Chapter 6
On-Board and Off-Board Technologies for Hydrogen Storage

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ABSTRACT

Future energy systems will be determined by the increasing relevance of renewable energy resources due to global warming, energy crisis, and pollution. Hydrogen is considered one of the promising alternative fuels to replace oil, but its storage remains a significant challenge. The main hydrogen storage technologies can be broadly classified as physical, chemical, and hybrid methods. The physical methods rely on compression and liquefaction of hydrogen, and currently, compressed hydrogen storage is the most mature technology that is commercially available. The chemical methods utilize materials to store hydrogen, and hydrogen can be extracted by on-board regenerable or off-board regenerable chemical reactions depending on the type of material. Hybrid methods take advantage of both physical and chemical storage methods. The most prominent hybrid method is the cryo-adsorption hydrogen storage which utilizes physisorption-based porous materials. The chapter describes these technologies and discusses alternative/novel hydrogen storage material technologies.

I. INTRODUCTION

Due to emerging Economies, global energy demand is increasing continuously. Relic fuels supply nearly 80% of energy demand worldwide; further, if reliance on Relic fuels is continued, the principal source of this energy may have foreseeable Imminent (Economics, 2018). Global Warming, Energy crisis and Pollution are the major problems facing by the current modern society due to the excessive utilization of Fossil Fuels. Finite production of fossil fuels possess Bell-shaped Curve with reference to the theory of Hubbert's peak (Maggio & Cacciola, 2012; Houghton, 2005; Asif & Muneer 2007; Barbir et al.1990).

After Discovery of Certain reservoir for fossil fuel production it is leading to increase exponentially, then the rate of production decreases reaching peak point of depletion of fossil fuel and reduction in feasibility of extraction (Hubbert, 1956). So, it is understood that oil and other relic fuels, get exhausted in the near future. In the conveyance sector, oil is most important source of energy i.e., used excessively by mankind and according to the current estimates, the fuel that is likely to be depleted before end of twenty-first century is oil (Agrawal et al. 2007; Kerr, 2011).

A huge share in the world trade was contributed by oil economy, and any significant changes in it might take many years before it is completely comprehended; hence, it is domineering to act in present day towards finding cleaner replacements to oil. Even though the exhaustion of oil is vital concern which is required to be addressed at possible earliest, much more insistent issue requiring immediate attention is global warming. Increase in temperature of earth precisely due to anthropogenic emissions of CO_2 which is caused by use of excessive fossil fuel is Global warming (Asif & Muneer 2007). Sea level rise and extreme weather are the impacts of global warming which in turn can cause worldwide environmental change and colossal community. Being time-sensitive problem an effective measure for prevention of irreversible changes in atmosphere needs to be designed and executed immediately (Yi,1996). Oil spills and air pollution caused by combustion are also a grave problems requiring attention. Particulates like NO_x, CO_x (where X=1 or 2), SO_z (where Z= 2 or 3) and benzene are emitted from mobile platforms are harmful to health. Densely populated areas are responsible for problematic air pollution. On the other hand, Aquatic life and Surrounding communities have long devastating effects due to large scale oil spills. Lastly, excessive utilization of fossil fuels threatens energy security. Oil reserves are usually present in unsteady areas of the world (Mendelssohn et al. 2012). The countries importing oil are facing the problems in meeting oil demands as a consequence of disrupted supply from the time to time. Due to this disruption failure in supply of oil, the countries will have grave economic, political and social impacts. Several countries have their individual natural reserves which are diminutive energy security and another long-term energy security policy to drive away from oil in near future (Asif & Muneer 2007).

From the preceding conversation, it is clearly evident that the alternative fuels are necessary to protect mother earth which also helps in reducing risks related with extreme oil use. Due to owing their unique property of high energy density, fuels derived from oil have extensively been used in transportable applications and becoming a formidable task to replace this oil (Asif & Muneer 2007).

Hydrogen is understood to be among the strongest contenders, that replaces the oil in transportable applications. Though hydrogen might not be an energy source similar to oil, it acts as an energy carrier, connotation hydrogen availability on earth is not direct, which requires its production through other sources. At present, a noteworthy share of hydrogen energy is produced from methane through the process of "steam methane reforming (SMR)". Amongst other processes for the production of hydrogen is through water electrolysis; as this process uses production of electricity from renewable energy technologies since there is a possibility of hydrogen production from renewable energy sources.

After the production of hydrogen, transportation, distribution to end-user and storage for later use are some important stages that are needed to be addressed. The three stages of production, transportation and storage of hydrogen are called as hydrogen economy.

II. HYDROGEN ECONOMY

Hydrogen economy has been proposed as an alternative system to the oil economy in the early 1970s. The main motivation of hydrogen economy being non emittance of pollutants but only H_2O when it is used in an internal combustion engine or in fuel cells as divergent to employing hydrogen carbons. In order to combat environmental issues along with global warming hydrogen must be produced from renewable energy sources as debated in the introduction.

Figure 1. Hydrogen Economy
(Redrawn with permission from Crabtree et al. 2004)
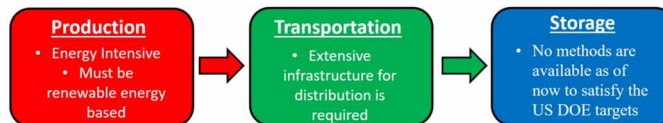
The economy of hydrogen comprises of 3 parts as shown in the above Fig.1 (Crabtree et al. 2004). Production of hydrogen through the process of SMR is cost-effective and most efficient (83%) option available today (Abbas & Daud, 2010). While, other methods of production like photocatalytic water splitting have an efficiency of 10-14% H_2 production and these are not yet competitive with SMR (Gerboni & Salvador,2009).

Issues with the production of hydrogen are:

- The process should be High energy-intensive
- The raw material should be renewable energy resource.

Extensive distribution systems are generally required for the transportation of hydrogen; it might be transported through tube trailers, pipelines and liquids (Felderhoff et al. 2007) by cryogenic tanks and as well as Cylinders in gaseous form.

Hydrogen has low energy density but has high energy capacity. Hydrogen energy density can be increased by liquefication and compression but these are cost-effective processes. For instance, to liquefy the hydrogen one-third of hydrogen's lower heating value is required. Therefore, on the basis of cost-effectiveness, end-use storage technology and safety, the medium of transportation is selected i.e., either gaseous or liquid (Lattin & Utgikar, 2007; Konni et al. 2020).

In some reports, it has been revealed that Hydrogen storage distribution cost is nearly 15 times much expensive than a liquefied hydrocarbon fuel. From the preceding conversation, it can be understood that elevated costs included in production and transportation are cause for deprived hydrogen economy. Nevertheless, the hydrogen storage step is the main obstacle in comprehending hydrogen economy (US

DOE, 2009). Till date, none of hydrogen storage technology is available which can fulfil the targets of the Department of Energy (DOE) 2020 (US DOE, 2009). Due to its noteworthy energy losses in each step Figure.2 (Bossel et al. 2009), hydrogen economy is criticized. However recent research in this field is providing hope for the Hydrogen economy to overcome the disadvantages that are facing in the current technology (Shinnar,2003; Høyer & Holden, 2007; Eberle, et al. 2009; Konni et al. 2020; Konni et al. 2019).

