



Hydrogen storage methods: Review and current status

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ABSTRACT

Fossil fuels comprising coal, crude oil, and natural gas are non-renewable and greatly harmful to the environment. Hydrogen, on the other hand, is both sustainable and environmentally friendly. However, due to its light weight and gaseous nature, it presents challenging problems of its storage, and the practical hydrogen storage is perhaps the biggest hurdle in the success of the hydrogen economy on a large scale. Hydrogen can be stored in a variety of physical and chemical methods. Each storage technique has its own advantages and disadvantages. It is the subject of this study to review the hydrogen storage strategies and to survey the recent developments in the field.

1. Introduction

Hydrogen has the highest energy content per unit mass (120 MJ/kg H₂), but its volumetric energy density is quite low owing to its extremely low density at ordinary temperature and pressure conditions. At standard atmospheric pressure and 25 °C, under ideal gas conditions, the density of hydrogen is only 0.0824 kg/m³ where the air density under the same conditions is 1.184 kg/m³. This low density of hydrogen results in an extremely low volumetric energy content of hydrogen that is 0.01 MJ/L H₂ at ambient conditions and 8.5 MJ/L H₂ for the liquefied H₂ (LH₂) [1,2]. In comparison, the volumetric energy contents of methane and gasoline are 0.04 MJ/L and 32 MJ/L, respectively. The low volumetric energy density of hydrogen is certainly a great hurdle in the economic and efficient storage of hydrogen and ultimately in the success of the hydrogen economy. In a developed hydrogen economy, hydrogen is expected to be used both for the stationary as well as for the on-board purposes. Hydrogen storage for a stationary application is far less challenging than for an onboard application. For the stationary applications, the weight of the storage system that is gravimetric hydrogen density is less of a concern than the volume of the storage system or volumetric hydrogen density. For the on-board applications, on the other hand, both the gravimetric as well as volumetric densities are crucial though volumetric energy density is relatively less important for a large-sized vehicle. For the on-board storage adequate amount of hydrogen is required to travel a reasonable distance without refueling the vehicle. A storage method that gives both a high gravimetric energy density and a high volumetric energy density is, therefore, a

requirement. Additionally, moderate operating conditions, low enthalpy change, and fast kinetics of the hydrogen storage and release are the requirements. Safety, low cost, and public acceptance are the other important factors. There are numerous physical and chemical hydrogen storage techniques with their own features and storage capacity that may be proved favorable in the development of a future hydrogen economy. It is the purpose of this study to review the currently available hydrogen storage methods and to give recommendations based on the present developments in these methods.

2. Hydrogen storage methods

The followings are the principal methods of hydrogen storage:

Compressed hydrogen
Liquefied hydrogen
Cryocompressed hydrogen
Physically adsorbed hydrogen
Metal hydrides
Complex hydrides
Liquid organic hydrogen carriers (LOHC) or Liquid organic hydrides

Fig. 1 pictorially represents the concept of these hydrogen storage methods whereas Table 1 gives a comparison among them.

In the following sub sections, the above mentioned hydrogen storage methods will be discussed and their characteristic features will be highlighted.

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2.1. Compressed hydrogen

The most widely used method of hydrogen storage is the compressed hydrogen at high pressure [2,3]. The compression of hydrogen is not only a well-developed technology [2, 4–7], but it also offers high rates of hydrogen filling and release [3]. Additionally, no energy is used for the release of hydrogen [8,9]. However, compression of hydrogen to a high pressure consumes about 13–18% of lower heating value of hydrogen [8, 10] which affects the overall economics of the process. The good news is that the increase in pressure only slightly increases the power required for the compression [9]. Hydrogen is stored in cylindrical vessels as spherical vessels are difficult to fit onboard. A light weight and low cost vessel material that can withstand high pressure is required. The selected material must be able to resist hydrogen diffusion and the likely embrittlement caused by the stored hydrogen.

Based on the above criteria, four different types of vessels are used for the storage of compressed hydrogen gas [7, 11–13].

Type I: These are the cheapest option [13]. The vessels are made of metallic materials and capable of withstanding pressure up to 30 bar [11,12]. For high hydrogen pressures or densities, the metal wall needs to be relatively thick. This increases the weight of the storage vessel and substantially decreases the net hydrogen gravimetric energy density. The vessels offer extremely low gravimetric energy density as about 1 wt % H₂ is only successfully stored [11,12,14] in a practical manner. The most common material of construction is steel or aluminum alloy [6,11].

