogen production cost where 450 USD/kW_e CAPEX as well as 2000-8000 full load hours are utilized [62]. Mass production and full load hours have great effect on production and storage costs of Hydrogen. Hydrogen and Energy related reports/studies, such as [62], provide some of this information which is considered as a strength parameter for the study.

Table 6 : calculated hydrogen production cost (based on [57]–[62])

Ocean energy type	LCOE (\$/kWh)	H ₂ price (\$/kg H ₂)
Tidal	0.12 - 0.41	5.8 - 20.8
Wave	0.12 - 0.40	6.14 - 20.44
OTEC	0.17 - 0.75	8.53 – 31.4

High price variation are shown even for the same Hydrogen production technology. The main reason for such variations is the difference in generated electricity cost based on employed technology, generation place as well as efficiency and capacity for the utilized components. HS has been considered a key issue for the high-scale deployment of FC applications [63]. According to Dou et al. [64], the production cost of Hydrogen is about 15–30 \$/GJ which may increase to 35–50 \$/GJ due to storage, transportation and distribution [65]. Biogas, produced from wastes elsewhere, reduces the transportation distance to only 50 or 100 km. Therefore, distributed production technologies are more preferred compared to the corresponding centralised technologies such as Steam methane reforming (SMR). Distributed production technologies decrease trucks greenhouse gases emissions [66]. Hydrogen transport as a compressed gas by trailer is well established for relatively small quantities over short distances up to 200 km (as in Europe). Compressed hydrogen can be transported by cylinders or bundled tubes on tube trailer on trucks with pressures between 200 and 500 bar. At 200 bar condition, trailer capacity reaches 420 kg H₂ [67]. The capacity might increase to 666 kg H₂ with the involvement of composite material [68], [69]. The new jumbo trailer could transport 1100 kg of compressed hydrogen at 500 bar [70].

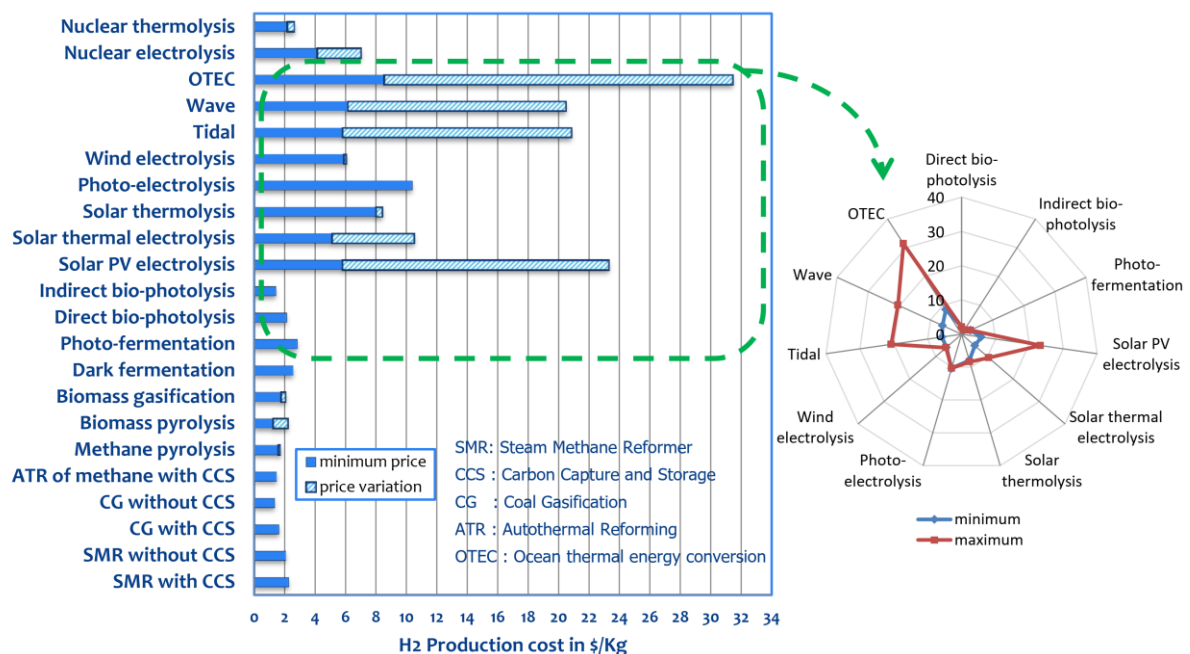


Fig 2: Hydrogen production cost with different production methods (published in 2019 [56]).

Liquid Hydrogen is more efficient for larger volumes or longer distances (as in America) [71]. Cost-effective energy carriers could play an important role towards the widespread of hydrogen technology in transport field [46]. Piping transportation for Hydrogen, costs 2 \$/GJ, is less than one tenth the other transportation techniques such as train or trucks ranging around 20-40 \$/GJ [65]. According to Veziroglu [72], pipeline transportation has been employed to closer consumption networks. Hydrogen piping has the advantage of utilizing the existing natural gas networks and even their compressors with small modifications. Lower pressure losses in Hydrogen pipelines allow the distance between the re-compression stations to be twice the case of natural gas. However, Hydrogen has its critical drawbacks such as embrittlements, sealing, fatigue stress, larger diameter piping and more compression power. Although the transmission cost of Hydrogen is about 1.5-1.8 times that of natural gas, Hydrogen becomes more economical than electricity transmission for more than 1,000 km [73].

HS is classified into physical-based and material-based technologies. Fig. 3 shows the different Hydrogen storage technologies (HST) and their classification. Physical storage (PS) methods include compressed gas, liquid and the cryo-compressed form. PS depends on changing storing conditions such as pressure in compressed gas or temperature in liquid storage or both parameters as in cryo-compressed gas storage. On the other hand, material-based, or solid state, storage involves absorption or adsorption technique. Fig. 4 shows the hydrogen storage capacity in one litre known as the volumetric capacity along with the energy content for different main hydrogen storage methods.

3. Physical Storage Technologies

3.1 Compressed Gas Hydrogen Storage (CGH₂)

Hydrogen has a very low density (0.089 kg/m³) at normal conditions. High pressure storage is the most accomplished way to store Hydrogen [74]–[77]. However, high development and manufacturing costs are the main obstacles against its democratization [78]. Almost 80% of hydrogenation processes all over the world utilize the high pressure HST in both hydrogen storage and transportation fields [49]. However, extremely high pressure up to 700 bar or 1000 bar is required for vehicle application [77], [79]. To pressurize Hydrogen to 700 bar, the consumed power is about 10% of the gas energy content [80].

To satisfy industrial requirements such as the volumetric capacity, the internal pressure must be increased up to 70 MPa [81]. As pressure increases from 1 bar to 700 bar, the Hydrogen density increases from 0.1 g/L to 40 g/L and consequently energy volumetric density increases from 0.0033 kWh/L to 1.32 kWh/L respectively. Both gravimetric and volumetric hydrogen storage densities increase by raising Hydrogen pressure. However, safety issues arise. Pressure vessels are divided into five types according to their components which consequently control their characteristics as shown in Table. 2. For industrial applications, Hydrogen is usually stored between 20 and 30 MPa in the metallic Type I cylinders of deficient gravimetric capacity (about 1 wt. %). This value remains far from targets for energy applications [79]. Type II which is partially covered by carbon fibres could attain slightly higher storage capacities than type I. Moreover, it could withstand high pressure values. Besides, classic metal pressure vessel is not capable of developing high strength/stiffness to weight ratios. On the other hand, Type IV utilizes polymer liner instead of metallic one and hence it has a better gravimetric performance. After the polymerization process the carbon fibre reinforced polymer (CFRP) possesses sufficient mechanical properties and thus works as the unit bearing the main load [79], [82]. Accordingly, composite filament wound technology could improve the storage performance due to lightweight, high strength, and adequate resistance for both fatigue and corrosion [83], [84]. In favour of these features, composite filament wound technology will be compatible with aerospace, military and hydrospace and vehicular applications. Therefore, the accelerated commercialization of hydrogen in the automotive industry will be witnessed [85].

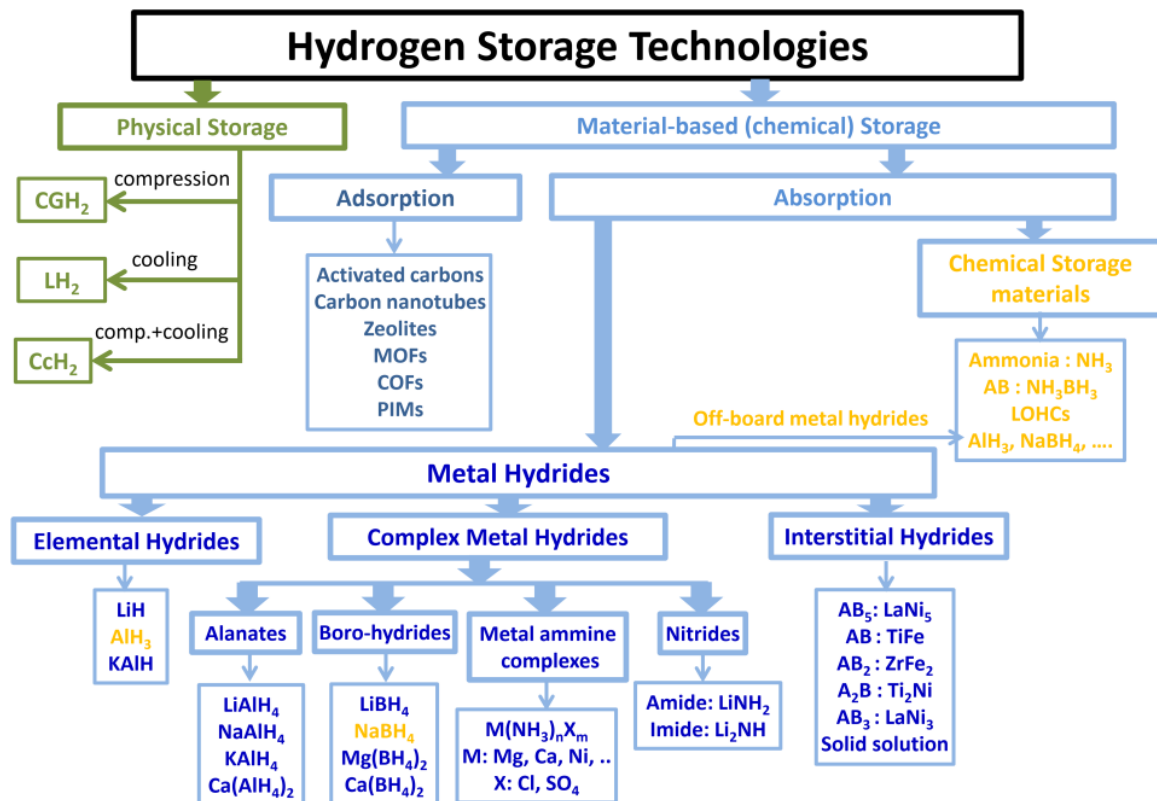


Fig. 3: Hydrogen storage technologies ([86], [87]).

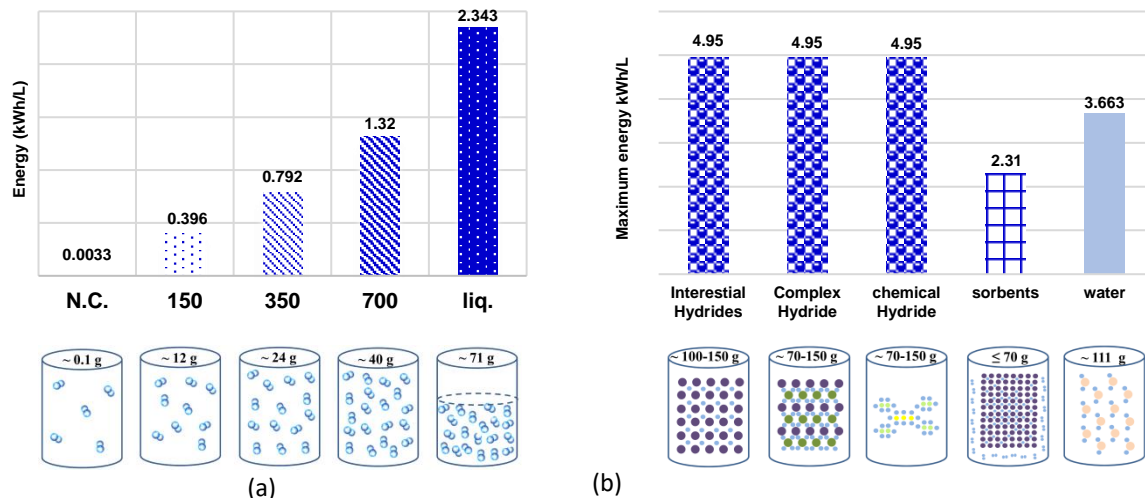







Fig. 4: Volumetric capacity and energy density for (a) physical and (b) material based Hydrogen storage methods [88].