Hydrogen Storage Classification

See Figure 2.

Figure 2. Classification of Hydrogen Storage Technologies.
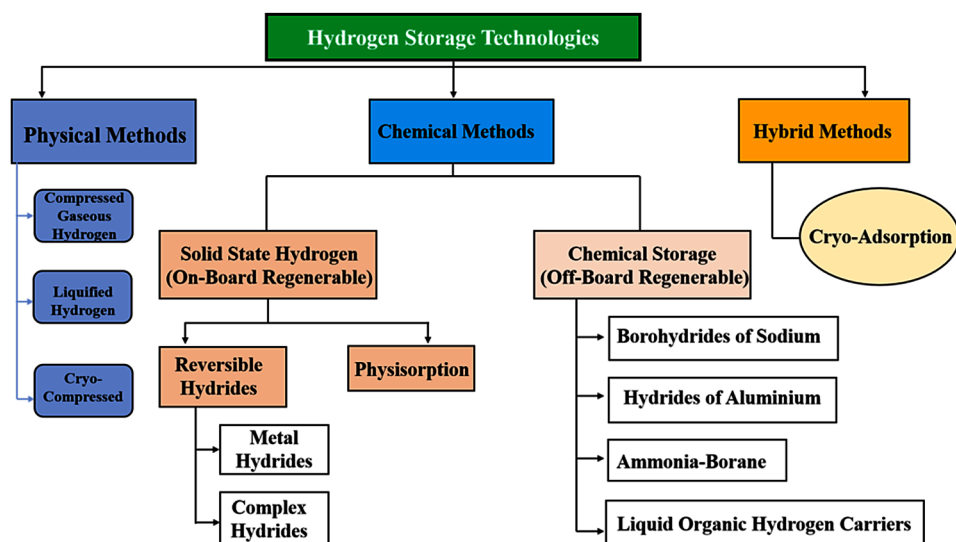
III. HYDROGEN STORAGE

Hydrogen Storage Technologies Classification

Technologies for hydrogen storage can be sketchily classified under three main classes:

1. Methods of physical nature
2. Materials-based hydrogen storage (also called chemical methods), and
3. Advanced or hybrid methods

Methods included under the class physical nature include liquefied hydrogen, compressed gaseous hydrogen and cryo-compressed hydrogen. Chemical methods include chemical storage and solid-state storage. Further, hybrid method of storage consists of cryo-adsorption which adopts both physical and chemical methods.

Hydrogen will not react with storage media in physical method, whereas in the chemical method, it will interact with storage media by the robust covalent/ionic bonds or by feeble Vander Waals forces. Hydrogen storage materials are included in chemical methods always to store the hydrogen. Since 2000s these methods drew attention, but due to they are in physical storage methods.

Further, chemical methods are classified into:

1.   Solid-state storage and
2.   Chemical storage

The key dissimilarity between the above two is that regeneration of solid-state materials can be done merely through charging with hydrogen, while chemical storage materials require to be regenerated in centralized facilities off-board (Eberle et al. 2009). Moreover, key elements for market of fuel cell vehicles are on-board regenerable materials (Chalk & Miller, 2006). A hybrid process with combination of physical and chemical methods, Cryo-adsorption possess advantage of physisorption, compression and liquefied material-based technologies for hydrogen storage.

IV. DOE HYDROGEN STORAGE TARGETS

DOE targets aimed at hydrogen storage systems intended for light-duty vehicles is summarized in Table 1 (Ganguly et al. 2019; Konni et al. 2017). Volumetric and gravimetric capacities are the present most stringent doe targets.

In addition, fuel purity, reversibility (i.e., operational cycle life) and fast kinetics (i.e., system full time) are problematic for complex hydrides. Besides storage materials weight, balance plant elements like storage tank, the control system, tubing, valves are also required to be accounted for. Two times of gravimetric storage capacity with that of the targets of system level is given by DOE as the main thumb rule towards achieve the good targets. Recently, kg H_2/kg are gravimetric hydrogen storage capacity units as given by DOE presented in table 1, previously gravimetric hydrogen capacity was expressed in wt.%. (Read et al. 2007; Konni et al. 2018).

If the system comprises hydrogen storage material, weight of the hydrogen storage material must be added to the weight of the system. Both the units of gravimetric hydrogen storage capacity (i.e., kg H_2/kg system and wt.%) are employed in the entire chapter.

V. RECENT STATUS OF HYDROGEN STORAGE

In table 2 the present status of storage technologies for Hydrogen is summarised. The capacity of different technologies spans is in the range of 1.9 to 6.8% (Gravimetric) and 13 - 39 g/L (Volumetric capacity). Chemical methods for hydrogen storage fall behind over the physical methods. Volumetric capacity targets are easier when compared to the gravimetric capacities and this can be observed in table 2. usually, lowest storage capacity is observed in solid storage materials. A weight percentage, of range 1.9 – 2.5% can only store by Complex hydrides and the physisorption materials like activated sorbents can store hydrogen up to 3wt%. Chemical hydrides can perform superior than solid-state store materials and store hydrogen up to 3.5 wt.%. 5.5 wt.% of hydrogen can store at 70Mpa in the compressed hydrogen storage

Table 1. US DOE hydrogen storage targets for on-board hydrogen storage systems for light-duty vehicles

Storage Parameter	Units	2020	Ultimate
System gravimetric capacity	Kg H_2/kg system	0.055	0.075
System volumetric capacity	Kg H_2/L system	0.040	0.070
Operating ambient temperature	$^{\circ}$C	-40/60 (sun)	-40/60 (sun)
Min/max delivery temperature	$^{\circ}$C	-40/85	-40/85
Operational cycle life	Cycles	1500	1500
Well to power plant efficiency	%	60	60
System fill time (5 kg H_2)	min	3.3	2.5
Fuel purity	% H_2	99.7% (dry basis)	
Loss of useable H_2	(g/h)/kg H_2 stored	0.05	0.05

(Ganguly et al. 2019).

tank. Cryo compressed and Liquefied hydrogen technologies are the best technologies to store hydrogen in terms of gravimetric storage capacity.