Type II: In these vessels, the metallic wall is wrapped with fiber resin composite on the cylindrical part [11,12]. Compared to Type I, they have 30–40% less weight at the expense of 50% more cost [13].

Type III: These are made of carbon fiber composite materials (carbon fiber reinforced plastic, CFRP) lined with metal such as aluminum [2]. They are strong and light weight, but have low thermal conductivity which may pose problem for low rate of heat release during the compression of hydrogen [2]. They are suitable for applications requiring 450 bar pressure [13]. However, they can be used up to 700 bar hydrogen pressure.

Type IV: Similar to Type III, these are made entirely of composite materials. However, they are different from Type III in that the liner in Type III is mostly metal liner which contributes $\geq 5\%$ of mechanical strength [11,13]. For Type IV, the liner is mostly polymeric as that of high density polyethylene (HDPE) and hardly a metal [11,12]. They are also used to store hydrogen at 700 bar pressure. Type IV cylinders of Hexagon Composites [15] or NPROXX [16] are polymer lined, filament wound carbon fiber reinforced polymer (CFRP) structures.

Table 1

Comparison of various hydrogen storage methods [1,7,11,84,89,92,99,125, 126].

Storage method	Hydrogen content (wt% H ₂)	Volumetric density (g/L)	Volumetric energy density (MJ/L)
Compression			
1 bar, RT	100	0.0814 ^a	0.01
350 bar, RT	100	24.5 ^b	2.94
700 bar, RT	100	41.4 ^b	4.97
700 bar, RT, (incl. Type IV tank)	5.7	40.8	4.9
Liquid hydrogen			
1 bar, –253 °C	100	70.8	8.5
1 bar, –253 °C (incl. tank)	14	51	6.12
Cryo-compression			
350 bar, –253 °C	100	80	9.6
Metal hydrides			
MgH ₂	7.6	110	13.2
FeTiH ₂	1.89	114	13.7
Complex hydrides			
NaAlH ₄	7.5	80	9.6
Physical adsorbents			
Activated carbon @77 K and 30–60 bar	5.0	38.5	2.4
Zeolite (NaX) @77 K and 40 bar ^c	2.55	20	2.4
MoF (MOF-210) @77 K and 80 bar	7.9	25.8	3.1
Liquid hydrogen organic carriers			
Methylcyclohexane/toluene	6.2	47.3	5.68
perhydro-benzyltoluene/benzyltoluene	6.2	56.0	6.72

^a Calculated from ideal gas law.

^b Calculated from the standard form of the Peng-Robinson equation.

^c Assuming same density as activated carbon.

A kind of Type V vessel is a modification of Type IV with reinforcing space filling skeletons [17] and designed to have even higher hydrogen volumetric and gravimetric densities. These vessels are, however, yet not available commercially. More detailed construction features of the hydrogen storage vessels are given by Barthelemy et al. [11].

Hydrogen stored at 700 bar in Type III or Type IV vessel may provide a practical solution with refueling time less than 3 min and driving 500 km [10]. At 700 bar with Type IV vessel, hydrogen has energy density of