Gravimetric capacity of composite pressure vessels could exceed four times that of steel vessels working on the same pressure [89]. Therefore, such targets will be attained by composite pressure vessels (Types III & IV) as shown in Table 2. Hydrogen storage parameters concerning storage density and cost may vary from study to another due to the utilized references for each study. These studies utilize sensitive parameters, such as location and cost of system components, which could lead to enormous differences in the overall storage cost. According to [90], DOE targets for gravimetric and volumetric capacities, for light duty vehicles for 2020, have been 4.5 wt. % and 0.030 kg-H₂/L [90]. Type IV has achieved 4.2 wt. % and 0.024 kg-H₂/L at 700 bar [90]. In addition, realizing a travel distance of more than 450 km with less than 3 minutes fuelling time is a real target. Moreover, metallic parts in composite vessels are minimal and consequently are safer while burst. Pressure vessels, which are utilized in vehicular applications, are composed of four layers. The principle layer is made of Aluminium alloy lined internally with plastic and covered externally by carbon fibres. A fibre glass layer is externally added to work as a shock absorber [91]. Hydrogen storage, as a compressed gas, in a small to

medium scale could utilize pressure vessels above ground. Salt is extremely gas tight and inert with respect to Hydrogen. Therefore, underground technology, especially salt caverns, is more suitable for large scale storage or long discharge time [10]. Apart from advantages of composite pressure vessels, cost is still an obstacle in the way towards Hydrogen economy future in the field of energy applications. Therefore, economic studies are of great importance for compressed hydrogen systems [92].

Table 2: Pressure vessels types [[7], [79], [93]].

Type			I	II	III	IV	V	
Schematic								
Components and related failures	Metallic	part	Fully metallic	Metallic enclosure	Metallic liner	Boss	-	
		Failure	- Hydrogen Embrittlement, mechanical properties degradation and premature cracks. - Premature failure for fatigue for metal liner and liner damage ^a . Reason: contact between metal and Hydrogen, surface impact ^a .					
	Composite	part	Not applicable	Some fibre over-wrap	Full composite over-wrap		Fully composite	
		Failure		Fiber breaks, delamination and matrix cracking, composite thickness decrease. Reason : accidental mechanical impacts and subsequent pressure loads.				
	Polymer	part	not applicable				Polymer liner	Under consideration
		Failure					Permeation, leakage Reason : contact between polymer and H ₂ charge/discharge conditions	
Pressure limit			≤ 50 MPa	Not limited	≤ 45 MPa	≤ 100 MPa		
Vessel price			++	+	-	-		
Gravimetric capacity wt. % or tank mass			-	±	+	++		
Popularity & maturity			****	**	*	*		

3.2 Liquid Hydrogen Storage (LH₂)

Among HST, liquid hydrogen (LH₂) storage, requiring 20 K, is characterized by significant storage density of 70.9 kg-H₂/m³ as well as safety benefits with respect to the storing pressure [77], [94]–[98]. First, large-scale liquefiers such as 501M and 503 of 180 and 300 kg/h capacities respectively have been built in the late 1960s. The 501M plants have utilized high-pressure refrigerating cycle for Hydrogen liquefaction while medium pressure refrigerating cycle with a turbo-expander have been used for 503 units [99]. Total power consumption for LH₂ storage is about 35% of the energy content of the stored hydrogen which loses much more energy than other HST [100]. Therefore, LH₂ is limited to flight and space applications where high volumetric and gravimetric energy storage densities are required regardless of its high power consumption. In addition, LH₂ has been properly used for gas delivery using trucks of capacities up to 60,000 L [79]. Hereafter, cryo-compressed Hydrogen storage technology will be investigated in which high volumetric and gravimetric could be attained with less energy consumption.

3.3 Cryo-compressed Hydrogen Storage

The density of hydrogen at high pressure (70MPa) and room temperature is only 39.1 kg/m³ while that of liquid hydrogen is 71.0 kg/m³ at 20 K and a relative low pressure of 0.4 MPa. However, gaseous hydrogen

above 15 MPa can have higher density than liquid hydrogen if stored at temperature near liquefaction temperature [100]. Thus, both temperature and pressure for Hydrogen storage could be optimized in order to obtain high storage performance. According to Yanxing et al. [100], temperature and pressure ranges for most effective hydrogen storage, regardless of ortho-to para-hydrogen conversion are: 35-110 K and 5-70 MPa respectively corresponding to hydrogen densities of 60.0-71.5 kg.m⁻³. In [100], the authors introduced two effective indices ψ and ω expressing the density of hydrogen per consumed power and the ratio of total power consumption to heat of combustion of hydrogen respectively. The value of ω for LH₂ and for CCH₂ respectively has maximally been 35% and 25%. In addition, better ψ values for CCH₂ makes it a suitable candidate for Hydrogen storage process. Apart from all these advantages, CCH₂ has been seriously affected by heat leakage than CGH₂ and LH₂ systems [100]. Moreover, its power consumption is more than that of CGH₂ as well as Hydrogen embrittlement effect which could lead to severe deterioration for the pressure vessels.

4. Physical Storage vessels

4.1 CGH₂ pressure vessels

Pressure vessel is a promising technology to store hydrogen gas in commercial applications [46], [101], [102] offering rapid refuelling with a relatively less infrastructure. Hydrogen is the lightest and smallest element [35]. Therefore, it has a permeation problem which becomes more serious at high pressures. Seamless and multifunctional layered vessels are better options to meet low-cost storage [77]. The multi-layered steel vessel is mostly preferred due to its design flexibility, fabrication, feasibility, and safety considerations [77]. However, only composite vessels could achieve the required storage densities. Hereafter, pressure vessel research studies, mostly Finite-element-based, will be intensively discussed.

Finite element (FE) is a powerful method to solve numerical problems for complex structures [103]. It could be useful in optimizing the design of pressure vessels and to predict the maximum, or burst, pressure and to evaluate the failure under different operating conditions. FE would be another alternative for multiple destructive tests before manufacturing process. Design and manufacturing of pressure vessels include several parameters such as that related to winding, dome and vessel thickness. Several experimental [104]–[106] and numerical [107]–[110] studies have ensured that failure of pressure vessels is not abrupt but rather progressive with multiple failure modes. It involves matrix cracking, fibre/matrix interface debonding, and fibre breakage. By combining the continuum damage mechanics (CDM) and the finite element analysis (FEA), the progressive failure analysis of the composite vessel is used to account for the stiffness degradation and to predict the burst pressure [111], [112]. Liu et al. [113] have explained, in the form of flow chart, FE modelling, optimised parameters and utilized software. This review has investigated failure analysis and strength evaluation involving damage constitutive model, failure criteria, progressive failure analysis and burst prediction. Leh et al. [110] have provided a progressive failure model, based on two different criteria, enabling burst simulations for type IV Hydrogen pressure vessel. Mixed FE criteria have showed low execution time while solid model have predicted more accurate stresses. Simulation results have been validated against displacement and pressure experimental measurements. Leh et al. [110] have established a progressive model to predict the burst pressure of type IV Hydrogen pressure vessel. This work has proposed a perfect method to predict the multi-sequence lay-up of a dome for several winding angles and thicknesses [63]. Ramirez et al. [104] have utilized the FEA along with experiments to provide a reliable model in order to predict the burst pressure of type IV hydrogen tank. Chapelle and Perreux [114], Iaccarino et al. [115], Bogetti et al. [116] have studied the non-linear stress–strain response as well as progressive failure analysis of type III vessel through classical laminate theory. Xu et al. [49] have studied the same parameters employing four failure criteria including the maximum stress, Hoffman, Tsai–Hill and Tsai–Wu criteria respectively. Tsai–Wu failure criterion leads to most accurate failure pressure. Camara et al. [117] have performed a statistical study to estimate lifetime and failure probabilities for Hydrogen pressure vessels as a function of internal pressures. FE has been utilized for damage evaluation. Bie et al. [105] have employed a theoretical model based on micromechanics and continuum damage mechanics to evaluate fatigue lifetime. Simulation results have been verified via

experimental ones. In framework of OSIRHYS IV project, Samtech model have been established and integrated in LMS Samtech Samcef software based on FE in order to simulate type IV hydrogen pressure vessel under 70 MPa. This study has performed identification for material parameters at coupon level and compared simulation results of burst with experimental ones at room temperature [78], [118]. Liu and Tsai [119] have proposed progressive quadratic failure criterion in order to perform the failure analysis. Naik and Krishna Murty [120] have employed different failure criteria with respect to the stress.

The main techniques of composite laminates modelling are the laminate-based and the ply-based modelling [121], [122]. Dae-Sung and Seung-Hwan [107] have investigated three FE techniques to model type III hydrogen pressure vessel. A laminate-based modelling, away from its simplicity, underestimated stresses particularly at the boundary between cylindrical part and dome. Hybrid modelling technique overestimated these stresses due to mismatches of material properties and FE types. Full ply-based modelling has been the best technique to predict accurate stress distribution and consequently it have been recommended for design process. For design and optimisation purposes, FEA has been numerously utilized. Liu et al. [111], [123]–[125] and Zheng et al. [126] have predicted the burst pressure of composite vessels with specific design parameters. Zhang et al. [81] have obtained the dome thickness using Wang's method and variable polar radii. Variable polar radii-based filament winding could significantly reduce the thickness accumulation near polar openings. However, dome thickness has not been uniformly distributed. Under the internal pressure of 70 MPa, the maximum stress for boss and liner has been 295.7 MPa and 49.2 MPa respectively which did not exceed yield strength.

Liu et al. [113] have discussed grid and composite laminate theories for design process. This review has also displayed optimal design based on safety coefficient or reliability and life time techniques. In the framework of OSIRHYS IV project, simulation models and methods have been developed and validated for design and optimization purposes for composite high pressure [78]. Design and manufacture of these vessels are enhanced by new advanced filament wound technologies [127]. Filament winding, where fibres are in yarn form, is the most suitable method for composite pressure vessel and cylinder fabrication [128], [129]. Carbon fibre contributes with approximately 50-70 % of composite tank cost [130]. Therefore, several studies have investigated involving low cost fibres or reducing high strain fibres amount and/or their cost. Optimal winding pattern is an important step in the design of filament wound composite pressure vessels which determines roving stability, fibres accumulation and laminate thickness distribution [131]. FEA has been utilized to model thin composite vessels fabricated by the filament winding without considering the exact dome geometry [49], [83], [84], [132], [133].

Modern unidirectional composites have strength to weight ratios greater than 1.5 times metal. Fibres, contrary to metals, provide the strength only in one direction (circumferential or axial directions). Therefore, axial layers must be added [134]. Optimal thickness of the composite cylinder is 1.5 times more than that of the corresponding metallic shell. Composite cylindrical vessels are mostly formed with a hoop layer with angle 90° in addition to helical layer. Helical winding allows the fabrication of a cylindrical part and domes of the vessel whereas hoop winding provides the optimal structure of the cylinder [134]. Several studies have investigated winding pattern such as plane [135], geodesic [136]–[141], semi-geodesic [142]–[144], non-geodesic [131], [145]–[150], delta- axisymmetric [151] and spline winding [152] while others have worked on methods for calculating ply thickness [84], [153]–[156]. Geodesic winding is valid for toroidal pressure vessels. It offers great stability on the supporting surface. Semi-geodesic winding with slippage coefficients allows high pressure storage and hence increases storage capacity for composite vessel [121], [157]. Unlike geodesic winding, non-geodesics increase the design space for optimal winding patterns [157]. Dome regions, described in figure 5a, suffer high stresses. Therefore, geometrical determination of the dome is a critical part in the vessel design process. Based on the non-geodesic trajectories, Zu et al. [158] have proposed an efficient method to design an isotensoid tank with unequal polar openings, shown in figure 5b, which could strengthen its structure. To optimize meridian profile, non-geodesic trajectories are involved in the design process of combined overwound structure [131], [158]. Zhang et al. [159] have predicted the burst pressure using FE method for composite elbows involving both the geodesics and non-geodesics. Based on netting theory [160]–[162] with certain mandrel size, winding parameters dissatisfy process requirements leading to non-uniform layer thickness and winding angle change.