1. Physical Methods Of Hydrogen Storage

a. Compressed Gaseous Hydrogen Storage

The compressed gaseous form of hydrogen storage is one of the convenient storage methods available today. At 15-20 Mpa; steel cylinder tank is used for hydrogen storage and volumetric density of 10-12 kg/m^3 and gravimetric density of 1.5 wt.% can be reached by these methods (Tarasov & Lototskii, 2007). The DOE targets for 2020 i.e., 5.2 wt.% and 40 kg/m^3 (table 1) can be achieved but it requires High pressures. But increase in pressure will reduce the thickness of the Steel tank and this is not a solution for enhancing the storage capacity of hydrogen and it is also found that gravimetric hydrogen storage

*Table 2. Current status of hydrogen storage technologies*

Hydrogen Storage Method		Gravimetric Capacity (wt %)	Volumetric Capacity (g/L)
Physical storage	Compressed (350 bar)	2.8-3.8	16-18
	Compressed (750 bar)	2.6-4.4	19-25
	Liquid	4.8-6.8	31-39
Chemical storage	Complex hydride	1.9-2.5	16-28
	Carbon (porous)	2.9-3.1	13-15
	Chemical hydride	2.6-3.5	22-29
Hybrid storage	Cryo-compressed	5.0-5.8	28-38
Targets	2020	5.2	40
	Ultimate	7.0	70

(Read et al. 2007, Baroutaji et al. 2019)

capacity decrease with increasing pressure. Therefore, to achieve the targets of DOE, storage tank materials which are lighter are necessarily required. The carbon fibre reinforced composite tanks (figure 3) are developed to store the hydrogen at two different pressure levels of 35 and 70 Mpa. In order to reach the hopes of users on par with gasoline-powered vehicles hydrogen-fuelled vehicles should have a range of 300 miles and this requires storage of 4–7 kg of hydrogen, depending on the vehicle size (Tarasov & Lototskii, 2007; Hua et al. 2007).

Figure 3. Quantum Technologies type IV compressed gaseous hydrogen storage tank
(Reprinted from Ref. (von Helmolt & Eberle, 2007) with permission from the Journal of Power Sources. Copyright Elsevier)
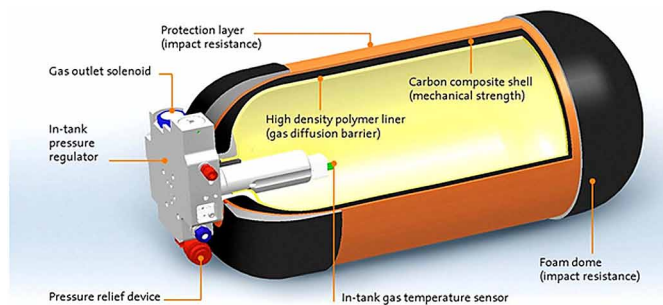

The main components of storage tanks are as follows:

- **Liner**: Hydrogen can permeate through many materials due to its smaller size. Hydrogen permeation from the tank can be prevented and eliminated by the liner. Polymeric materials are generally used as a liner when compared to the metallic liner materials due to its lightweight (Felderhoff et al.2007).
- **Shell**: These are the components of a storage tank loaded with bearing components (Hua et al. 2011).
- **Protection Layer**: this the outer most protective layer of the tank and also useful to withstand the impacts,
- Temperature sensor vehicle electrical interface, pressure sensors, pressure relief device, pressure regulator, vent line ports, connector, refuelling port, stone shield and fill line check valve are the other essential components required to balance the plant.
- **General considerations:** 1 litre of liquid hydrogen occupies 780 L of gas at normal temperature and pressure. Boiling temperature of hydrogen is at 1 atm of 20.2 K. Therefore, the boiling rate and compressibility are the two important considerations while designing and implementing the Cryo-method.

Storage tanks of capacity 35 and 70 Mpa does not satisfy the targets given by the DOE while performing a technical assessment. It is to be noted that 5.5 wt.% (35Mpa) system possess higher gravimetric capacity that 5.2 wt.% (75Mpa). However, 17.6 kg/m^3 of 70Mpa has high volumetric capacity than 26.3 kg/m^3 (35Mpa) System (Hua et al. 2011).

An amount of compression work is the major drawback of the compressed gaseous hydrogen storage. Compression work is 12 to 15% lower than the heating values of hydrogen which is essential to reach 35 and 70Mpa. With increasing pressure, the significance of compression work lowers as shown in figure 3.To keep the temperatures and pressures at safe levels and to fill the hydrogen as much as possible during the compression of hydrogen, the hydrogen tank needs to be cooled. The energy penalty will be added during the cooling process. Estimates state that compression is greater than that of liquefaction cost for hydrogen (Zhou, 2005).

Figure 4. Hydrogen compression work as a function of pressure
(Reprinted with permission from Ref. (Felderhoff et al. 2007). Copyright Royal Society of Chemistry)
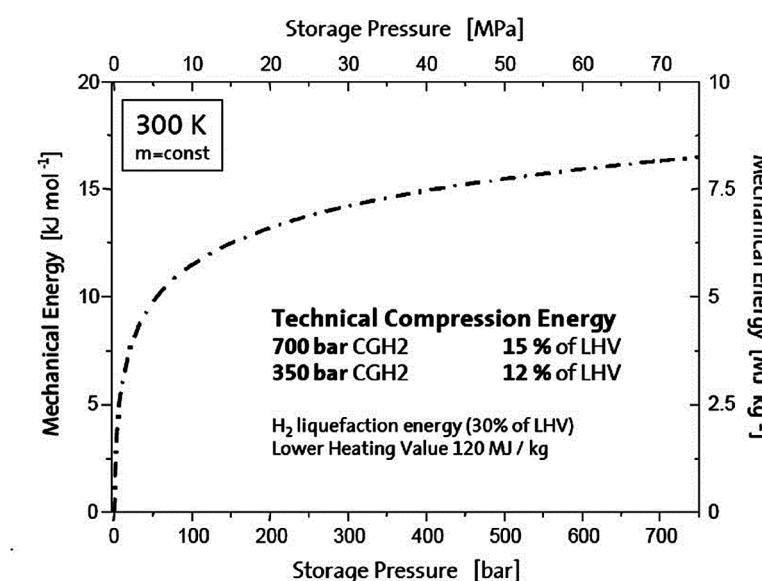
Storage technologies for gaseous hydrogen usually include storing at room temperature only (i.e., 300 K). Cryo-compressed technologies like keep hydrogen at high pressures in cryogenic temperatures in order to attain greater storage capacity. Gaseous storage is considered as most practical option upon its shortcomings by automotive industry which is the only technology that has been adopted commercially (i.e., Toyota Mirai) thus far (Hamilton et al. 2009).

b. Liquefied Hydrogen Storage

Liquified hydrogen storage is another physical storage method. As shown in Table 2, high volumetric and gravimetric densities can be achieved by this method. Comparing to the compressed hydrogen storage, liquified hydrogen storage pressures are lower (<1 Mpa) and this helps in eliminating the load-bearing (in terms of Cost) carbon fibre reinforced composite materials generally utilized in compressed hydrogen storage. Drawbacks of this storage system are boil-off losses and liquefaction energy penalty. Components of typical liquid hydrogen storage tank are presented in Fig. 4. The hydrogen storage tanks are insulated in between the double-walled vessels.

The temperature between liquefied hydrogen (20K) and ambient (300K) are generally different, the inner vessels are insulated with the multilayers consists of altering metal foil layers (vacuum super insulation) and padding materials and this helps in minimizing ambient heat gain.