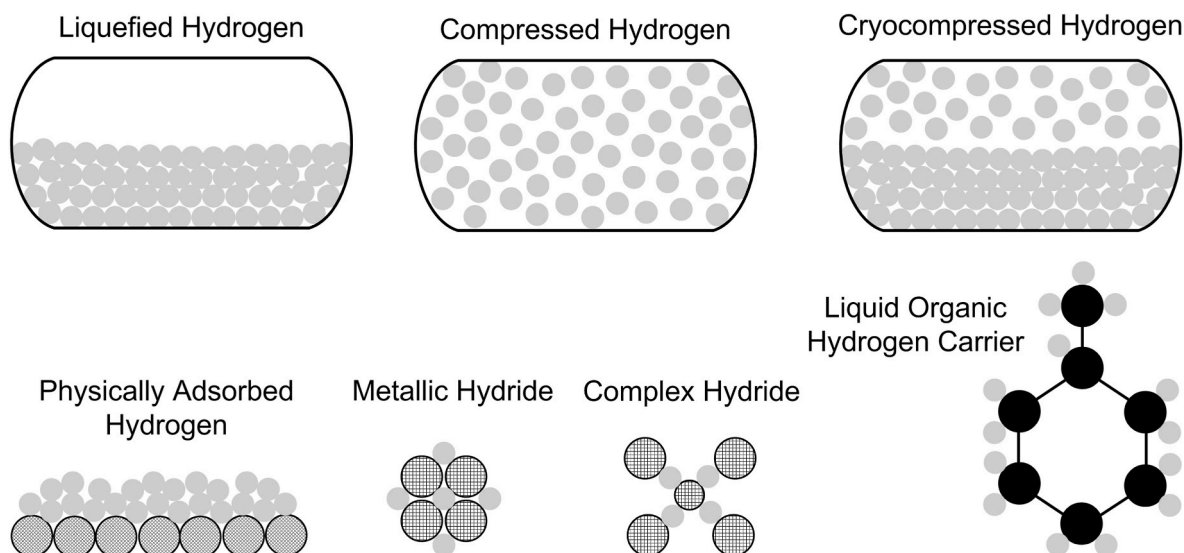


Fig. 1. Concept of hydrogen storage methods.

5.7 MJ/L [7]. However, onboard pressurized vessels have less public acceptance [4] and have increased risks of explosions due to sudden possible shocks. Sophisticated valve technology is required to decrease the pressure of 700 bar to engine inlet pressure. Ideally, energy can be recovered during the expansion process [8], but it requires complicated design and extra weight of turbine on the vehicle. Practical problems of refueling at 700 bar [18] and associated safety issues at the filling stations are also there. Moreover, hydrogen fuel infrastructure including its transportation and dispensation (filling stations) is required [4,19].

Fuel cells vehicles working on compressed hydrogen are commercialized and more and more vehicles are sold and running on the roads. Examples are Toyota Mirai (2021) and Hyundai Nexo (2018, an improvement over the previous generation, Hyundai Tucson) both of which use compressed H₂ at 700 bar, three Type IV cylinders, and travel more than 600 km in single charge [20,21]. Commercial Hyundai truck uses hydrogen at 350 bar and can travel ~400 km in one fill [22]. Hydrogen fuel infrastructure is also developing in different parts of the world though at rather slow pace. One such example of hydrogen storage and distribution is developed by Hexagon Composites Company [23].

Compressed hydrogen gas can also be stored in glass microspheres of the size, say, 5–500 μm [9]. The microspheres offer reasonable (5.4 wt %) gravimetric H₂ density [24]. The microspheres can be loaded with high pressure hydrogen gas (350–700 bar) [24] on off-site and delivered to the filling station [2,4], thus eliminating the need for the hydrogen infrastructure [2]. They appear to be safer than compressed hydrogen in cylinders as the bulk hydrogen storage is at low pressure. Moreover, the glass spheres do not necessarily require a cylindrical or spherical shape of tanks. However, the glass microspheres or similar structures offer low volumetric energy density and require energy [9] and high temperature for the release of hydrogen, i.e., temperatures of 200–300 °C [24]. They slowly release hydrogen at ordinary temperatures thus hydrogen is lost during the handling and transportation and they are susceptible to breakage during charging, discharging, and transportation [9].

Underground geological caverns can also store hydrogen [1,6,25,26]. This solution is suitable for long period of storage [1,6], however, there may be issues of hydrogen purity due to impurities present in the caverns [1]. HyUnder project in Europe [25] is an example of underground hydrogen storage in salt caverns.

2.2. Liquefied hydrogen storage

In the liquid or cryogenic form hydrogen (LH₂) has much higher density and therefore volumetric energy density increases to a large extent. The density of liquid hydrogen reaches to around 71 g/L at –253 °C [6] where its energy density becomes equal to 8 MJ/L H₂ [2]. It can, therefore, be said that 4 cylinders of LH₂ are equivalent to 1 gasoline tank. Considering the weight of insulation and the tank weight, though, a lower value is achieved. The critical temperature of hydrogen is –240 °C (above which hydrogen cannot be liquefied), therefore hydrogen has to be cooled below its critical temperature for the liquefaction. Hydrogen is liquefied to –253 °C (normal boiling temperature of hydrogen) [27] for storage as liquid. Similar to compression of hydrogen, liquid hydrogen storage is a well-established technology [7]. Liquefied hydrogen offers high rates of hydrogen release similar to compressed hydrogen [7] and low adiabatic expansion energy at cryogenic condition [13,27,28]. The low adiabatic expansion energy is useful in avoiding damage when H₂ will be suddenly leaked through an opening. As the liquid hydrogen density is nearly 1.5–2 times as that obtained with hydrogen compressed at high pressure, the tank size reduces to an acceptable value. Storage is at low pressures so rather thin and cheap storage tanks can be used. In the liquid form hydrogen is non-corrosive [29] and stainless steel and aluminum alloy vessels with sufficient insulation are used for the cryogenic storage. However, the cost of liquefaction is high so is the energy used for the liquefaction [1,9,18]. It is realized that about 30–40% of net heating value of hydrogen