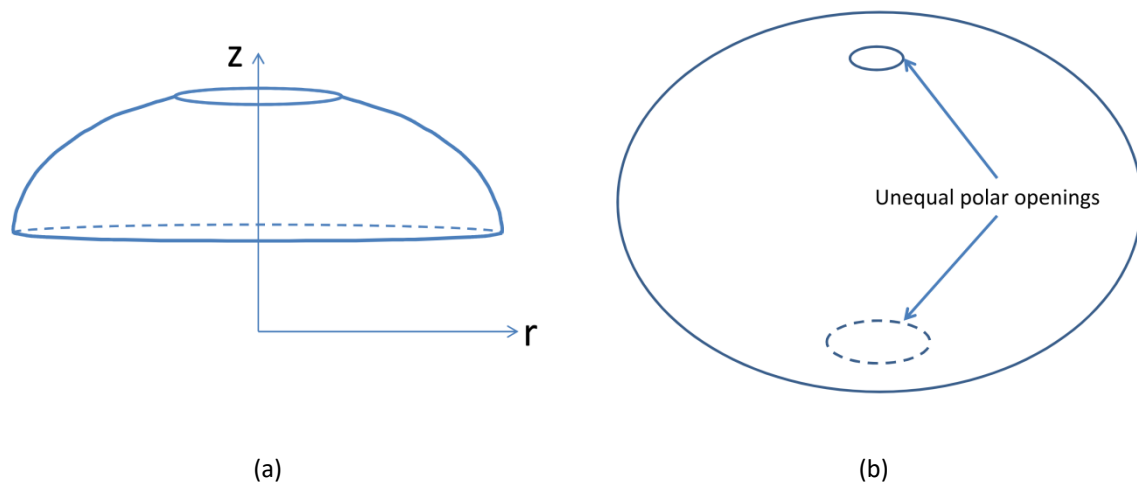


Fig. 5: Schematic for (a) dome shape and (b) isotensoid tank with unequal polar radii [158]

According to Park [142], the winding angle and thickness determination are dependent. Zu et al. [131] have established a FE model (on ABAQUS) of the pressure vessel based on the optimisation results of non-geodesic winding parameters. According to this study, winding angle decreases with increasing the slippage coefficient at certain polar opening radii. Fibres seriously overlap around tangent points when roving bandwidth increases. However, layer thickness of the dome increases with roving bandwidth decrease.

Dome behaviour and its impact on the cylindrical section of the vessel are too difficult to determine [46]. Parameters such as dome shape, lay-up in the domes or in the cylindrical section have been optimised [84], [102], [114], [121], [163], [164]. Dome-shape optimisations leads to a better stress redistribution in dome region by integrating a mechanical criterion, minimisation of strain energy, into the optimisation process [63], [133], [150], [165], [166]. Leh et al. [46] have proposed a method in order to predict both winding angles and ply thickness of the end-closures for multi-sequence composite pressure vessels. Through this work, a perfect correlation has been obtained between simulation and experimental results based on radiographic images of the tank. Leh et al. [63] have established a continuous damage model combined with a winding model so as to predict the evolving geometric characteristics and to optimise vessel parameters automatically. A 30 % reduction in mass has been obtained. During this work, metamodelling optimisation technique has been proposed. Unlike classical optimisation, the joint use of metamodelling allows computation launch on multiple machines very easily which consequently increases the method's CPU performance with substantial gains in its time. Magneville et al. [78] have shown the importance of quantifying manufacturing uncertainties and how it could be applied into robust FE analyses.

Most composite pressure vessels are porous. Therefore, these tanks must contain some kind of liner. Load share and strain compatibility between liner and composite in pressure/depressurization cycles must be considered [167]. Metallic liner has several advantages such as anti-collision, impermeability and distinct plasticity enhancing the widespread of the associated, type III, tank [81]. Zu et al. [131], [168], [169] analysed type III pressure vessels with various shapes of metallic liners. Research participates in finding innovative material for liner and parts such as valves. Autofrettage process generates compressive residual stress in a metal liner. It has been intensively studied to enhance static and fatigue strengths [170]–[172]. Son et al. [45] have predicted the required autofrettage pressure based on several failure criteria of anisotropic composites. Hong et al. [109] have re-analysed the autofrettage pressure proposed by [45] considering material degradation of composite due to temperature increase. Due to working with high pressures, the development of rubber rings of high leakage resistance is intensively investigated. On the other hand, type III has its critical drawbacks such as Hydrogen environment embrittlement (HEE). HEE occurs due to direct contact between Hydrogen and metallic parts. Its serious effects increase while operating with Hydrogen of high purity at certain conditions such as high pressure and room temperature or even lower [173]. Mechanical properties of material might degrade in hydrogen atmosphere depending on the rate of Hydrogen reactions at the metal

surface. Solubility, diffusivity and trapping characteristics of Hydrogen in addition to the real stresses/strains of the material are involved in degradation process [173].

For deep pressure cycles, liner is often made of polymer such as polyethylene and polyamides so as to avoid hydrogen embrittlement of metals [174]. The gaseous hydrogen storage at high pressure with type IV vessels is currently the best technology [63]. Therefore, it has been deeply investigated. Type IV pressure vessels suffer permeation problem due to direct contact between Hydrogen and polymer liner. Firstly, permeation rate increases with time until equilibrium is reached [175]. Thermoplastic liner utilization guarantees low hydrogen permeation rates [176]. Permeation and leak tests are involved to check the gas tight capability of the tank. In addition, pressure cycle tests are separately performed under ambient and extreme temperatures [177]. Gas accumulates at the outer surface of the liner which, during rapid emptying, exerts pressure on its external side leading to large deformation of the liner [178]. This phenomena is known in the field of oil and gas as “buckling collapse” and have recently proved for Hydrogen pressure vessels [179], [180]. Different gas pressure between the composite interface and the liner plays an important part in liner deformation. Therefore, an integrated device is recommended in order to monitor solvent differential pressure and hence to detect liner collapse [174], [181].

Critical solvent pressure, corresponding to liner collapse, require large number of tests to be accurately detected due to manufacturing variability of cylinder which will result in pressure range not a single value [181]. Hydrogen depressurisation tests funded by French national research agency (ANR) have been carried out in order to investigate permeation and deformation for type IV tank at 70 MPa [179], [180]. Blanc-Vannet et al. [174] have evaluated liner deformation during Hydrogen emptying tests utilizing CT scan for different initial pressures, maximally 700 bar, and flow rates up to 7 bar/min. This work has concluded a correlation between the severity of the collapse and the maximal pressure on the liner-composite interface which itself depends on initial and final pressure and on emptying flow rate. Permeation tests were made on sample-scale to determine parameters required for gas diffusion calculations and hence pressure at the liner-composite interface, or solving pressure, could be obtained. For sever hydrogen emptying, the composite shell could be inadequately affected especially when it has manufacturing defects as a result for Hydrogen desorption [174].

4.1.1 Thermo-mechanical behaviour

Quick charging of hydrogen gas causes temperature to rapidly rise in a vessel [109] with high temperature variation. Mechanical properties of carbon/epoxy composites vary with temperature due to epoxy resin, participating around 40%, which is highly affected by temperature variations [109]. The inverse proportion between mechanical properties and temperature for polymer-based composites has been experimentally proved [182], [183]. AE methods could predict thermo-mechanical properties under fatigue cycling [184]. According to Son et al. [45], [107], vessel might fail under excessive pressure due to a transverse tensile fracture mode which is significantly affected by temperature change. However, Metallic materials could withstand temperature change between -50 and 40 °C and pressure range from 45 to 80 MPa [173]. Shimokawa et al. [185] have experimentally confirmed the dependency of static and fatigue strengths on temperature for carbon/bismaleimide composites. Walker [186] has analysed the compressive strength for carbon/epoxy composites under different temperature conditions (-129 °C, 21 °C, and 177 °C). Hong et al. [109] has established a FE model for type III hydrogen pressure vessel in order to obtain temperature distribution during various pressurization conditions. Based on temperature distribution, reduced properties have been evaluated in order to check for possible failures. Even for minimum burst pressure of 164.5 MPa, maximum temperature only has reached 90.6 °C and consequently high degradation rate have not been noticed.

AE may estimate the damage within hydrogen filling process [187]. A temperature prediction numerical model for both Hydrogen and its container during fast fuelling is necessary. Gentilleau et al. [188] have considered thermo-mechanical stresses caused by rapid filling. The effect of temperature and matrix cracking on the composite pressure vessel with a polyurethane liner has been studied. Dicken and Merida [189] have assessed the temperature variation of type III pressure vessel (35 MPa capacity) according to the charging time and compared these results with analytical ones. Through fast fill, the temperature tank goes up to 85 °C at 87.5 MPa due to the compression heat [173]. It comes back, within minutes, to the automotive normal

temperature range (-40 to 40 °C). Moreover, the tank temperature could reach -80 °C when driving at full speed at -40 °C ambient temperature.

Reviews [78], [104], [113], [117], [127], [190]–[192], have analysed burst strength for pressurized wound storage at room and moderate temperature (80°C) based on analytical and FE techniques. These studies have proved a great relation between the temperature and material properties. The thermal strain compatibility of the liner and composite under thermal cycling, stress-rupture and creep compatibility of the composite under long-term pressurized loads are of great importance. The thermo-mechanical behaviour has been deeply investigated both for ambient and extremely hot (85°C) and cold (-40°C) temperatures [78]. According to [167], Leak-before-burst capability of liner and composite system must be included in the design.

Magneville et al. [78] have employed a thermo-mechanical behaviour law to study the burst behaviour of hydrogen vessels under high pressures. Thickness of storage structures prevents direct testing on conventional mechanical test machines. Therefore, coupled mechanical-thermal-decomposition model has to be identified from representative samples cut in wound tubes [190]. Hu et al. [132] have coupled thermal and mechanical damage in a FE model and predicted the profile of resin content in the hydrogen storage vessel. The mechanical strength of composite vessels is highly sensitive to thermal load and especially to fire [193]–[195]. Unlike metallic vessels, burst of composite tanks when fired is not due to pressure increase. Matrix of outer layers is directly exposed to fire and is consequently degraded. Composite transforms into char whose mechanical properties are severely reduced [196]. Fire danger has led to extensive research work due to its great importance. This chemical reaction substantially modifies the stress distribution within the structure. Stresses are transferred from outer burnt layers to inner ones. Damage threshold is reached and hence the global strength is deeply reduced. INERIS is a French National Institute for Industrial Environment and Risks which contributes to the evaluation and prevention of the risks that are induced for the environment, health and safety of people and goods. In this context, it has performed a full-scale conventional bonfire experiments, using heptane pool.

Experiments have included both steel and composite pressure vessels in order to determine the fire conditions to test the thermo-mechanical behaviour [190]. Halm et al. [190] have developed a reliable thermo-mechanical model. To get this model, pressure and temperature measurements, during and after the fire, has been carried out through FireComp project. The methodology has satisfactorily predicted results in spite of simple assumptions such as axisymmetric geometry, homogeneous flux and burst at first fibre failure. Without thermally activated pressure relief device (TPRD), highly pressurized vessel will burst when subjected to fire [190], [197]. Pressure limit determines the threshold between leakage and burst failures when subjected to fire [176]. Liner melts, leading to depressurization through composite shell, if heat transfer is faster than properties degradation. Otherwise, deteriorated wall would burst [176]. To prevent tank rupture, an additional TPRD shall be involved and CFRP wall thickness shall be designed based on 2.25 times NWP [177], [198].

During the bonfire tests, it can be observed that the liner melting temperature is significantly higher than determined by DSC at atmospheric pressure [176]. Melting temperature of the liner could be pressure dependent [176]. Zheng et al. [199], [200] have performed CFD simulation of bonfire tests in order to investigate the effects of fuel type, fuel flow and filling medium on internal temperature rise of pressure vessels subjected to engulfing or localized fire. Bustamante-Valencia et al. [82] have evaluated the fire resistance for 100 L tank, through measuring time to burst, under different pressures. Blanc et al. [193] and Halm et al. [190] have obtained time to burst for different initial pressures as well as deduced that 36 L tank has a pressure limit of 250 bar. Huppa et al. [176] have analysed failure mechanism for COPV for different thermal loads, including fire, considering heat transfer to liner as well as degradation of mechanical properties. According to this work, an increase in the temperature or the impingement area of the fire leads to a considerable decrease in the fire resistance time. In addition, lower initial hydrogen pressure leads to an increase in fire resistance time.