Multilayer insulation design is showed in Figure 5

Figure 5. (a) Liquid hydrogen tank design by Linde and (b) the vacuum super insulation
(Reprinted from Ref. (von Helmolt Eberle, 2007) with permission from Journal of Power Sources. Copyright Elsevier)
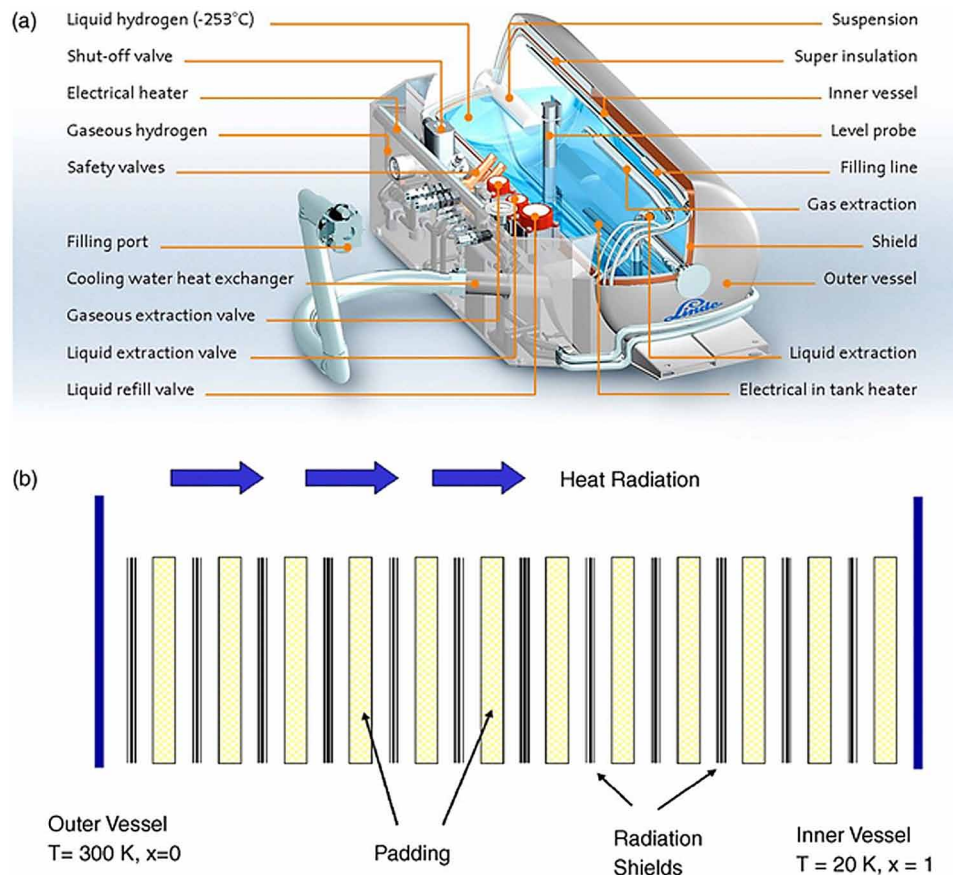
The efficiency of insulation (Manoharan et al. 2019) will be enhanced by the space between vessels. Insulation acts as the most important component in the liquid hydrogen tank. While designing a tank for all heat transfer mode are necessary to be examined. Radiation heat transfer is efficient in between ambient and liquid hydrogen as conduction occurs through pipes, ports and mountings.

The shape of the tank is additional important aspect in the thermal design of a liquid hydrogen tank. Cylindrical tanks will minimize the heat flow and this results in minimization of surface to volume ratio. In the current vehicle designs cylindrical tanks will occupy more space. Conformable tanks are preferable in case of cylindrical tanks in some cases, but these tanks show inferior thermal preferences when compared to cylindrical tanks. In addition, conformable tank manufacturing is more labour-intensive process and costly (von Helmolt & Eberle, 2007).

Elimination of input heat to the current storage tank though with vacuum super insulation is impossible; due to the heat input the hydrogen inside the tank evaporates continually resulting in increase of pressure inside the tank constantly. Excess of any hydrogen is required to be emitted to atmosphere, catalytically burned or captured (Felderhoff et al. 2007). If the pressure of the tank inside reaches around 1Mpa. Hydrogen not utilized or excess hydrogen is called boil-off losses. "Dormancy" is time period between parking the vehicle to the venting process. Longer dormancy periods are favoured, owing to longer dwell times and lesser loss through adiabatic or isothermal processes.

Applying innovative cooling methods will enhance the dormancy and the normal state-of-the-art tank designs possess dormancy period of 3 days. In comparison with the other storage, methods liquefied hydrogen storage shows the best volumetric and gravimetric storage densities (Manoharan et al. 2019). The liquefaction cost of hydrogen is 30% lower having value of hydrogen as shown in Figure. 4.

Overall cost of liquid hydrogen storage effortlessly surpass cost of gaseous hydrogen storage when considered in combination with boil-off losses. At present, liquid hydrogen storage is the lone attractive method for short-term storage (i.e., space applications) due to the above-mentioned limitations.

c. Cryo-Compressed Hydrogen Storage

High pressures and Cryogenic temperatures (< 77k) are used to store hydrogen in this method. This method overcomes the drawbacks of other hydrogen storage methods. The major flaw of cryo-compressed Hydrogen Storage is low volumetric and low gravimetric densities (at high pressures even). Energy densities can be enhanced by cooling the hydrogen to cryogenic temperatures at immense pressures, by avoiding the penalty associated with Liquefaction. Maximum 1 MPa pressure (low pressure) can be stored by liquid hydrogen tanks and this leads to the shortfall of dormancy period. Dormancy period of these tanks can be increased by enhancing the pressures. In comparison with low-pressure tanks, vaporised hydrogen can be stored in high-pressure tanks longer. The liquid hydrogen and cryo- compressed hydrogen helps in charging the cryo-compressed tank in a dual-phase region. Resilience of this nature makes storage system apt for diverse needs; for example, liquid hydrogen can be used when range of driving is more important than tariff (Sdanghi et al. 2019).

According to the assessments, this storage system can reach the DOE (Ahluwalia et al. 2010) targets i.e., volumetric, gravimetric densities and dormancy, but shortfalls in reaching the cost of manufacturing and well-to-Wheel efficiency. Amongst other technologies of hydrogen storage Cryo-Compression storage shows grater volumetric and gravimetric densities (see Table 1). In addition to that, it also eliminates and reduces the boil-off losses in comparison with liquified hydrogen Storage. Cryo-compression hydrogen storage have evolved to be a promising hydrogen technology in comparison with others.

## 2. Chemical Methods of Hydrogen Storage

Preceding discussion makes it evident that liquid hydrogen storage and compressed hydrogen storage (i.e., Physical Methods) have many drawbacks resulting in search for improved hydrogen storage methods. Till 2000s, researchers mostly focussed on metal hydrides and efforts on chemical storage methods were very limited. In the early 2000s, awareness of environmental problems was increased and research on hydrogen storage has gained more importance.