[11,30] is used in the liquefaction process. Another issue is the boil-off phenomenon, which is the loss of hydrogen due to energy input from the surroundings. It is estimated that about 1.5–3% of hydrogen vaporizes per day [3,31]. The boil-off phenomenon also requires more open spaces for public parking and garages [32,33]. A double walled vacuum vessel with excessive and expensive insulation can be used to decrease the boil-off. Moreover, larger the container having smaller surface to volume ratio, the smaller will be the evaporation loss [9,31]. The special design and insulation may increase the weight of the vessel thus reduce the gravimetric energy density. Liquid hydrogen infrastructure [1,14] and possible public acceptance are additional challenges [30]. Although, BMW and GM/Opel have developed test vehicles such as BMW Hydrogen 7 (hydrogen consumption in an internal combustion engine) and GM Hydrogen 3 (hydrogen to be used in a series of fuel cells), respectively based on liquefied hydrogen [2,31], but owing to the extreme low temperature conditions and boil-off phenomenon there is no potential for the liquefied hydrogen to be used on-board [11] especially in small to medium vehicles. Where the dormancy period is small, liquefied hydrogen has the potential. Commercially it is used in spacecrafts where cost has no issue and dormancy period is not available. Recently, Sinot has developed a 112 m long fuel cell yacht, Aqua, that runs on liquid hydrogen [34].

2.3. Cryo-compression

In the cryo-compression the aspects of both the compressed gaseous hydrogen and the cryogenic hydrogen are combined. The hydrogen is stored at cryogenic temperatures and under minimum hydrogen pressure of 250–350 bar [3,27,35,36], much higher than the critical pressure of hydrogen (13 bar). In comparison to the liquefied hydrogen, the cryo-compressed hydrogen offers higher densities, ~80 g/L [4,11,13], nearly 10 g/L higher than the density of liquefied hydrogen, and greatly reduced boil-off losses [11,12]. Ahluwalia et al. [37] observed dormancy period that lasts more than 7 days without the loss of hydrogen while filling the cryo-compressed hydrogen vessel 85% to its full capacity. However, a more expensive double walled, Type III vessel is to be used [11] and increased energy input is required [12]. The rates of hydrogen release and refueling the tanks remain rapid [13,36] and the availability of hydrogen infrastructure as demanded by compressed hydrogen and liquefied hydrogen is still a challenge [1].

2.4. Metal hydrides

Hydrogen chemically interacts with metals and metal alloys to form metal hydrides. The hydride is formed when a hydrogen molecule is dissociated into atomic hydrogen at the surface and then diffuses into the bulk and chemisorbed in the metal or alloy structure [11,18]. This chemisorption may cause the lattice to expand to about 20–30% of its original volume [10]. The hydride formation occurs either by direct reaction of hydrogen with the metal or by the electrochemical dissociation of water molecule [16,31]. The two reaction mechanisms are shown below [9,38]:

Mechanism 1: Direct hydrogen reaction: $\text{M} + x/2\text{H}_2 \leftrightarrow \text{MH}_x$

Mechanism 2: Electrochemical dissociation of water: $\text{M} + x/2\text{H}_2\text{O} + x/2\text{e}^- \leftrightarrow \text{MH}_x + x/2\text{OH}^-$

where, M is a metal or alloy.

When the hydride is formed the heat energy (of chemisorption) is evolved, whereas in the reverse reaction (desorption) to release the hydrogen to be utilized in a commercial facility, an equal amount of energy has to be provided from an outside source. The reversible reaction is caused either by decreasing the pressure or by increasing the temperature [39]. An understanding of the thermodynamics of the process is thus important. An account of thermodynamic pressure-composition-temperature (PCT) measurement of a metal

hydride can be read in Møller et al. [10] and Graetz [39].