4.1.2 Failure detection

Pressure vessels shall be regularly inspected and monitored. Manual methods are expensive, time-consuming and could give high result variability due to subjective judgements. Therefore, non-destructive methods such

as ultrasonic scan [187], X-ray tomography [187], and the promising acoustic emission (AE) technology [184], [187], [201], [202], could be utilized. AE methods could detect the damage caused by pressure loading [202]. Damage mechanisms are associated with parameters of AE features [203], [204]. Moreover, critical AE signals could be accurately identified based on neural network algorithm in spite of being time consuming [205], [206]. Empirical mode decomposition (EMD) and Hilbert-Huang spectral analysis were used to obtain the frequencies associated with the composite damage mechanisms [207]. Marec et al. [208] used fuzzy c-means clustering method combined with principal component analysis (PCA) which gave better description for damage mechanisms. Liao et al. [47] has utilized AE methods to describe damage mechanisms of Type IV pressure vessels. AE parameters including amplitude, frequency, and energy are analysed. The amplitude, absolute energy, and energy are correlated to matrix cracking, fibre/matrix interface debonding, and fibre breakage which represent damage mechanisms. According to this study, the amplitude, absolute energy, and energy of the matrix cracking are generally the lowest while those associated with fibre breakage are the highest. Fibre breakage, being the least failure, signals mainly appears near the highest pressure of 158 MPa.

The safe, reliable and economic performance for composite hydrogen vessel is related to excellent prediction of damage evolution and failure pressure [114], [121] especially with the possibility to assess damage during in-service use [209]. Therefore, master curve have been developed in order to evaluate damage considering the intrinsic safety factor as shown in fig.6 [209]. Pressure vessels could be regularly compared with the master curve during its in-service life. Unusual operating conditions such as overheat could accelerate damage. However, it can confidently return to service provided that vessel's damage is lower than that of master curve.

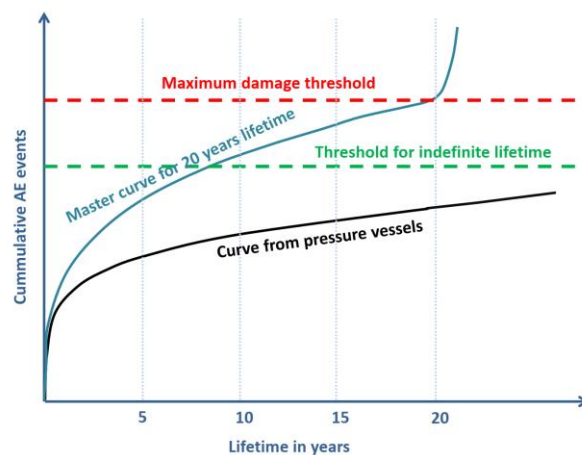


Fig. 6 : Pressure vessel damage evaluation during in- service use [209].

4.2 Cryogenic vessels for LH₂ and CCH₂

LH₂ temperature is approximately 20 K, far less than ambient conditions, which stimulates heat leakage and evaporation loss particularly in long-term storage [210], [211]. Therefore, it requires high efficiency (vacuum) insulated vessels where an inner pressure vessel is introduced into an external protective jacket. For further enhancement, perlite (powder structure) or super insulation are employed. Intensive research has been performed on both passive insulation and active technologies in order to attain zero-boil-off (ZBO) liquid hydrogen storage [212]–[217]. Spray on foam insulation (SOFI), hollow glass microspheres (HGMs) and multi-layer insulation materials (MLI), perlite and aerogel are candidates for insulation materials [218]–[228] which could be optimized in single or composite form [227], [229], [230]. Variable density multi-layer insulation (VDMLI) and self-evaporation vapor cooled shield (VCS) have been recently introduced to such systems to increase their effectiveness. Zheng et al. [231] have analysed the insulation performance for different arrangements being MLI, VDMLI, MLI + VCS and VDMLI + VCS. According to this study, combination of VDMLI and VCS could reduce heat flux by 83.12% than MLI and 66.32% than VDMLI. That work has optimized the position of VCS in VDMLI and MLI. With respect to MLI system, Single-VCS and Double-VCS integration could reduce heat flux by 50.16% and 59.44% respectively with little effect for the subsequent VCS involvement [232].

Moreover, the insulation performance under different vacuum conditions and emergencies has been investigated [231], [232]. Wang et al. [233] have optimized both HGMs-MLI and HGMs-VDMLI insulation systems and have studied the influence of WBT and vacuum pressure on the insulation performance. HGMs-VDMLI system has showed better thermal, for same weight, and economic performance than foam-VDMLI. Thermal insulation performance of VDMLI is 58% better than MLI [234]. Sun et al. [235] have proposed a design for passive ZBO system without requiring highly qualified insulation material which could store liquid hydrogen for two years without evaporation. To improve insulation performance, vapour-cooled shield [236], [237] has been proposed in conventional insulation systems to recover the sensible heat of H₂. On the other hand, Zheng et al. [238] have optimized a system composed of thermo-acoustic refrigerator shield (TRS), utilizing H₂ combustion heat, and self-evaporating vapour cooled shield with different insulation materials in order to reduce the temperature of the insulation material and hence the heat leakage amount [239], [240]. According to [238], the heat flux into tank with VCS decreased by 70.98% and TRS by 90.81%.

Several studies have investigated active cryocooler technologies to achieve zero boil off, re-liquefy the evaporated Hydrogen, for liquid Hydrogen storage [212], [213], [216]. Turbo-Brayton cryocoolers have excellent characteristics with respect to performance, reliability, vibration, maintenance, lifetimes, size, and mass [241], [242]. Deserranno et al. [243] have designed a 20 W, at 20 K, cryocooler with Carnot efficiency of 23%, being 3 times better than any 20 K cryocooler. Moreover, capacity and Carnot efficiency could increase to 80 W and 25% respectively. According to this work, utilization of a 100 K liquid oxygen tank to provide shielding to the 20 K liquid hydrogen tank reduces the required cooling amount at 20 K to become 0.02-0.25 W/m². Stirling pulse tube cryocooler (PTC) type has become the first option in space application due to its high qualifications [203], [244]–[246]. Increasing the storage temperature and hence the pressure of LH₂ greatly reduces PTC input power but Hydrogen density significantly decreases [244]. Zheng et al. [244] have optimized a PTC cryocooler integrated with cold shield and MLI to minimize its power consumption. According to this work, optimal temperature and position of the cold shield could reduce power consumption by 69.5% and 74.4% for single and two cold shield cases respectively. Shuang et Liu [247] have established a transient CFD model for liquid Hydrogen tank in order to study the effects of injection liquid velocity, injection liquid temperature and pressure drop range on the efficiency of the pressure drop process under the microgravity operating conditions. According to that work, temperature decrease or velocity increase of the injection process could increase the efficiency of depressurization process.

Apart from these previous studies, Borges de Sousa et al. [248] have benefited from evaporation process of liquid Hydrogen. Here, researchers have proposed a device, based on gas/liquid Hydrogen in order to store heat energy in the 15K-17K range, to be utilized as a thermal stabilizer for cryogenic chains in satellites. It has been validated in different working conditions in respect to gravity and heat load application. However, liquid Hydrogen cell is about 17 cm³ in volume; it requires about 56 L for the hydrogen gas expansion to maintain low temperature for the cell.

On the other hand, the BMW Group has utilized cryo-compressed hydrogen tank with large storage capacity for hydrogen vehicles [249], [250]. For that purpose, type III composite pressure vessels, contained in an insulated jacket, are employed. The design of the cryo-compressed storage tank has been discussed in [251].

5. Material based Hydrogen Storage

Material based Hydrogen storage depends on materials which have the ability to reversibly store hydrogen in either hydride or molecular hydrogen. Hydrogen storage materials should have certain characteristics such as rapid kinetics, good reversibility, affordable price and high storage capacities at reasonable operating temperatures and pressures [252], [253]. Based on the storing technique, material based hydrogen storage could depend on adsorption or absorption. As previously discussed, physical storage has some drawbacks such as storage capacity, consumed energy and vessel requirements to withstand high pressure or to prevent heat leakage as in liquid or cryo-compressed. Moreover, there are safety issues related to extreme pressure such as leakage, burst and fire hazards. Consequently, research has sought out new technologies which could achieve high Hydrogen storage capacities while being capable of operating under moderate pressures and

temperatures. For material based hydrogen storage technology, storage density has been mentioned in more studies without determining whether all storage system components are included or only the storage material. Compared to physical storage, material based storage is predicted to have higher hydrogen storage capacity at room temperature [254] as well as being safer [51] owing to lower hydrogen storing pressure and slower hydrogen release rate.

Recently, there have been research projects related to material based hydrogen storage such as STORHY [255], [256], NESSHY [255], [257], HyFillFast [255], SSH2S [258] as well as HyCARE project [259], utilizing metal hydride to store quantities up to 50 kg Hydrogen and McPhy, GKN [260] to enhance deployment of solid state hydrogen storage. Moreover, first unmanned aerial vehicle (UAV) test flight with Cella solid-state hydrogen storage has been developed which is considerably lighter than that utilizing the Li-ion [261]. Hereafter, material based storage will be intensively investigated.

5.1 Adsorption technologies

Adsorption is a surface process, mostly reversible, involving the transfer of a molecule from a gas or liquid to a solid surface [262]. Based on adsorption, there are several promising hydrogen storage materials such as carbon nanostructures, metal organic framework (MOFs), covalent organic framework (COFs), polymers of intrinsic micro-porosity (PIMs) and zeolites. These structures have been intensively investigated due to their fast kinetics, good reversibility as well as high hydrogen storage capacity [35]. Efficient hydrogen storage in nanostructured materials is challenging because of their very low density [263] especially at moderate temperatures.

5.1.1 Carbon based materials

Several carbon based substrates like porous carbon and carbon nanotubes and nanofibres of various structures have hydrogen storage properties [264]. Activated carbon is one well-known material for hydrogen adsorption, especially under cryogenic conditions and high hydrogen pressure. The chemical treatment, to prepare the activated carbon, governs its porosity and surface properties, thus directly affecting its hydrogen storage behaviour [265], [266]. Carbon nanostructures, especially of high specific surface area, have great potential for hydrogen storage [267]. Carbon nanotubes are graphite sheets rolled up in a cylindrical shape whose adsorption capacities depend on the pore size and the curvature of the tubes [268]. Owing to their nanometre scale diameter, these materials allow high density hydrogen gas condensing of about 5–10% by weight [268]. The typical adsorption capacities of activated carbon range from 1-7 wt. % at 77 K and pressures of 1–20 bar respectively. At pressures slightly above ambient (viz. 2–4 bar), the gravimetric capacities reported are about 2–3% [264]. Super-activated carbon could reversibly store up to 5 wt. % and 1.3 wt. % at 77 K and 296 K respectively [269] with more capacities near liquefaction temperature. Hydrogen uptake parameters depends on the structure of nanotubes including single or multi-walled, fibres or ropes as well as the presence of some elements or doping agents [270]. Doping of the carbon sites by various elements or the presence of elements like oxygen has also been shown to have only a negligible effect [271], [272]. In addition, reactive ball milling has been suggested for carbon nanotube material in hydrogen atmosphere for prolonged duration to enable higher hydrogen adsorption [273]. However, it is considered as unstable at room temperature and could have relatively low volumetric H₂ storage capacity due to low packing density [267].

5.1.2 Metal organic frameworks

Metal organic frameworks are porous crystalline materials with large surface area (up to 4800 m²/g) involving organic linkers and inorganic metal oxide units [274]. Based on 4000 MOF species, specific surface area of 3100–4800 m² g⁻¹ have the maximum theoretical storage capacity [264], [275]. MOF-5 (Zn₄O (BDC)₃ where BDC is 1,4-benzenedicarboxylate) is a mature candidate for hydrogen storage at both ambient and cryogenic conditions. It has hydrogen adsorption capacity up to 4.5 wt. % at cryogenic conditions and 1 bar pressure whereas, 1% under ambient conditions and 20 bar pressure [264], [276]. More polarized links and reduction in

pore dimensions have shown a positive effect on the hydrogen adsorption capacity [277]. Dissociative chemisorption onto the porous network has increased the hydrogen uptake capacity of MOF-5 and IRMOF-8 by 8 times [264], [278], [279]. Finding suitable agents, such as metal ions, shall be intensively studied in order to favourably modify MOF properties for hydrogen storage under ambient temperature and moderate pressures. Introducing metal ions such as Li^+ , Cu^{+2} , Mg^{+2} into MOFs have been intensively studied in order to improve the hydrogen storage performance [279] whereas, research shall deeply investigate adequate mechanical strength of the MOF structure and thermodynamic properties. According to [280], MOF-5 has greatly approached the 2020 targets provided by U.S. DOE for performance and cost parameters of the automotive material based Hydrogen storage as shown in table 3. However, the requirement of cryogenic conditions and relatively high hydrogen pressure could be the main obstacle to the widespread utilization of MOFs-based hydrogen storage system.