Material- based hydrogen storage is also called as chemical methods of hydrogen storage which are founded on interaction of hydrogen with hydrogen storage materials. The hydrogen interaction with hy-

Figure 6. Cryo-Compressed Hydrogen Storage.
Reprinted from Ref. (Barthelemy et al. 2017) with permission from the International Journal of Hydrogen Energy. Copyright Elsevier
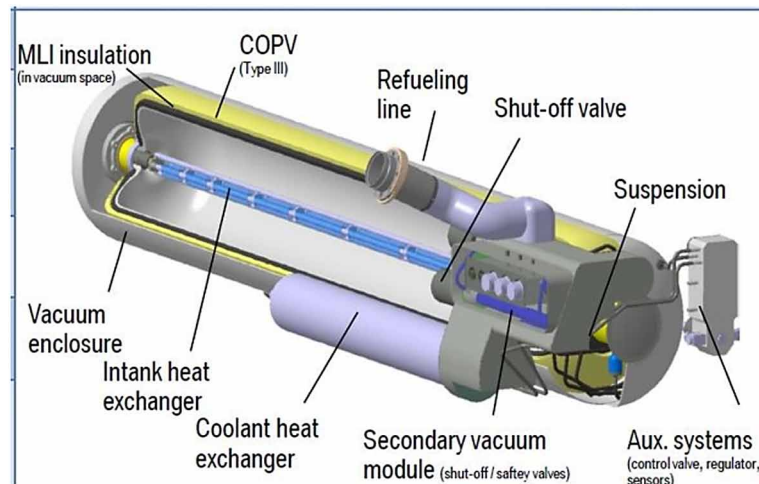
drogen storage materials in strength can be ionic and covalent bonds(strong), Kubas interaction(moderate) or van der Waals forces (weak) (Hoang & Antonelli, 2009). The operation condition like charging/discharging, pressure, temperatures etc., can be dictated by the strength of the interactions in the hydrogen storage method. In comparison with compressed or liquified hydrogen storage, hydrogen can be stored more efficiently in firm materials like $LiBH_4$, (complex hydride) can store 18.4 wt.% (gravimetric) and 121 kg/m^3 (volumetric), respectively (Züttel et al. 2003).

The plant components like a storage tank, safety features, cooling /heating equipment, does not take into consideration in materials-based storage capacity. Hydrogen storage capacity is half of the material storage capacity and it is a basic thumb rule (Read et al. 2007).

Chemical hydrogen storage methods can be categorized into

1. on-board regenerable and
2. off-board regenerable

The difference between these two storage materials has unfavourable thermodynamics or kinetics or both. Hydrogen on board vehicles can be recharged by the solid-state storage materials, whereas off-board can be regenerated. Off-board regeneration is more difficult in comparison with on-board regeneration. Off-board regeneration is costly and impractical. Charging of On-board regenerable materials can be done directly using hydrogen and doesn't require any further intermediate steps. The overall cost and fuel cycles will be increased in off-board regeneration as it requires processed spent fuels in the central facility.

a. Solid-State Hydrogen Storage (On-board Regenerable Materials)

The on-board regenerable materials are classified into two types based on the interactions and strength between hydrogen and storage materials

1. reversible hydrides (based on strong interactions) and
2. physisorption materials (based on weak interactions).

Reversible hydrides are further classified into metal hydrides and complex hydrides. Complex hydrides (Jain et al. 2010) and Porous materials (Thomas, 2007) consist of a significant portion of hydrogen storage materials and that can regenerate onboard hydrogen storage. The complex Hydrides have high gravimetric and Volumetric densities and these characteristics help in storing a high amount of hydrogen. Withal, they experience sluggish kinetics, high operating temperatures and reversibility. Contrarily, pours materials that are based on physisorption have complete reversibility and fast kinetics; nonetheless, at cryogenic temperatures they can store significant amount of hydrogen because the material matrix of porous nature i.e., with less adsorption enthalpy have weak interaction with hydrogen at room temperatures (Felderhoff et al. 2007).

Reversible Hydrides

Metal Hydrides

The old class metal hydrides with reversible hydrides are AB_5 ($LaNi_5$) and AB_2 ($ZrMn_2$) – type alloys that date back to 1960s (Zaluska et al. 2001). The metal Hybrids that are broadly studied are listed in Table 3. Movement of hydrogen atoms into the crystal matrix and its interaction with metals by dissociation from Metal Hybrids. AB_2 and AB_5 are termed as intermetallic hybrids, as their interstitial crystal lattice (Chandra et al. 2006) contain hydrogen atoms. Prime disadvantages with these hybrids are low gravimetric densities ($LaNi_5H_6$); require high temperatures for operation (MgH_2) and great price of rare earth metals (i.e., titanium and Lanthanum).

The metal hydrides consist of less gravimetric densities (1-2 wt.%) and not appropriate for a mobile application, but appropriate for the stationary application (Chandra et al. 2006); due to their favourable operating conditions and reversibility of hydrides. MgH_2 hydride among other Metal Hydrides gained significant attention because of its high gravimetric capacity (7.6 wt.%). Magnesium hydrides show both covalent and ionic characters; and also has immense operating temperature (Table 3) (Noritake et al. 2002). The studies on MgH_2 focussed on reducing desorption temperatures and increasing kinetics by destabilization by various metal oxides and transition metals (Oelerich et al. 2001; Liang et al. 1999).
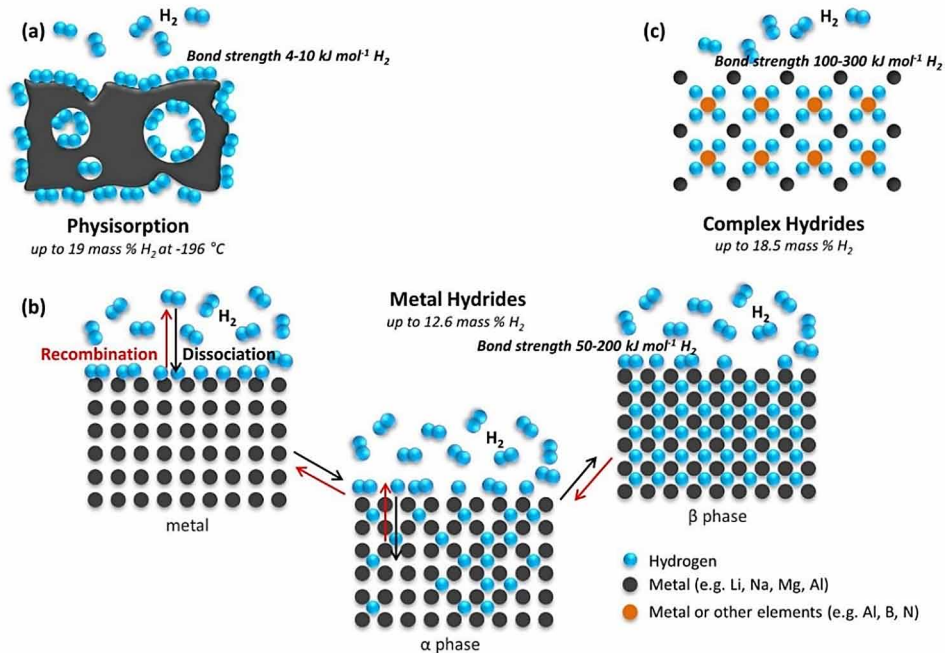
Complex Hydrides

Bogdanović & Schwickardi, 1997 doped the Ti with $NaAlH_4$ and made a complex hydride and bought attention to the hydrogen storage community. They added 2 mol% of Ti to $NaAlH_4$ and showed that adding this small amount can regenerate the complex hydrides by applying high hydrogen pressure. High gravimetric capacity for storage of hydrogen can be attained only by doping the metals that are lighter than Mg (i.e., Li and Na). Thus, during the last decade researchers focussed on light metal complex hydrides. These hydrides show both covalent and ionic bonding characters. In $LiNH_2$, Covalent characters are shown by N-H bonding in NH_2 (anion), whereas Mixed characteristics i.e., covalent and ionic characters are shown by Li-N.