The metal hydrides can offer higher hydrogen storage capacity than the compression and the liquefaction [2,3,6,11,18] and store hydrogen at moderate temperature and pressure [2,3,18]. As the operating conditions are less severe than the gas compression and the liquefaction, the use of metal hydride is a safer option than the two [27]. Moreover, the loading and the release of hydrogen can be carried out as many times as required unless impurities hinder the operation [40]. Moreover, generally many metal hydrides require moderate energy (20–55 kJ/mol H₂) [39]. On the other hand, metal hydrides have drawback of having low sorption and desorption kinetics, high hydrogen release temperature, and formation of undesirable gases during discharging the hydrogen [39,41]. For the on-board applications, there should be enough energy in the exhaust gases that can be used for the hydrogen release service. Otherwise, a part of hydrogen must be burned to provide the remaining energy requirements which decreases the hydrogen energy density of the hydride [39]. It is important to mention here that Proton Exchange Membrane (PEM) fuel cells may not be able to provide the heat energy at more than 80–100 °C [31,39]. The optimum range where PEM cells operate are 1–10 bar and 0–100 °C, and enthalpy change of 30–48 kJ/mol H₂ [31]. Moreover, on the refueling station, the exothermic heat has to be managed and thus thermal management may be a problem for this type of hydride [42].

Metal hydrides are binary or intermetallic hydrides. Binary light metal hydrides offer high volumetric and gravimetric energy densities [10]. However, the dehydrogenation/hydrogenation conditions (temperatures and/or pressures) are high, e.g., LiH has 7.7 wt% energy, but it requires minimum of 900 °C [33] for the dehydrogenation. In other cases these hydrides do not undergo reversible reaction under low to moderate operating conditions. Among the metal hydrides, MgH₂ is an interesting material as it contains 7.6 wt% hydrogen content equivalent to 9 MJ/kg Mg [43], and the hydrogen release temperature is relatively low, 350–400 °C [44], though still high for PEM fuel cell applications. Intermetallic hydrides are formed by combining two metals with hydrogen. They are formed from heavy transition metals and are reversible at low temperature and pressure conditions [11,45]. It is possible to achieve high volumetric energy densities, however, low gravimetric densities, < 3 wt% hydrogen [27,41,45], are not favorable to use these materials in commercial applications. LaNi₅, FeTi, and Mg₂Ni are examples of intermetallic hydrides and their gravimetric energy density is 1.4 wt%, 1.89 wt% [6], and 3.59 wt%, respectively. LaNi₅ and FeTi are of special interest as they offer low desorption temperature and pressure [1]. A list of selected metal hydrides along with their hydrogen capacities is shown in Table 2.

So far, we have learnt that generally the metal hydrides can have good energy densities, but the kinetics of the hydrogenation and dehydrogenation is slow. Moreover, the hydrogen release temperature is relatively high. The improvement in these properties can possibly be made by decreasing the particle size, reducing the crystal grain size, alloying, adding additives to produce composites, using catalysts,

nanostructuring, and nanoconfinement. For example, it is known that ball milling decreases the particle size and the crystal grain size, decreases the diffusional resistance, and creates defects in crystals [31]. Reducing the particle size increases the surface area of the material and thereby the rate of adsorption is enhanced (as adsorption is a surface phenomenon). Shorter diffusional paths decrease the time for hydrogen to reach at the active sites of the metal or alloy. Crystal defects create more amorphous phase which improves the thermodynamics [2,46]. More elaborated discussion about the above mentioned methods for improving the properties of the metal hydrides can be found in Ren et al. [41], Reardon et al. [47], Wu [48], Pukazhselvan et al. [49], Wang and Wang [50], Zhu et al. [51] and Abe et al. [6].

Among the metal hydrides, MgH₂ has gained much attention in the literature and widely studied by the researchers. It has been found to store a large amount of hydrogen, i.e., it offers high gravimetric energy density and the volumetric energy density of MgH₂ is nearly two times the volumetric energy density of liquid hydrogen [43]. Also, as Mg metal is inexpensive and abundantly available [3,10], MgH₂ can be easily and cheaply produced in bulk quantities. However, magnesium hydride is formed at high temperature and pressure conditions. It is formed at temperature ~300 °C and a pressure of >30 bar [43] where 75 kJ/mol is released during the hydrogenation [44]. Moreover, the kinetics of the MgH₂ formation is quite slow [31,43] and, as discussed above, the hydrogen release temperature is not suitable for PEM cells.