5.1.3 Zeolites

Zeolites are crystalline aluminosilicate materials having highly ordered structures and uniform pore sizes. They are good adsorbents for various gases such as hydrogen carbon dioxide as well as moisture. In physisorption-dominated hydrogen uptake, the maximum storage capacity depends on the available surface area for adsorption [264], [281]. Hydrogen can be forced into the porous structure of zeolites, known as encapsulation, at very high pressures (up to 900 bar) and relatively high temperatures (up to 350 °C) where it can remain confined even at room temperature [282]. NaX zeolites have capacities up to 2.55 wt. % at 77 K and 40 bar [264], [283], [284]. Moreover, hydrogen storage capacity has been improved at room temperature by doping the zeolite structure with palladium and similar metals [285] or by utilizing techniques such as bridging and spillover mechanism which enhances hydrogen uptake [286].

Table 3: Performance and cost analysis of material based Hydrogen storage systems for automotive applications: current status vs. targets [280].

	Storage Technology (material)	Gravimetric Density (kg H ₂ /kg system)	Volumetric Density (kg H ₂ /L system)	Cost (\$/kg H ₂)
Current status	NaAlH ₄	0.012	0.012	\$1,430
	MOF-5	0.038	0.021	\$490
	Off-Board (AB)	0.046	0.040	\$550
Targets	2020 Target	0.045	0.030	\$333
	Ultimate Target	0.065	0.050	\$266

5.2 Absorption technologies

Several hydrides such as ionic, covalent and complex hydrides are prosperous candidates for Hydrogen storage. For reversible hydrogen storage, both absorption and desorption shall be applicable. According to desorption technique, additional components shall be included in the storage system. These components add to the system weight and hence reduce the actual hydrogen storage densities of the system as it does not contain extra hydrogen. Three methods are employed to desorb hydrogen; hydrolysis, ammonolysis and thermolysis [267]. Hydrolysis generates irreversible by products $[\text{M}(\text{OH})_x, \text{MAIO}_2, \text{MBO}_2, \text{NH}_4\text{BO}_2]$ [267], [287], [288].

5.2.1 Metal Hydrides

Several metallic based materials have the ability to absorb hydrogen under moderate pressure and low temperatures [289]. Metal hydrides composed of lightweight elements such lithium (Li), boron (B), nitrogen (N), magnesium (Mg) and aluminium (Al) have shown great potential for use as hydrogen storage materials [290]. Moreover, it appears to be the safest method of storing hydrogen owing to relatively low operating

temperatures as well as endothermic hydrogen release [291], [292]. However, metal hydrides suffer from the disadvantage of weight for hydrogen on-board storage [293] as well as slow kinetics, low reversibility and high dehydrogenation temperatures [294]. The most promising metal Hydrides are listed in Table 4. Substitution is one of the most modification process for the purpose of achieving adequate kinetics or economic effectiveness. In this article, metallic based hydrides are classified into elemental, intermetallic and complex hydrides.

5.2.1.1 Elemental Hydrides

Several metals such as Mg, Na, Li, Ca and Al are promising candidates for Hydrogen storage. Among these metals, research has focused on the utilization of magnesium based alloys for hydrogen storage [295] owing to the following reasons: (1) favourable hydrogenation characteristics, [296], (2) high hydrogen storage densities up to 7.6 wt. % [297], [298], (3) light weight (4) excellent heat resistivity and good recyclability [299], (5) abundant availability, (6) reasonable prices [300]. Mg-based alloys have a hydrogen storage capacity of approximately 5 wt. % [252]. However, Mg-based alloys have poor thermodynamic characteristics and sluggish kinetics [301] owing to the strong bonding between Mg and hydrogen [252]. Consequently, high decomposition temperature (~573 K) is required [302]. To improve the storage performance of MgH₂, alloying, surface modification [252], doping [303] as well as reducing particle size to nanometre scale [304] could be employed. Zhang et al [305] have intensively overviewed different techniques, such as nanocatalysis and nanostructuring, which could enhance the hydrogen storage performance of MgH₂. Transition metals based nano-catalysts such as Na₂Ti₃O₇ [306], NbH_x [307], Ni nanofibres [308], (Ti_{0.5}V_{0.5})₃C₂ [309] have great effect on the kinetics while metal carbon composites could additionally improve cycling stability effects. On the other hand, nanostructuring of Mg/MgH₂ may improve both thermodynamics and kinetics characteristics.

Moreover, technologies such as mechanical alloying, reactive ball milling and mechanical grinding have been suggested [310], [311]. According to [312], Hydrogen absorption/desorption kinetics of Mg are affected by three parameters: (1) the magnesium oxide layer, (2) limited hydrogen dissociation, (3) low hydrogen mobility of the magnesium hydride phase [313]. On the other hand, the hydrolysis reaction of MgH₂ is very slow due to the formation of insoluble layer of Mg-hydroxide. To accelerate H₂ yield in hydrolysis, acetic acid and catalyst are employed [267]. Owing to the importance of heat transfer; Thiangviriyi et al. [314] have proposed central tube heat exchanger for hydrogen storage systems utilizing MgH₂-TiF₄-multi-walled carbon nanotubes (MWCNTs). Heat exchanger has doubled absorption/desorption kinetics and consequently neither agglomeration nor sintering has occurred.

Aluminium hydride AlH₃, or alane, is a hydrogen storage material with high gravimetric and volumetric hydrogen storage capacities of 10.1 wt. % and 7.47 kgH₂/100 L respectively. However, it requires a very high pressure in the order of GPa in order to reversibly store Hydrogen as well as being unstable [315], [316]. Consequently, this alloy will be classified as chemical, or off-board, hydrogen storage system. Elemental hydrides such as LaH₂, YH₂, ZrH₂ and TiH₂ are very stable and consequently need very high temperatures whereas others such as NiH and FeH are very unstable and hence require very high pressures [317]–[319]. Multiple studies have investigated NaH, LiH and CaH₂ compounds which vigorously react with water [320], [321] with more than 90% conversion in 1 min [321].

Table 4: The most promising metal hydrides alongside their modifications.

Category	Candidate	Modification	Features	References	
Elemental Hydrides	MgH ₂	Without modifications	storage density up to 7.6 wt. % with sluggish kinetics, poor thermodynamic properties requiring 300°C decomposition temperature.	[297], [298], [302]	
		mechanical grinding and doped with 1 mol% of Nb ₂ O ₅	absorbance of 4.5 wt. % of hydrogen within 15 s at RT and 1 MPa.	[322]	
		disks of nano-composite (MgH ₂ /8wt.% Nb ₂ O ₅ +2 wt.% Ni)	5.5 wt. % hydrogen storage density and fast absorption/desorption kinetics of 2.6/3 minutes at 250 °C with 400 h life cycle.	[323]	
		MgH ₂ coating with Ni powder (3 layers)	hydrogen storage capacity of 6.1 wt. % , good cyclability up to 600 cycles as well as good absorption/desorption kinetics at 150/200 °C and 10/0.2 bar within 5.1/11 minutes.	[324]	
		utilization of MgH ₂ /MoS ₂	hydrogen storage density of 6.15 wt. % with a peak dehydrogenation temperature of 402 °C	[325]	
		gradual temperature variation from RT to T _{max} during hydrogenation	Mg nanotrees form has offered the maximum storage density of 6.19 wt. % within 150 minutes at T _{max} = 300 °C.	[326]	
Interstitial Hydrides	AB ₅	LaNi ₅	without modifications	hydrogen storage up to 1.5 wt. % theoretically	[327]
			partial Ni substitution with Co	enhanced cyclic and anti-electro-oxidation ability	[328]
			partial Ni substitution with Mn	reduced formation pressure without reducing storage density	[328]
			LaNi _{5-x} Sn _x (0 < x < 0.4) prepared by arc melting,	low equilibrium pressures, fast kinetics, adequate resistance against cyclic degradation.	[329]
			partial La substitution with Ce	increased equilibrium pressures, positive effect on the low-temperature capacity, increased hydrogen equilibrium pressure.	[329] [330] [331]
			CeNi ₄ Zr and CeNi ₃ Zr ₂ alloys	larger storage density than CeNi ₅ with capacity increase with an increase in Zr content.	[292]

Category	Candidate	Modification	Features	References	
Interstitial Hydride	AB	TiFe	Without modifications	reversibly absorption of hydrogen up to 1.9 wt. %.	[332]
		The substitution of Fe with Ni (TiNi)	up to 1.2 wt.% capacity at desirable operating condition with improved life cycle, formation of undesired surface oxides, TiFe _{0.8} Ni _{0.2} is the most promising	[332] [333] [332]	
	AB ₂	ZrFe ₂	Without modifications	1.7 wt. % capacity with hydriding/dehydriding P _{eq} of 69.9/32.9 MPa at 20°C.	[334]
		ZrFe _{1.8} Mo _{0.2} (M=V, Cr, Mn) ZrFe _{1.8} Mo _{0.2} (M=Fe,Co,Ni,Cu) ZrFe _{1.8} Mo _{0.2}	about 1.8 wt. % Hydrogen storage density, approximately 1.7 wt. % Hydrogen storage density, 1.6 wt. % Hydrogen storage density	[335]	
		Zr _{1.05} Fe _{1.7} Mn _{0.2} V _{0.1} (Zr _{0.6} Ti _{0.4}) _{1.05} Fe _{1.2} Mn _{0.8} (Zr _{0.5} Ti _{0.5}) _{1.05} Fe _{0.95} MnV _{0.05} (C14)	lowest hysteresis, lowest plateau slope, 1.64 wt. % Hydrogen storage density and dehydriding pressure of 6.82 atm. at 298 K.	[336]	
		without modifications	hydrogen content up to 5.6%, slow kinetics, poor reversibility, severe dehydrogenation conditions, two-step decomposition reaction	[337]–[340]	
Complex metal Hydrides	Alanates	NaAlH ₄	doping with Titanium or Zirconium	improved performance	[42], [341]– [344]
		doping with Chlorides of zirconium, vanadium, and several lanthanides	Improved kinetics similar to Ti	[345]	
		addition of TiCl ₃ catalyst with 4 mole %	improved reversibility, thermodynamic and kinetic properties	[345]	
		TiF ₃ catalyst instead of TiCl ₃	comparable effects with less costs	[252], [337]	
		doping with scandium (Sc)	fast kinetics, hydrogen storage capacities within a range of 4.0-4.9 wt. %, very expensive.	[340]	
		NaAlH ₄ nanocomposite doped with carbon, porous and nonporous	high storage capacities up to 7.0 % at 673 K.	[346]	

Category	Candidate	Modification	Features	References	
Complex Metal Hydride	Alanates	LiAlH ₄	without modifications	high hydrogen capacities up to 10.6 wt. % requiring very high pressure and temperature, thermodynamically unstable	[347], [348] [196], [340], [349]
		Doping with Ti-based or V-based catalysts	reduced decomposition temperature	[350]	
	Borohydrides	LiBH ₄	without modifications	high gravimetric capacity up to 18.5 wt. % at room temperature difficult hydrogenation process, very high decomposition temperature experimental capacity around 50% of theoretical.	[351] [352] [353] [349]
			SiO ₂ utilization	hydrogen release starts at 473 K, hydrogen storage capacity of 13.5 wt. %	[354]
			doping with fluorine (such as LiBH _{3.75} F _{0.25})	9.6 wt. % hydrogen storage capacity at predicted temperature of 373 K	[355]
			addition of Mg and Ti-based catalysts	hydrogen storage capacities up to 8 wt. % at temperatures above 598 K	[353]
			doped with LiNH ₂ at a molar ratio of 2:1	release hydrogen more than 10 % by weight	[348]
			LiBH ₄ /CaH ₂ system	better reversibility than LiBH ₄ with a theoretical hydrogen storage density of 11.7 wt. %	[356]
			LiMn(BH ₄) ₃	low activation energy, more desorbed Hydrogen up to 8.0 wt. % at relatively lower temperature	[352]

5.2.1.2 Interstitial Hydrides

Intermetallic compounds have a great affinity to absorb hydrogen forming the intermetallic, or interstitial, hydrides on the form of $A_xB_yH_z$ [252] where A and B are mostly rare earth and transition metals [329]. Intermetallic compounds have certain formulas including AB_5 , A_2B , AB_2 , AB , A_3B and vanadium based solid solutions [252]. Khan et al. [357] have described new intermetallic groups such as A_2B_7 with $Y_2Ni_7H_8$, $La_2Ni_7H_8$ and $La_{1.5}Mg_{0.5}Ni_7$ as candidates [318], [358], [359]. Research has focused on certain metals such as uranium, zirconium, titanium, lanthanum, cobalt, nickel as well as iron [264]. Among intermetallic compounds, uranium based hydrides have the best hydrogen storage performance. However, availability issues limit it to nuclear industries [264]. For hydrogen isotope storage, especially in the field of fusion research, ZrCo is the closest element to uranium [264]. Palladium offers a relatively low temperature of 350 °C for palladium hydride regeneration as well as having easy handling in non-pyrophoric powder form. However, it could store little amount of Hydrogen [360]. On the other hand, BCC structures such as $Ti_{0.22}Cr_{0.39}V_{0.39}$ absorbs and desorbs 2.2 wt. % of hydrogen at low temperature and dissociation pressure [361]. Apart from hydrogen storage, intermetallic compounds such as $LaNi_5$ could be employed in Hydrogen systems for sensing, catalytical and purification purposes [362].