Theoretical gravimetric densities of complex hydrides: $LiBH_4$(18.4 wt.%) (Orimo et al. 2005), Li_3N (11.5 wt.%) (Chen et al. 2002), $LiAlH_4$ (10.6 wt.%) (Chen et al. 2001) and $NaAlH_4$ (7.5 wt.%) (Bogdanović & Schwickardi, 1997; Song & Guo, 2006) and their reversible capacities of gravimetric

Figure 7. Schematic representation of current approaches to store hydrogen with materials.
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are about 4-5 wt.% under experimental operating temperatures and pressures (Sakintuna et al. 2007). The most studied complex hydrides of their reversible capacities are LiBH4–LiNH2–MgH$_2$ (4–8 wt.%, 200–280⁰C) (Sudik, 2008), LiNH$_2$–MgH$_2$/LiH (4–6 wt.%, 200–250⁰C) (Luo, 2004; Nakamori & Orimo, 2004), NaAlH$_4$ (3–5 wt.%, 120–150⁰C) (Resan et al. 2005) and LiAlH$_4$ (3–5 wt.%, 150–200⁰C) (Chen et al. 2001). Studies on these hydrides are mainly focussed on noxious toxic/poisonous gas emissions, sluggish kinetics, destabilization issues (Sakintuna et al. 2007; Borgschulte et al. 2011; Ichikawa et al. 2004; Demirocak et al. 2013).

Table 3. Extensively studied metal Hydrides

Metals	Hydrides	Capacity (wt.%)	Temperature for 1 Bar H$_2$ (⁰C)
Mg	MgH$_2$	7.66	279
Mg$_2$Ni	Mg$_2$NiH$_4$	3.59	255
FeTi	FeTiH$_2$	1.89	-8
ZrMn$_2$	ZrMn$_2$H$_2$	1.77	440
LaNi$_5$	LaNi$_5$H$_6$	1.37	12

(Principi et al. 2009)

Physisorption Based Materials

Porous Materials

Porous materials have large surface area and materials based on physisorption (Morris et al. 2019; Mohan et al. 2019), these materials include inorganic and organic ordered (Zeolites) and Amorphous (activated carbon) structures (Rowsell & Yaghi, 2004; Davis, 2002; Zhang & Cooper, 2005). These materials have various applications in ion exchange (Davis, 2002), gas storage (Morris et al. 2019), biomaterials (Karageorgiou & Kaplan, 2005) catalysis (Corma,1997), purification (Toyoda et al. 2003), and separation (Nakanishi & Tanaka, 2007; Horcajada et al. 2006). Based on the pore dimensions these materials are classified. Pores are separated into three categories on the basis of their measurements in accordance to International Union of Pure and Applied Chemistry; micropores (<2 nm), mesopores (2–50 nm), and macropores (>50 nm) (Ssing et al. 1985).

High surface area novel porous materials development like polymers of intrinsic porosity (PIMs) (McKeown & Budd, 2006), metal-organic frameworks (MOFs) (Rowsell & Yaghi, 2004), covalent organic frameworks (COFs) (Han et al. 2008), porous aromatic frameworks (PAFs) (Ben et al. 2009), templated carbons (Yang et al. 2007), conjugated microporous polymers (CMPs) (Jiang et al. 2008) and hyper crosslinked polymers (Germain et al. 2006), during the previous decade lead to extensive research attempts on storage materials (Morris et al., 2019). Owing to their reversibility, debauched sorption kinetics and capable gravimetric storage capacity these materials have been studied extensively.

Hydrogen storage in the above mentioned porous materials having large surface areas is comprehended by the interface of H_2 on porous material surface via physisorption (i.e., adsorption) and mainly on the basis of weak van der Waals forces (Rzepka et al. 1998). At cryogenic temperatures, a good amount of hydrogen uptake can be achieved by physisorption method. The storage capacity of hydrogen at room temperatures are usually less than 1 wt.% at modest temperatures (100 atm) (Thomas, 2007; Kajiura et al. 2003). The adsorption enthalpy pore size, pore volume and surface area the key parameters for hydrogen storage capacity (Bhatia & Myers, 2006; Frost et al. 2006). The adsorption enthalpy is low in porous materials (<6 KJ/mol) (Schmitz et al. 2008) and for uptake of hydrogen at room temperatures need to be improved (20–40 kJ/mol) (Jhi & Ihm, 2011).

Multiple alteration procedures like optimizing pore size (Bhatia & Myers, 2006) increasing surface area and nobbling with impure atoms (B, N, alkali/transition metals (Chung et al. 2008; Goddard and Han, 2009; Li & Yang, 2006; Zhou et al. 2008) will tune the enthalpy or improve the hydrogen uptake capacity.

Therefore, many researchers focussed on improving the adsorption enthalpy (i.e., creating open metal sites in MOFs) (Zhou et al. 2008), increasing surface areas (Farha et al. 2012), and fine-tuning pore size-dimensions of these materials (Katoch et al. 2019).

Chemical Hydrogen Storage (Off-board Regenerable Materials)

The term Off-board Regenerable materials in this section are used to describe, the materials that cannot be redeveloped simply (as the thermodynamics and Kinetics for these applications are unfavourable). Chemical Hydrides is another term that is frequently used in the literature to describe the materials with the same class.

Examples of chemical Hydrides used for chemical hydrogen storage: Sodium borohydrides ($NaBH_4$) and Aluminium hydrides (AlH_3). (but there are not places under the reversible hydride group due to their

difficulty in reliability). Most studied hydrogen materials in the literature available are ammonia-borane (NH_3 _ BH_3 or simply AB) (Staubitz et al. 2010), $NaBH_4$ (Netskina et al. 2019), AlH_3 (Graetz et al. 2011) and Cyclohexane-benzene (liquid organic hydrogen carriers) (Crabtree, 2008; Teichmann et al. 2011). In detail about these materials are discussed below. Further, Methanol's (alcohol), Hydrocarbons (Eberle et al. 2009) and ammonia (NH_3) (Klerke et al. 2008) also reflected as chemical hydrogen storage materials. Main problem associated with such materials as energy carriers are, they will not provide solutions for sustainable development as these materials are based on relic fuels.