Being promising, much attention is given in improving the properties of MgH₂. This includes decreasing the temperature and enhancing the rates of the hydrogenation/dehydrogenation. Good kinetics of the hydrogenation/dehydrogenation has been obtained at 150 °C by micro- and nano-structuring, or particle size reduction by ball milling [31]. Zaluska et al. [44] found that ball milling effectively reduces the crystal grain size and greatly reduces the time of loading the hydrogen in MgH₂. Ruele et al. [52] reported that ball milling MgH₂ increases the desorption rates and decreases the desorption temperature. They reasoned that the effect increases with an increase in milling time which causes a decrease in the crystal size.

Alloying to form Mg₂NiH₄ has better kinetics and shows lower enthalpy change of hydriding, 65 kJ/mol [43], with temperature of hydriding as 280 °C at 1 bar [31]. Mg₂FeH₆, Mg₁₇La, and Mg₁₇Al₁₂ are the other examples of alloying that have shown fast kinetics. Alloying, however, reduces the gravimetric density, e.g., Mg₂NiH₄ contains 3.6 wt % hydrogen [50] and Mg₂FeH₆ shows 5.5 wt% H₂ [50]. Both these values are less than the parent MgH₂ capacity (7.6 wt%). Sometimes the hydriding energy actually increases as in the case of Mg₂FeH₆ reaction, the enthalpy change is higher and equals to 77.4 kJ/mol [53]. Apart from alloying with a metal, two different hydrides or a hydride and, say, carbon can be mixed to utilize the better part of each component in the final hydride composite [31,50]. Johnson et al. [54] used a mixture of LiBH₄ (complex hydride) and MgH₂ and found improvement in the kinetics. The weight percent H₂ capacity of MgH₂ increased to 11.4 wt% and the corresponding enthalpy change for the reaction lowered to 45 kJ/mol H₂. Li et al. [55] used graphite with MgH₂ and observed that the hydrogen loading temperature decreases to 200 °C. Other examples of hydride composites are MgH₂-NaAlH₄, MgH₂-Mg(AlH₄)₂, and MgH₂-AlH₃. No improvement in the kinetics of desorption is observed when Si is used as additive [52]. A catalyst presence is also observed to enhance the kinetics of the process. Zaluska et al. [44] observed the effect of Pd and Fe catalysts and found that both are very effective. They observed that with Pd catalyst, the hydrogen absorption time was reduced to more than half the value when there was no Pd present. They also employed other catalysts but found less favorable results. Cui et al. [56] employed Ti with MgH₂ and observed that at 250 °C, 5 wt% hydrogen is desorbed in first 15 min. Borkhordarian et al. [57] studied the effect of a series of metal oxides on the kinetics of hydrogen desorption/sorption. Nb₂O₅ was found the best performing catalyst. At temperature of 300 °C and under vacuum conditions, in the presence of 0.5 mol% Nb₂O₅, nearly entire 7 wt% H₂ was desorbed within 90 s

Table 2

Hydrogen storage characteristics of metal hydrides [6, 31, 43, 44, 50, 53, 54, 74, 83, 127–130].

Metal hydride	H ₂ capacity (wt%)	Desorption temperature (°C)	Desorption enthalpy (kJ/mol H ₂)
MgH ₂	7.6	>300	75
Mg ₂ NiH ₄	3.59	>280	65
Mg ₂ FeH ₆	5.5	>300	77.6
FeTiH ₂	1.89	>30	28
LaNi ₅ H ₆	1.4	>100	31
MgH ₂ -LiAlH ₄ (1:1 M)	9.4	>250	45
MgH ₂ -NaAlH ₄ (1:1 M)	7.6	>175	–
MgH ₂ -LiBH ₄	11.4	>350	45

whereas at 300 °C and 8.5 bar, nearly 7 wt% was absorbed within 60 s. A rather detailed review of the catalysts used with MgH_2 is provided by Jain et al. [58].

The MgH_2 metal hydride is successfully used for the stationary hydrogen storage applications [10], however the limitation discussed above restricts its use for the on-board applications. Additional research is demanded to further improve the properties of MgH_2 to be used for the on-vehicle applications.