5.2.1.2.1 AB_5 – type alloys

$LaNi_5$ is the most investigated AB_5 alloy which has favourable storage characteristics such as fast kinetics, low equilibrium pressures as well as high reversibility at ambient conditions [363], [364]. However, it has low gravimetric hydrogen storage capacity (theoretically 1.5 wt. %) [327]. To develop cost-effective materials, lanthanum (La), nickel (Ni) or both shall be partially substituted with low-cost metals [365]. The utilization of elements such as Rh, Ir, Pt, and Au could decrease the absorption pressures and stabilizes the formed hydrides [364]. On the other hand, $CaCu_5$ is the most promising compounds owing to their good cyclic abilities, low equilibrium pressures, fast kinetics despite having less than 1.5 wt. % gravimetric capacities [366].

5.2.1.2.2 AB – type alloys

AB -type alloys are characterized by their light molar mass and high weight capacities. TiFe alloys are the most well-known AB -alloy which could reversibly absorb hydrogen up to 1.9 wt. % [332] with lower cost than $LaNi_5$ [98]. However, it suffers from poor kinetics, relatively low gravimetric capacity, high equilibrium pressure and complex activation procedure [332]. On the other hand, Akamaru et al. [367] have concluded that hydrogen storage of Pd-Cu-H and Pd-Au-H hydrides decreases with an increase in Cu and Au content. Moreover, Pt and Ir substitution have a pronounced effect on the plateau pressure of the hydrides compared to Cu substitution.

5.2.1.2.3 AB_2 – type alloys

In this group, A represents titanium (Ti) or zirconium (Zr) which could limit their use owing to their high cost. Consequently, several attempts have been made to substitute rare earth metals [368]. Vanadium is utilized to enhance the hydrogen storage density of Zr and Ni-based hydrides due to its relatively large atom and few electrons in its outer shell [369]. Young et al. [370] have studied the effects of cobalt (Co) with yttrium (Y) amount on the hydrogen storage properties of $Zr_{21.5}V_{10}Cr_{7.5}Mn_{8.1}Co_{8.0}Ni_{32.2}Sn_{0.3}Al_{0.4}$ alloys at a temperature of 303 and 333 K. The maximum reversible hydrogen capacity has been 1.36 wt. % at 333 K with a Y content of 2%.

5.2.1.2.4 A_2B – type alloys

Ti_2Ni alloys have the most attractive hydrogen storage properties. Moreover, partial Ti substitution with Zr increases the hydrogen desorption capacity as well as decreasing the thermal stability [252].

5.2.1.2.5 AB_3 – type alloys

AB_3 -type alloys (where A = La, Ce, Y) [328] has relatively low hydrogen storage capacity. The $LaNi_3$ is a common candidate for this group. Partial Ni substitution with Mn could lead to larger reversible Hydrogen storage capacity [371].

5.2.1.2.6 Solid solution alloys

Vanadium-based solid solution alloys, having body-centred cubic (BCC) structures, are proven to allow high gravimetric densities up to 4 wt. % with relatively low operating temperatures as well as relatively perfect kinetics [252]. For further modifications, several studies have investigated element substitution, annealing treatment, and surface modification for Vanadium-based solid solution alloys [372]. The increase in Al content in $V_{1-x}Al_x$ alloys decreases the enthalpy and stability [373].

On the other hand, Ti-based alloys including Ti-V-Cr, Ti-V-Mn and Ti-Cr-Mo alloys, such as $Ti_{0.5}V_{0.5}Mn$, could have high gravimetric storage densities of almost 2 wt. % with fast kinetics near ambient conditions [374]–[376]. Prabhukhot et al. [36] have studied promising hydrogen storage materials such as Mg_2CoH_5 and Mg_3CoH_5 which could store up to 4.5 and 5.4 wt. % respectively. Zaïdi et al. [377] have studied Mg_2NiH_4 which could store up to 3.6 wt. % at 1 bar and 245 °C [5], [35], [75], [378], [379]. Novel hydrides, known as high entropy alloys (HEAs), such as $TiVZrNbHfH_{2.5}$ [380], [381] and $TiVCrNbH_8$ [382] could store up to 2.7 and 1.96 wt. % [318]. This could indicate that HEAs are cost efficient hydrogen storage material with high gravimetric capacity at room temperature. Apart from all advantages for intermetallic alloys, they still offer low hydrogen storage capacities, slow kinetics and complicated activation procedure [252], [264].

5.2.1.3 Complex Metal Hydrides

Complex metal hydrides involve a metallic cation and anionic group to form compounds such as alanates, borohydrides. These compounds could make bonds with four hydrogen atoms with an alkali metal [354]. Complex hydrides are promising candidate for hydrogen storage applications owing to their high hydrogen storage capacities as well as mild dehydrogenation pressure and temperature [383]. However, most of the complex hydrides have high thermodynamic stability and slow kinetics [384]. In addition, their performance and stability after multiple cycles, difficulties in handling as well as their highly stable decomposition products are very challenging parameters which limit their refuelling with hydrogen on board a motor vehicle [42], [385]. Consequently, thermodynamic destabilization, nano-confinement, and catalysis could be utilized [252].

5.2.1.3.1 Alanates

Alanates have the general form of $MAIH_4$ where M could be Alkali or Alkaline earth metals. Aluminium based compounds have been intensively investigated for hydrogen storage [373] owing to their high storage capacities [386] as well as mild pressures and temperatures [387].

5.2.1.3.1.1 Sodium alanates

Sodium alanates, $NaAlH_4$, are excellent inexpensive metal hydrides having high hydrogen content up to 5.6%, as well as favourable operating pressures and temperatures [338]. However, they have slow kinetics, poor reversibility, severe dehydrogenation conditions [340], two-step decomposition reaction [337] with Hydrogen release of 3.70 and 1.85 wt. %, respectively [339]. Intensive work is still required for $NaAlH_4$ to achieve US DOE targets for on board vehicular applications [352].

5.2.1.3.1.2 Lithium alanates

Lithium alanates, $LiAlH_4$, could have high hydrogen capacities up to 10.6 wt. % [347]. However, they require very high pressure during hydrogenation and high temperature up to 673 K during decomposition which occurs in three steps [347], [348] as well as being very thermodynamically unstable [196], [340], [349]. Consequently, they are not suitable for on-board vehicular applications [348]. Li_3AlH_6 have better thermodynamic properties compared to $LiAlH_4$. However, it has slower kinetics and lower reversible hydrogen capacities [388].

5.2.1.3.1.3 Potassium alanates

Potassium alanates, $KAlH_4$, have high theoretical hydrogen storage capacity without the need for a catalyst. However, it requires high temperature up to 623 K [340].

5.2.1.3.2 Borohydrides

Alkali-transition metal borohydrides, such as LiBH_4 , NaBH_4 , $\text{Mg}(\text{BH}_4)_2$ and $\text{Ca}(\text{BH}_4)_2$, are stable hydrides having high gravimetric hydrogen storage capacities up to 9.6 wt. % [267] as well as adjustable characteristics [253], [350], [352]. However, they have drawbacks such as high thermodynamic stability, slow kinetics in addition to borane formation which is undesired volatile by-product [389].

To improve their characteristics, implementing destabilization or doping techniques could be utilized [352]. Pt- LiCoO_2 and Pt- CoO highly accelerate H_2 generation in the hydrolysis reaction up to 100% of Hydrogen in 15 min without catalyst running out [267].

5.2.1.3.2.1 Lithium borohydrides

Lithium borohydrides (LiBH_4) could have high gravimetric capacity up to 18.5 wt. % at room temperature [351]. However, LiBH_4 have difficult hydrogenation process [352], very high activation energy [355] and very high decomposition temperature [353] with experimental capacity around 50% its theoretical one [349].

5.2.1.3.2.2 Zinc borohydrides

Zinc borohydrides, $\text{Zn}(\text{BH}_4)_2$, have high theoretical hydrogen storage densities up to 8.4 wt. % [383]. However, it has slow thermal decomposition at high temperatures as well as being unstable at room temperature [390]. The addition of nano-Ni into $\text{Zn}(\text{BH}_4)_2$ leads to faster kinetics as well as lower the temperature for melting and decomposition [383].

5.2.1.3.2.3 Sodium borohydrides

Sodium borohydrides, NaBH_4 , have high theoretical hydrogen storage capacities about 10.7 wt. % and 5.72 $\text{kgH}_2/100 \text{ L}$ [267]. Hydrogen is released by hydrolysis which is an irreversible process. Moreover, toxic and damaging compounds, for FC, are formed during the thermal decomposition process [340]. Although sodium hydroxide (NaOH) addition stabilizes NaBH_4 , it leads to worst storage performance [391].

5.2.1.3.2.4 Calcium borohydrides

Calcium borohydrides ($\text{Ca}(\text{BH}_4)_2$) are favourable hydrogen storage materials owing to their high theoretical hydrogen capacities up to 8.3 wt. % [267].

5.2.1.3.3 Nitrides

Metal-nitride-based systems composed of amide and binary hydrides could release hydrogen in appropriate conditions [252]. Mixtures of lithium amide and lithium hydride ($\text{LiNH}_2 + \text{LiH}$) have high gravimetric hydrogen storage densities. However, they have high decomposition temperatures and very high dehydrogenation enthalpy [252]. The reversible gravimetric and volumetric storage densities of lithium nitride Li_3N could achieve 11.5 wt. % and 7.35 $\text{kgH}_2/100 \text{ L}$ [392].

5.2.1.3.4 Metal ammine complexes

Metal ammine complexes are in the form of $\text{M}(\text{NH}_3)_n\text{X}_m$ where M is a cation such as Mg, Ca, Cr, Ni and Zn whereas X is an anion such as Cl and SO_4 . They have greater reversible hydrogen storage densities. However, ammonia release at certain temperature is a strong disadvantage which requires certain storage containers [393].

Each hydrogen storage material could be suitable for certain applications and not suitable for the others. Table 5 lists some of stationary and mobile applications and the corresponding suitable materials. Some mentioned studies have been already applied by great manufacturers such as Toshiba [394], McPhy [395], HySA [396]–[398], Nilar [318], and Ferroamp [318]. In addition, recent complex hydrides such as $\text{Na}_2\text{Mg}_2\text{NiH}_6$ [399], $\text{Na}_2\text{Mg}_2\text{FeH}_8$ [400], $\text{Na}_2\text{Mg}_2\text{RuH}_8$ [400] and Li_4RuH_4 [401] could be promising materials for Hydrogen storage.

Table 5: Suitable applications for hydrogen storage materials [255].