Borohydrides of Sodium

Hydrogen is released from sodium borohydride ($NaBH_4$) through hydrolysis reaction as reported by subsequent reaction path where half of the hydrogen is produced from water:

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2$$
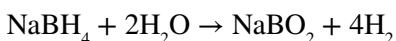
These borohydrides have 10.8 wt.% storage capacity of hydrogen by theoretically; Withal, in operating conditions, 2.9 – 7.5 wt.% storage capacities were reported (Netskina et al. 2019). The major issues linked with these hydrides with water system ($NaBH_4$–H_2O system) are the solubility of $NaBH_4$ and $NaBO_2$ is low in Water and this requires more quantity of water that can be stowed on-board and slow rate of reaction for hydrogen generation necessitates a catalyst to enhance the speed of reaction. However, over a longer duration, the catalyst durability may be induced and performance of the reaction may be degraded. These are the reason DOE restricted the above hydrides (as aqueous solutions) not to be used for hydrogen storage (Netskina et al. 2019).

Hydrides of Aluminium

Hydrides of aluminium (AlH_3- Aluminium hydride) has 148 kg/m³ Volumetric and 10.1 wt.% gravimetric storage capacities of hydrogen. Hydrogen is liberated from AlH_3 with small amount of input heat (~7 kJ/mol) in accordance with endothermic reaction (Graetz, 2009).
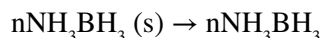
$$AlH_3 \rightarrow Al + \frac{3}{2}H_2$$
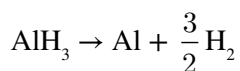
Hydrogen delivery can be fastened by manipulating the size of crystallite, as crystallite with smaller size will decompose the AlH_3 faster and this will help in increasing the rate of reaction. Pressure (~700 MPa) is nearly required for regeneration of AlH_3 which is a major challenge at room temperatures. The Electrochemical hydrogenation and ethereal reactions (with $LiAlH_4$ and $AlCl_3$) are the other alternative ways for AlH_3 Regeneration.

Ammonia-Borane (AB)

A gravimetric storage capacity (theoretical) of 19.6 wt.% was achieved with this Ammonia-Borane (white crystalline solid) which is a non-explosive and non-flammable substance (Staubitz et al. 2010). Extraction of Hydrogen from AB can be achieved by many ways such as thermolysis (with or without the presence of a catalyst), hydrolysis and decomposition (Huang & Autrey, 2012).

Thermolysis and Hydrolysis were discussed briefly:

$$nNH_3BH_3 \text{ (s)} \rightarrow nNH_3BH_3$$

$$nNH_3BH_3 \text{ (l)} \rightarrow [NHBH]_n \text{ (s)} + nH_2 \text{ (g)}$$

$$[NHBH]_n \text{ (s)} \rightarrow [NB]_n \text{ (s)} + nH_2 \text{ (g)}$$

The thermal decomposition of Ammonium-Borane requires onset temperature of 70^0C and maximum is 110^0C. (~1.1 mol H_2 can be yielded by 1 mol of Ammonium-Borane) and this decomposition will release a by-product polyaminoborane ($[NH_2BH_2]$ n) (Peng & Chen, 2008). Trace amounts of ammonia and borazine will be liberated by the decomposition of ammonium-borane and these are required for operating proton exchange membrane fuel cell and needs to be captured or eliminated (Demirocak et al. 2013).

Other concern of thermolysis of AB is induction duration before release of hydrogen; for example, AB starts to produce significant quantities of hydrogen just after 3 h at a temperature of 85^0C (Peng & Chen, 2008). The major concern with these substances (during thermolysis) is an induction period to release hydrogen a minimum 85^0C preheat for 3h is required. By mixing ionic liquids (Bluhm et al. 2006) with ammonium-borane can overcome the induction period or by doping the ammonium-borane with porous materials also decrease this problem (Gutowska et al. 2005). The overall storage capacity of hydrogen will be retarded by the above methods as they add dead weight to the system.

Ammonium-borane Hydrolysis process is mainly depending on pH. The aqueous Ammonium-borane is highly stable in basic and neutral solutions. However; by the interaction of aqueous ammonium-borane with an acid solution, the rate of reaction is fastened and will be hydrolysed rapidly.

Hydrogen should be available on-demand in the current world; so, reacting acidic solution with aqueous Ammonia-borane will liberate more amount of hydrogen. Prime problem of producing hydrogen by a hydrolytic pathway through ammonium-borane is production of highly stable compounds i.e., borate (B-O). Due to this stable bond formation regenerating of Ammonia-borane needs extensive energy and requires high capital (Stephens et al. 2007).

Liquid Organic Hydrogen Carriers (LOHC)

LOHC carriers of energy and the hydrogen can be unloaded and loaded with LOHC in cyclic way (Teichmann et al. 2011). A significant manufacturing benefit is there in carrying liquid as a hydrogen carrier rather than solid. Initially, the end-users are easily benefited and can be transported easily with the existing infrastructure and required quantities can be pumped easily to reaction chamber where it is rehabilitated into heat. Heating of whole hydrogens storage materials is not required due to this reason (Crabtree, 2008). Extensive studies on LOHC like N-ethyl carbazole and cyclohexane-benzene was done according to the literature available (Crabtree, 2008; Teichmann et al. 2011). Comparing LOHC with Chemical hydrogen storage materials, LOHC has a 6-8 wt.% (theoretical) hydrogen storage which is relatively low. Works are ongoing on this type of carriers and in detail especially on regenerating methods of LOHC (Crabtree, 2008; Teichmann et al. 2011).

Hybrid Methods of Hydrogen Storage

To overcome the shortcomings of different storages technologies, hybrid methods (use two or more different methods) are used and this will help in enhancing the storage. Cryo-adsorption is one of the main methods of the hybrid method. Physical-chemical process of hydrogen storage, Cryo-adsorption takes benefit of liquefied, compressed and physisorption materials based hydrogen storage technologies.

Cryo-Adsorption Hydrogen Storage

Hydrogen is stored at high pressures at cryogenic temperatures in physisorption based materials. The storage capacity of the system is mainly related to porous materials adsorption. To enhance the storage capacity pore size, pore-volume, surface area and heat are critical (Frost et al. 2006). Several researchers have investigated the performance of cryo-adsorption of different materials such as MOFs (Hirscher, 2011), zeolite (Li et al. 2009) and Activated carbon (Ahluwalia & Peng, 2009). Instead of empty tank for storage of hydrogen, porous materials will enhance the storage capacity at same temperatures and pressures. Hydrogen storage capacities of high-pressure porous materials presented in literature are the difference between saturation and the zero pressure (Figure 8).