AlH_3 is also a promising binary metal hydride [2,9,46]. It has high hydrogen content 10.1 wt% [2,46,59] and high volumetric energy density as the density is 1.48 g/mL [2,46]. It dehydrogenates at relatively low temperature of ~ 100 °C [49]. However, AlH_3 is difficult to undergo reversible reaction and needs immensely high hydrogen pressure for the hydrogen charging [59]. The regeneration of hydride cannot be carried out on-board. Additional work is required to modify the hydride properties to follow more practical conditions of hydrogen loading and release.

2.5. Complex metal hydrides

Complex metal hydrides are formed when hydrogen atoms covalently bond to a central atom in a coordination complex such as $[\text{AlH}_6]^{-3}$, $[\text{AlH}_4]^{-1}$, $[\text{BH}_4]^{-1}$, and $[\text{NH}_2]^{-1}$ and a cation (e.g., Li, Mg, and Zn) stabilizes the anion [27,39,60,61]. The hydrides are mostly formed out of lighter elements of Groups I, II, and III of the periodic table [45] and therefore offer higher storage densities. The storage properties of some selected complex metal hydrides are shown in Table 3.

2.5.1. Alanates

Alanates are aluminum containing complex hydrides. They are either octahedrally coordinated or tetrahedrally coordinated by hydrogen atom [10,39]. In the former case they are hexahydroaluminates and in the latter case they are tetrahydroaluminates. Examples of alanates are sodium alanates, lithium alanates, magnesium alanates, potassium alanates, calcium alanates, and mixed metal alanates.

Sodium aluminum hydride (NaAlH_4) is widely studied complex hydride. It contains 7.4 wt% total amount of H_2 [62], however, practically only 5.6 wt% H_2 [1,12] can be released. The hydrogen is released according to the following two-step reaction [62–64]:



In the first step 3.7 wt% H_2 is released, while 1.9 wt% H_2 is released in the second step [38,65]. The average enthalpy change for the two reactions is 41 kJ/mol H_2 [66]. NaH produced in the second reaction requires excessive temperature (425 °C) for the hydrogen release [3], therefore, hydrogen available in NaH is considered irreversible. NaAlH_4 is easy to produce in mass productions [12,38] and it is relatively inexpensive [38,67]. On the other side, it requires high temperatures, 185–260 °C, for H_2 release [62–64] and undergoes low H_2 release kinetics [2,62,68]. It also poses difficulty of reversibility as it requires

Table 3

Hydrogen storage properties of complex metal hydrides [12, 38, 39, 58, 62–64, 66, 77, 79, 83].

Complex metal hydride	H_2 capacity (wt%)	Desorption temperature (°C)	Desorption enthalpy (kJ/mol H_2)
LiAlH_4	10.6/7.9 ^a	>160	5.8
NaAlH_4	7.4/5.6 ^a	>185	41 ^a
LiBH_4	18.5/13.5 ^a	>380	67 ^a
$\text{LiNH}_2\text{--LiH}$	10.4/5.5 ^a	>180	44 ^a
$\text{Mg}(\text{NH}_2)_2\text{--LiH}$	5.6	>150	54

Complex metal hydrides can be classified into the following three major categories: alanates, borohydrides, and amides-imides.

^a Reversibly released.

200–400 °C and high pressure in the range of 10–40 MPa for the rehydrogenation [62]. These drawbacks can be addressed and the improvement in the thermodynamics and kinetics can be achieved by catalysis, ball milling, alloying, and nano-engineering.

Bogdanović and Schwickardi [69] did a breakthrough work when they found that doping NaAlH_4 with Ti-containing species greatly decreases the kinetics and thermodynamics of the dehydrogenation and the rehydrogenation of NaAlH_4 . They observed an 80–85 °C decrease in the desorption temperature of hydrogen [68]. Also, they reasoned that increasing the amount of the dopant increases the kinetics, but decreases the gravimetric energy density of the hydride [62]. Only a small amount of 2–4 mol% is used as the optimum value [62]. Although Bogdanović and Schwickardi [69] used wet chemistry for doping Ti, but in a more preferred way, doping can be carried out by ball milling the catalyst and the hydride, under applicable hydrogen atmosphere. Many catalytic materials have been tried afterward with NaAlH_4 , but Ti halides such as TiCl_3 and TiF_3 have proved their superior catalytic properties when used with NaAlH_4 . Both of them improve the associated thermodynamics and kinetics and accelerate the reversibility. However, TiCl_3 is considered a standard catalyst for NaAlH_4 even though TiF_3 gives similar results and better energy density. This is due to the excessive cost of TiF_3 over TiCl_3 . ScCl_3 and CeCl_3 also show better promise than Ti catalysts, but again the costs are extremely high [62]. Pitt et al. [70] used a series of metal chlorides and concluded that ZrCl_4 is another qualified catalyst for improving the kinetics of the hydrogen sorption. Further detail about the catalytic effects on the properties of the complex hydrides is provided by Liu et al. [68].