Application		Utilized materials
Stationary	Off-grid systems	Metal hydrides [402]–[404] particularly AB₅ [394], [405]–[407] and MgH₂ [408], [409]
	Smart grid systems	Metal hydrides [410], [411] especially AB₅ [412], MgH₂ [395], [412], [413], NaAlH₄ [412] and Na₃AlH₆ [413]
	Thermal energy storage	Ti_{0.909}Zr_{0.052}Mn_{1.498}V_{0.439}Fe_{0.086}Al_{0.016}H₃ [414], TiFeH_x [415], MgH₂ [416], [417], NaMgH₃ [418], Mg₂FeH₆ [419], Ca₄Mg₄Fe₃H₂₂ [420], CaMgNiH₄ [420], Mg₂Si [421], LiBH₄-Ca(BH₄)₂ [422], CaAl₂ [423]
	Metal Hydride Hydrogen compressors (MHHCs) and purification units	LaNi₅ [255], [424], Ti-Zr-C-Mn (AB₂-type) [255], Ti_{0.7}Zr_{0.3}(Cr,Fe,Mn,Ni)₂ [255], VH₂ [425]
Innovative	Anodes for Ni-MH alkaline batteries	LaNi₅ , La_{1.5}Mg_{0.5}Ni₇ [426]–[428]
	Anodes for Li-ion batteries	TiH₂ , MgH₂ , AlH₃ , LiAlH₄ , and NaAlH₄ [429]–[431]
	Electrolytes for Li-ion batteries	LiBH₄ [432], [433]
	Full Li-ion batteries	TiH₂+MgH₂ (as anodes)+ LiBH₄ (as electrolyte) [318], [434]
Mobile	Submarines, AUVs and canal boat	Metal hydrides [255], [435]–[438]
	Mostly smaller trains, underground rail systems (such as mine vehicles)	Metal hydrides [439]–[441]
	Heavy duty (FC Forklift)	Ti_{0.065}Zr_{0.35}(Fe,Cr,Mn,Ni)₂ [396]–[398]
	Light passenger vehicles	AB₂ alloys involve Ti-Cr , Ti-Mn , Zr-Fe and BCC such as Ti_{0.32}Cr_{0.43}V_{0.25} [442]

5.2.2 Chemical Hydrogen Storage

This paper considers hydrogen storage materials which are hardly regenerated like ammonia borane, ammonia, lithium amide, and hydrazine as chemical ones. They have been investigated for on-board applications [443]. Compared to conventional metal hydrides, chemical hydrides involve lighter elements [444] and hence, they attain higher gravimetric densities along with hydrogen release easiness [445]. However, they are irreversible and generally utilized as single-use fuels in addition to the by-product removal issues [403].

Compared to liquid Hydrogen, they have less cost with respect to storage and transportation and hence have attracted great attention. Moreover, they could be utilized to transport energy from renewable rich areas to other places [318].

5.2.2.1 Ammonia

Ammonia is attractive hydrogen and energy carrier due to high hydrogen storage density of 17.8 wt. %/10.7 kgH₂/100 L and it is easily liquefied under about 1 MPa at room temperature. In addition, Ammonia is also burnable without emission of CO₂ [267]. Recently, ammonia was recognized as an energy carrier for direct combustion in International Energy Agency (IEA) [446] which could be converted into electric power without CO₂ [447], [448]. Hydrogen storage could be reversibly performed utilizing pairs such as [LiH-NH₃], [NaH-NH₃] and [KH-NH₃] which could generate Hydrogen at room temperature [449], [450]. The practical gravimetric density of TiCl₃-doped LiH-NH₃ (1 mol. %) is 6.1 wt.% [451]. Moreover, Ammonia absorbing materials could enhance the reaction yield [452].

5.2.2.2 Ammonia borane

Ammonia borane, NH_3BH_3 or AB, have desired characteristics needed for on-board hydrogen storage applications [453]. AB has successfully achieved DOE storage capacity targets for on-board vehicular applications as shown previously in Table 3. According to Lee and McKee [454], NH_3BH_3 has high hydrogen content up to 19.6 wt. % as well as having assured stability [455]. However, it has some drawbacks: (1) NH_3BH_3 hydrolyses easily in acids [454], (2) the synthesis of NH_3BH_3 is a complex process, (3) the decomposition of NH_3BH_3 results in the formation of B_2H_6 impurities, (4) sluggish decomposition kinetics at moderate temperatures below 373 K, and (5) harmful by-products. Several kinds of ammonia borane-based materials such as LiNH_2BH_3 (H_2 :10.9 wt. %) NaNH_2BH_3 (H_2 :7.5 wt. %), $\text{NaH-NH}_3\text{BH}_3$ (H_2 : 5.2 wt. %) have been synthesized [456], [457]. LiH or LiNH_2 addition might increase the Hydrogen discharge rate of NH_3BH_3 [458]. In addition, the substitution of amine protonic hydrogen in AB with a metal cation has been investigated [453]. LiNH_2BH_3 does not release borazine, a toxic by-product for PEMFC, as well as high storage density up to 15.6 wt. % and dehydrogenation temperature of 363 K [454].

5.2.2.3 Metal B-N-H compounds

Wang et al. [459] has overviewed metal B-N-H compounds which could be considered as derivatives for ammonia borane such as amine-metal-borohydride (AMB), metal amidoborane (MAB) and metal hydrazinidoborane (MHB) groups. $\text{Al}(\text{BH}_4)_3\text{-4NH}_3\text{-LiBH}_4$ is a promising AMB candidate having storage density of 16.1 wt. % as well as Hydrogen purity above 99% [460]. LiAB.AB [461] and $\text{NaLi}(\text{NH}_2\text{BH}_3)_2$ [462] are candidate for mono and multi- metal amidoborane which could have about 14.3 and 9 wt. % Hydrogen content respectively at low initial desorption temperatures. Finally, Both of NaHB [463] and KHB [464] is MHB candidate with hydrogen content of 7.6 and 7.3 wt. % respectively.

5.2.2.4 LOHCs

Liquid organic Hydrogen carriers (LOHCs) such as methyl cyclohexane-toluene, a variety of cycloalkanes and ammonia-borane-based systems have gained great attention for Hydrogen storage [465]. LOHCs are hydrogen carriers, where hydrogen is covalently bound to a liquid carrier and could be released when required. Hydrogen carrier shall have the following characteristics: (1) high hydrogen storage capacity, (2) small heat of formation (3) durability (4) easy handling (5) safety as well as being (6) abundantly available (7) in liquid phase. Unfortunately, LOHCs system suffers from some drawbacks such as high cost as well as high pressure and operating temperatures requiring different catalysts [466]. LOHCs involve main categories such as cycloalkanes, N-substituted heterocycles, 1,2-BN-heterocycles in addition to methanol and formic acid.

5.2.2.4.1 cycloalkanes

Cyclohexane [467], methylcyclohexane [468], decalin [469], [470] bicyclohexyl [470] are candidates for cycloalkanes group having high gravimetric capacity in the range of 6-8 wt. % and high boiling point. Their storage systems could reversibly store hydrogen with CO_x free hydrogen release and recyclable products. Large enthalpy and high temperature hydrogen release as well as endothermic dehydrogenation, requiring 64–69 kJ per mole of H_2 , reduce cycloalkane utilization [471].

5.2.2.4.2 N-substituted heterocycles

This group is characterized by its moderate reaction conditions, reasonable enthalpy, high storage capacity as well as relatively faster dehydrogenation. Particularly, dodecahydro-N-ethylcarbazole is a promising candidate for this group of organic hydrides owing to high Hydrogen storage capacity. However, it suffers from high melting point in addition to its little actual Hydrogen recovery [472]. Although Dodecahydrocarbazole has higher gravimetric capacity, dodecahydro-N-ethylcarbazole is preferred for its faster dehydrogenation reaction rate. Perhydro-4,7-phenanthroline is a promising candidate for this group which could store up to 7.2 wt.% [472].

5.2.2.4.3 1,2-BN-heterocycles

1,2-BN-heterocycles is considered as one of the most promising technologies of hydrogen storage and transport, owing to their high storage capacity and fast dehydrogenation. 1,2-BN-cyclohexane[473] and 1,2-BN-cyclohexane[474] are promising materials for hydrogen storage.

Formic acid is another liquid hydrogen storage material with Hydrogen contents of 4.4 wt. % and 5.3 kgH₂/100 L [475] while methanol has storage density of 12.6 wt % and 9.88 kgH₂/100 L [472].

5.2.2.4.4 Liquid inorganic hydrides

Hydrous hydrazine is a promising storage liquid having hydrogen content of 8.1 wt% and 8.3 kgH₂/100 L at ambient conditions [465], [476]. In addition, Hydrazine borane and Ammonia borane are promising inorganic hydrides.

The characteristics of hydride such as high operating temperature, sluggish kinetics as well as the stability limit their practical application. Nano-composite material could improve their storage performance [477]–[479]. Moreover, the combination of chemical hydrides could control their stability characteristics [267]. Concerning Li-Mg-B-H system, destabilization of LiBH₄ could be attained utilizing MgH₂ as an additive [480]. Moreover, the composite doped with TiCl₃ could reversibly store hydrogen up to 8.0-10.0 wt. % [267]. Other storage materials such as Mg(NH₂)₂-LiH [481]–[484], Ca(NH₂)₂+2LiH [75], combination of LiAlH₄ or Li₃AlH₆ with LiNH₂ [[267], [485]–[488] could have storage capacity in the range of 3-5.5 wt. %.

6. Material based storage vessels

Material based hydrogen storage is mostly accompanied by additional components to provide the suitable environment for the Hydrogen uptake/release processes. Recently, metal Hydrides have attracted great attention for Hydrogen storage applications. There are three main types of metal hydride reactors including tubular, disc and chamber, or tank, reactors. According to [489], tubular reactors are suitable for heat pump and compressors applications while disc and chamber reactors are recommended for kinetic measurements and storage systems respectively. Heat exchanger is one of the most important components to guarantee fast kinetics in MH reactors. During Hydrogen absorption, exothermic reaction, heat generates and consequently temperature increases which reduces the reaction rate. Therefore, efficient cooling technique is necessary. On contrary, Desorption is an endothermic reaction which requires an effective heating process to guarantee fast kinetics. Intensive research work has been focused on the heat transfer enhancement for best cooling/heating performances during Hydrogen absorption/ desorption processes. Research has included the integration of fins, metal powders and metal foam to increase thermal conductivity. In addition, the involvement of fluid bath, embedded cooling tubes, phase change materials have been assessed for providing effective heat transfer method.

Complex metal hydride, such as Sodium borohydrides, could require Hydrolysis process during Hydrogen release process. Hydrolysis includes additional components such as water, water tank and tank for collecting the unfavourable products. For Sodium borohydrides, Hydrogen storage capacities are approximately 10.7 wt. % and 5.72 kgH₂/100 L which decline to 1.3 wt. % and 0.5 kgH₂/100 L for the whole system [267]. On the other hand, chemical Hydrogen storage has great potential to be employed in Hydrogen storage applications owing to high storage capacities. Ammonia is attractive hydrogen and energy carrier due to high hydrogen storage density of 17.8 wt. %10.7 kgH₂/100 L and it is easily liquefied [267]. However, it has certain safety issues related to hydrogen purity and concentration of NH₃ and N₂ as stated by ISO 14687-2 which implies certain conditions to work with PEMFC. The theoretical hydrogen conversion efficiency NH₃ is 89.3%, [361]. High-performance ruthenium supported on MgO, Pr₆O₁₁ and La-Al₂O₃ cracking catalysts have shown NH₃ conversion of 99.7-99.8% (ammonia concentration of 1000 ppm) at 0.1 MPa and 773-823 K [267], [490], [491]. Ammonia storage materials such as zeolite, NH₄HSO₄ and MgCl₂ have been investigated in order to reduce the ammonia concentration in the simulated NH₃ cracking gas (H₂: 75%, N₂: 25%, NH₃: 1000 ppm) [492] which have been

reduced to below 0.02 ppm using the remover including zeolite (Li-X) packed column and dynamic adsorption method [492]. Several scenarios, for utilizing ammonia as hydrogen carrier, have been investigated including defect free dense-metal membrane [493], [494], plasma membrane reactor [495], and ammonia-fuelled solid oxide fuel cells [496]. In addition, Ammonia-Borane has successfully achieved DOE storage capacity targets for on-board vehicular applications.