It needs to recognize that applied operating environments are different from the real storage capacities of hydrogen in the system. As an example, pressure inside tank is certainly not zero as the fuel cell always operates at a pressure between 0.2-0.3 MPa (Wang et al. 2003). So, always there is a small amount of hydrogen remains in the tank. Temperature swing is the only way to mitigate this problem. Temperature

Figure 8. Schematic of on-board cryo-adsorption system.
Reprinted from Ref. (Ahluwalia & Peng,2009) with permission from the International Journal of Hydrogen storage. Copyright Elsevier
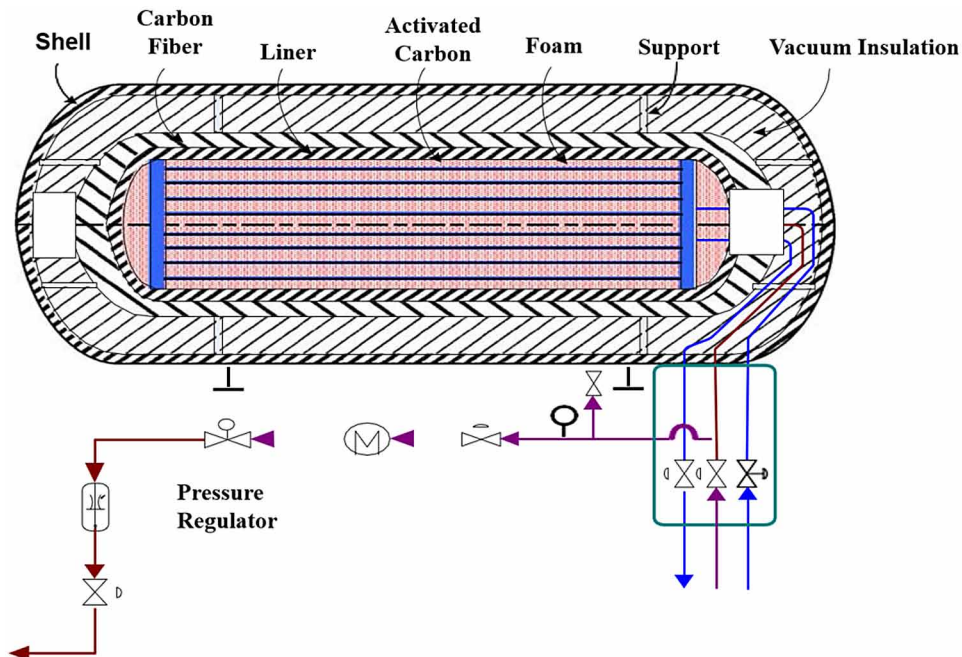
swing means enhancing temperature of tank by means of heat to desorb as abundant hydrogen as probable (Ahluwalia & Peng, 2009).

VI. CHALLENGES OF HYDROGEN STORAGE TECHNOLOGIES

Major challenges of hydrogen storage technologies are listed below:

1. **Compressed Hydrogen Storage**: High energy Penalty. For compression, a Lower heating value (up to 15%) is required. Storage tanks for tolerating high pressures are made by Carbon nanofibres which are very expensive.
2. **Liquefied hydrogen storage**: liquefaction requires quite great energy; lower heating values (up to 30%) are required. To minimise the heat gain from the surroundings the liquefaction tank must be super insulated. Frequent boils-off from the vent of the tank.
3. **Solid-state hydrogen storage**: as discussed earlier there are two chief technologies available for solid-state storage i.e., reversible hydrides and physisorption materials. Physisorption materials can store hydrogen only at cryogenic temperatures, so while filling the tank it needs to cool. Reversible hydrides require high temperatures and suffer from degradation over cycles and also emits toxic gases while discharging (NH_3).
4. **Chemical hydrogen storage**: off-board regeneration is required due to unfavourable kinetic and it is a costly process.

SUMMARY

From the beginning of the industrial era, modern society is uninterruptedly getting advantages from the exploiting of relic fuels undoubtedly. Though, relic fuels are the principal energy source (easy to store, High density. etc.) is a limited energy source. It is imperative to note that extensive utilization of relic fuels causes various environmental problem, one of the major concerns in the present scenario is global warming and climate change due to undue man-made CO_2 emissions. So, it is clearly evident that human community need to find an environmentally friendly alternative energy fuels alternative to relic fuel to move towards sustainable environment. Transportation sector majorly depends on oil that is anticipated to be extended before end of twenty-first century. CO_2 emissions emitted from automobiles are considered as a main source of CO_2 and there is no proven technology to capture the CO_2 that is economically viable. In near future, to mitigate climate change and to stop the reduction of oil it is needed to substitute with energy carrier which is environmentally sustainable. Amongst many options available for sustainable energy carrier, hydrogen is considered to be a promising candidate. This will not emit any noxious gases and free from carbon; when it is burned in internal combustion engines. Similar to the oil economy, hydrogen economy is a system that includes storage, production and transportation. At present, steam reformation methods are utilizing for the production of hydrogen. Renewable energy sources like wind or photovoltaic (PV) powered water electrolysis is required to produce hydrogen. Major challenges are being faced by the transportation of hydrogen are it requires an extensive networking system for distribution of energy which is so expensive.

Hydrogen storage is the last step in hydrogen economy and bottleneck in this economy. Many automotive industries are setting targets for the storage of hydrogen for vehicular application and collaborating with different countries in the world. The greatest rigorous targets are volumetric and gravimetric hydrogen storage capacities, resulting in comparison of different hydrogen storage technologies often times compared only on the basis of energy density irrespective of operating temperature, cost and efficiency. Storage technologies for hydrogen are comprised of solid-state, liquefied, compressed and chemical hydrogen storage technologies. The physical storage methods include liquified hydrogen and compressed storage systems, whereas chemical methods include solid-state and chemical hydrogens storage technologies. The key difference between physical and chemical processes is that hydrogen does not interact with the storage media in physical methods, while hydrogen interacts with the storage media in chemical methods. The conventional methods of hydrogen storage are liquified and compressed storage systems and these technologies have been used for decades. To enhance the gaseous storage, carbon fibre manufacturing methods with low cost were developed to reduce the costs of the tank. To minimise the boil-off losses vacuum super insulations are used and novel cooling technologies also enhanced the dormancy period. Compressed gaseous storage systems are commercialized and most successful technology among all other so far. Due to the shortcomings of liquified systems, majority of the research efforts concentrated on on-board regenerable (solid-state) and off-board regenerable (off-board regenerable). In comparison to solid chemical storage, more attention was gained by solid-state storage as they are reducing the costs concerned with spent fuels. Reversible hydrides and physisorption (porous) materials are the two subclasses of Solid-State storages materials.

A high temperature is required for the operation of reversible hydrides as they have reversibility issues. Porous materials store important quantity of hydrogen at cryogenic temperature, but the major drawback with these systems is price related with cooling. The challenge associated with solid-state materials is it is too difficult to bring the operating temperatures to the closer room temperatures. Hydrolysis process or thermolysis process is utilized to synthesis hydrogen in chemical hydrogen storage materials. By-products released during these processes are more stable to be renewed on-board merely charging by hydrogen required. The drawbacks associated with this material are complexity in regeneration and its cost. In conclusion, in this chapter advantages and disadvantages of hydrogen storage technologies and materials used for storage are presented in detail. Expedition for discovery of a benign fuel substitute to oil is still in process revealing hydrogen to be one of the best choices available in the present scenario. Further research is essential to progress hydrogen storage field frontward. Market diffusion of hydrogen storage technologies in near future is closely knotted to development of enriched hydrogen storage materials.

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