7. Safety considerations

7.1 Development of standards and codes

Pressure vessels had some catastrophic accidents such as the SS Sultana (1865) and the Grover Shoe Factory explosion (1904) [497]. Consequently, American Petroleum Institute (API) and the American Society of Mechanical Engineers (ASME) have established the Joint API/ASME Code for Unfired Pressure Vessels for Petroleum Liquids and Gases 1931-1934 [498]. Afterwards, recent accidents such as that of SS Norway in Miami harbour in 2003 have led to new standards for manufacturing and operation processes of pressure vessels. Pressure vessel design codes involve design criteria, material selection, stresses evaluation, inspection, quality control, testing, certification and responsibilities. Hydrogen and FC involvement shall be in accordance with specific codes such as ASME, NFPA2 and SAE. ASME VIII Boiler and Pressure Vessel Code is utilized for structural design while NFPA2 Code is employed in Hydrogen storage systems for test and operation processes [499]. Composite cylinders are constructed to several standards such as ISO 11119-1, ISO 11119-2, and ISO 11119-3. In addition, the ISO 11623:2015 standard contains the requirements for periodic inspection and testing of composite transportable gas cylinders intended for compressed, liquefied or dissolved gases under pressure [500].

Pressure vessels codes have several pressure-related expressions. Design, or maximum operating, pressure of the vessel is the pressure rating at its top. Maximum allowable working pressure (MAWP) is slightly larger than the design pressure due to selecting the larger standard components. Vessels could work above the MAWP for brief periods such as emergency situation but it should be checked before coming back into service [501]. Test pressure is generally 1.5 times design pressure or MAWP. This test is performed firstly at installation and repeated during re-installment inspection [501]. Slight distortion could occur near twice MAWP. Worst distortion scenario, with gasket blowing out, may occur at higher values up to four times MAWP. Therefore, vessel's burst pressure is in the range of 3.5 to 4 times MAWP with more uncertainty due to little experimental field tests [501]. Some codes such as ASME terminate at specific piping connections or certain shipment conditions [502]. Most pressure vessel codes such as Pressure Equipment Directive (PED) and ASME VIII accepts that the safety relief valve (SRV) is set at the maximum allowable working pressure [501].

Standards set regulations, tests and requirements which guarantee the system survival at working conditions throughout lifetime. For Hydrogen systems, burst pressure is one of the most important tests for Hydrogen tanks. It denotes the limit load-carrying ability of the vessel which is too difficult to predict due to complicated micromechanics [503], [504] as well as stiffness degradation as a response to continuous failure [113]. Pressure vessels are highly susceptible to various damages such as abrasion, scratch, impact, and aging [187]. Therefore, their load capacity and fatigue performance are reduced [505]. Research has become more essential for developing or modifying codes and associated tests for Hydrogen pressure vessels. Container shall not fail before specific number of cycles and must fulfil the requirements of leak and burst tests [177].

The yield distortion is easily detected and allows more safe pressure release. Therefore, small pressure vessels are mostly designed to enable yield at a relatively low pressure before any cracks. This design criterion is known as "yield before break". For large vessels, safe design implies that smallest crack shall have a length which is greater than the thickness of the vessel wall. This criterion is known as "leak before break" [506].

On the other hand, liquid hydrogen storage systems require perfect thermal insulation to achieve zero boil-off system. Design, manufacturing, inspection, tests and operating conditions for such cryogenic pressure vessels are discussed on ISO 21009-1 and ISO 21009-2 [79].

Infrastructure, especially fuelling stations, has a great impact on LH₂ involvement in car markets with respect to feasibility, economy and safety. Recently, hybrid Hydrogen-gasoline fuelling stations have been suggested for efficient use of space. On the other hand, safety considerations have become more complex. Several studies have conducted risk assessments and analyses for hydrogen fuelling stations [99], [507]–[521]. Nakayama et al. [513] have identified three worst-case scenarios in a Japanese hybrid hydrogen-gasoline fuelling station through hazard identification study (HAZID). Sakamoto et al. [99] have utilized Toxic Release Analysis of Chemical Emissions (TRACE) tool followed by ANSYS to perform risk assessment for hybrid hydrogen-gasoline fuelling stations during a 30 min pool fire. This study has considered tolerance ranges for temperatures and von Mises stresses and fatigue life. Emissivity of outer tank material should be less than 0.2 while distance between hydrogen tanks and gasoline dispensers must be more than 8.5 m which is close to the 8 m value recommended by the European Industrial Gases Association (EIGA) [522]. The back-gas is the displaced gas from the tank back to the filling station which is lost. Heat flow and pressure losses along the filling line highly participates the evaporation process for liquid Hydrogen and hence back gas amount. However, the contribution of the displacement of gas by liquid in the tank is only marginal [523]. Emans et al. [523] have experimentally determined that back-gas rate being more than 20%. According to [524], pre-cooling the filling line as well as reducing its length could greatly decrease heat leakage and hence the back gas amount below 10%. In this system, pre-cooling has been carried out through a connection, a bypass, between the filling line and the back-gas line. According to this study, the car-side bypass could be more effective than that in filling station side. Optimization of both filling station components and the vehicle tank could lead to zero back-gas [523].

Apart from much safety offered in material based hydrogen storage systems, there are several codes and corresponding tests provided to guarantee safe operation and transportation of the storing material. To develop a safe transportable material based hydrogen storage system, the design and construction of the container shall be performed in accordance with codes such as ISO 16111 [525]. The United Nations (UN) has developed testing criteria for the transportation of dangerous goods [526]. The modified UN procedures classify materials according to their pyrophoric action into two categories: flammability and water reactivity. Flammability tests involve the introduction of heat through three scenarios: self-heating, burn rate and pyrophoricity.

Burn rate test, mentioned in UN-RTDG part-3, test N1 [526], [527], involves the ignition of a sample of specified dimensions from one end while measuring temperature and burning propagation with time. Self-heating tests, included in UN-RTDG div. 4.2 [526], [527], involves setting the sample in a hot circulating air oven at different set temperatures for at least 1 h or until spontaneous ignition was observed. The test material fails when the temperature difference between the sample and the oven set temperature becomes greater than 60 °C. On the other hand, water reactivity tests involve water exposure with different intensities: water drop, water immersion and surface contact. Environmental reactivity has been evaluated for several materials such as LiBH₄ [528]–[530], NaAlH₄ [337], [531] and 8LiH:3Mg(NH₂)₂ [532]. James et al. [527] have not only determined the environmental reactivity of AlH₃ and NH₃BH₃ but also have reduced the sample sizes recommended in UN code [526] for burn rate and self-heating tests based on experimental validation. Consequently, this study saves materials which are lost during the tests.

Moradi and Groth [533] have intensively overviewed the different hydrogen storage and delivery technologies and the corresponding difficulties as well as risk and reliability analysis. Quantitative risk/reliability Assessment (QRA), includes hazard and cause analysis, consequence analysis and risk assessment, illustrates if the risk of failure in a system is As Low As Reasonable Practical (ALARP) or not. Several QRA have been established for Hydrogen generation and refuelling systems [510], [534], [535]. To develop good QRA for hydrogen system,

difficulties such as complexity of CFD, flame and gas detection accuracy as well as lack of failure and accident data shall be overcome. Sandia national lab has launched HyRAM project which is considered as a powerful tool for establishing Hydrogen system QRA and evaluating risk matrices [533], [536], [537]. Bayesian Networks (BN) is one of the most important methods to get risk and reliability models of low uncertainty. It has been employed for Hydrogen systems [508], [518], [533]. However, complex calculations as well as memory requirements could limit their utilization in large systems [533].

Material based hydrogen storage is a safe and compact option with high density storage capability. Moreover, it suffers from some drawbacks such as high cost, initial activation, side reactions with gases, volume expansion which induces large stresses, deterioration after several cycles, less recovered hydrogen, more weight as well as high capacity required for the heat transfer system [264], [538], [539]. Moreover, solid state hydrogen storage systems, for auxiliary power units (APUs), involve much higher GHG emissions, construction and operation costs, and consumption of resources than those of pressure vessels. However, operational energy demand tips the scale in favour of solid state systems [540]. In addition, chemical hydrogen storage has regeneration issues. Selecting the suitable material, according to the application, is always the principal challenge.

Table 7 : main characteristics and suitable applications for different HST

Storage system	Suitable applications	Gravimetric density	cost	Energy consumption	Response /kinetics	Purification /filter	Gravimetric density	Energy consumption	Response /kinetics	Purification /filter
A : Compressed Gas H₂							L-M	M	FR ⁽¹⁾	NA
Type I	stationary	VL	L	L	FR ⁽¹⁾	NA				
Type II	stationary	L	M	H	FR ⁽¹⁾	NA				
Type III	Industrial and vehicular	M	H	H	FR ⁽¹⁾	NA				
Type IV	- vehicles - industrial purposes (at high pressures)	H	VH	VH	FR ⁽¹⁾	NA				
B : liquid and Cryo-compressed H₂							H	H	FR	NA
L H ₂ systems	aerospace	H	H	VH	FR	NA				
cryo-compressed	vehicles	VH	H	H	FR	NA				
C : Material based H₂ Storage							L-H	L	L	require
MOFs	- stationary - vehicles(near targets)	H ⁽²⁾	M ⁽³⁾	L	MK	require				
Elemental hydrides	- stationary applications - Thermally (CHP)	L	-	L	SK	require				
Intermetallic hydrides	- stationary applications (like nuclear) - Thermally (heating + air conditioning) - MH batteries	VL	-	L	FK	require				
complex hydrides	- stationary applications - Thermally	M	H ⁽³⁾	L	MK	require				
chemical hydrides	- energy/Hydrogen carrier - single fuel use (vehicles) - direct combustion	H	M ⁽³⁾	L	FK	require				

Table symbols : V: very, L : low, M : medium, H : high, F : fast, R : response, K : kinetics, L- M : low to medium.

- (1) Rapid response with flow rate proportional to pressure value.
- (2) At cryogenic temperatures while low in room temperature.
- (3) Based on current status, from DOE, for vehicular applications.

Conclusions and Recommendations

In this study, different energy storage systems are investigated. Different researches have employed hybrid energy storage systems in order to achieve the best behavior with reasonable prices. For electricity storage systems, supercapacitors are suitable for covering peak loads while BESS and HSS are suitable for short and long term storage respectively. Hydrogen storage technologies are then analyzed according to operating principles, required vessel specifications, corresponding costs and storage density. Therefore, designer could select the proper HSS. CGH₂ is a mature technology utilizing pressure vessels for small scale storage and salt caverns for large scale storage. Thanks to Type IV tank high strength to weight ratio, it withstands 70 MPa with high hydrogen storage density and hence it is recommended for mobile applications utilizing CGH₂. However, up to 15% of Hydrogen energy content is consumed throughout pressurization. Moreover, high cost of the vessel, especially carbon fibers, is still a critical parameter. Therefore, optimal design has been deeply investigated based on FE and experimental validation process to decrease associated weight and cost. FE could be also utilized to predict and improve thermo-mechanical behavior especially during fire. LH₂ consumes high energy, up to 35% of energy content, and requires efficient insulation. Correspondingly, it is limited to certain applications such as aerospace. CCH₂ could attain greater storage densities than CGH₂ and LH₂ with moderate pressure and temperature range and hence it has been applied in BMW Company.

Material based storage has high volumetric hydrogen storage density as well as being safe and compact option. In addition, metal hydrides have the potential to store both hydrogen and thermal energy. Therefore, magnesium based hydrides are employed in applications such as concentrating solar power for high temperature thermal energy storage. Interstitial hydrides, such as AB₅, have <2% storage density with fast kinetics and hence could be employed for stationary applications such as nuclear systems. It is also employed in MH heating and air conditioning systems. These materials Complex metal hydrides, such as lithium borohydrides, sodium alanates have high hydrogen storage capacities up to 18.5 %. However, storage density deeply decline for the whole storage system with its additional components. According to achieving 2020 DOE vehicular targets with Ammonia Borane, it is suitable for vehicular hydrogen storage systems. However, it require specific purification systems not to cause harm to FCs. Chemical storage materials, especially liquid ones, have great opportunity to be employed as energy/Hydrogen carriers such as LOHCs. However, it is hardly regenerated and hence these materials are utilized as a single use fuel. Table 7 summarizes the findings of the paper.

Codes and standards shall be updated to cover all Hydrogen technologies for the diverse applications. Non-destructive failure detection methods such as AE will be widely employed in order to assess the status of the pressure vessel. It is recommended to consider splitting Hydrogen production cost into partitions such as fuel/electricity and capital expenditure parts. Hereafter, each partition could be evaluated as function of its corresponding parameters such as fuel/electricity price, capacity, full load hours and efficiency of utilized components as well as the effect of mass production and life time of these components.

For HSSs, system total volume/mass could be also divided into volumes/masses of the corresponding components. Then, it will be easy task to monitor the change of the storage density according to the subsequent variation in volume/mass of each component. The same principle could be easily applied for Hydrogen storage cost by accounting for change of components/partitions costs.

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