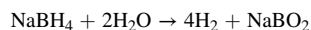
Ismail et al. [71], Ismail et al. [72], Rafi-ud-Din et al. [73], and Bendyna et al. [74] studied the thermodynamic properties and kinetic properties of the composite NaAlH_4 with MgH_2 , i.e., $\text{NaAlH}_4\text{--MgH}_2$ with 7.6 wt% H_2 . The composite showed improved desorption properties compared to the MgH_2 and NaAlH_4 hydrides when used independently.

LiAlH_4 is another high energy density complex hydride that has gravimetric energy density equals to 10.6 wt%. However, the reversible hydrogen contents are only 7.9 wt% due to the formation of aluminum hydride which requires excessively harsh operating conditions for the hydrogen release. Also both the kinetics of hydriding/dehydriding and the reversibility are poor [12]. In fact, it is characterized as irreversible hydride [38,39,62] owing to the extreme rehydrogenation conditions. LiAlH_4 is also not stable [38,62] and decomposed at low temperature [62]. Moreover, it is sensitive to oxygen and moisture [9] and the cost of LiAlH_4 is also higher than NaAlH_4 [62]. It is therefore suggested not suitable, in the form of LiAlH_4 , for the hydrogen storage applications. Catalytic effects and hydride addition as in $\text{LiAlH}_4\text{--MgH}_2$ (9.4 wt%) have shown to improve the properties of LiAlH_4 . KAlH_4 is though reversible, but the hydrogen capacity is lower than NaAlH_4 . The reversible hydrogen capacity is only 3.5 wt% [75].

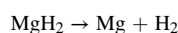
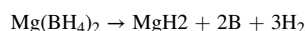
2.5.2. Borohydrides

Borohydrides contain high hydrogen content up to 10 to 18 wt% [58]. Examples of borohydrides are sodium borohydrides, lithium borohydrides, magnesium borohydrides, and calcium borohydrides. The hydrogen is released from a borohydride either by hydrolysis or by the decomposition reaction [3,8,62].

Hydrolysis:



Decomposition:



Intermediate products can also be present in some borohydrides such as in the decomposition of LiBH_4 [58].

Boron hydrides are more stable than alanates [2,18,76,77], but they

also show slow kinetics [77,78]. Alkali borohydrides have very high dehydrogenation enthalpy and high H_2 release temperature [39]. Moreover, toxic boron hydrides are produced as byproducts though in small amounts during the dehydrogenation reaction [76,77]. These byproduct boranes can contaminate the hydrogen supply and can damage the fuel cell system [76] and decrease the storage capacity of the hydrides with time [62,76]. Boranes are hygroscopic and require special needs to handle and store [18,79], however, they do not have explosive reaction with water [77].

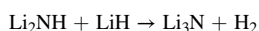
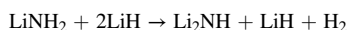
$LiBH_4$ is perhaps the most important complex hydride of this class [80]. It has hydrogen capacity of 18.5 wt% and enthalpy change of hydriding is 67 kJ/mol H_2 [39,77], but it is very hard to decompose [38] to release hydrogen. It releases 13.5 wt% H_2 [38,39] at $>380^\circ C$ [39] and 4.5 wt% hydrogen remained fixed in LiH. The decomposition of LiH requires extremely high temperature as discussed above. Moreover, $LiBH_4$ formation is even more demanding requiring greater than $650^\circ C$ and 150 bar H_2 pressure [38]. Adding SiO_2 to $LiBH_4$ is shown to improve the quantity of H_2 release at lower temperature. Züttel et al. [33] proposed that SiO_2 ensures 13.5 wt% release of H_2 at $200^\circ C$. $TiCl_3$, an extremely good catalyst for alanates, is not found suitable to be used with $LiBH_4$ as it causes the formation of stable and irreversible $Ti(BH_4)_3$ [77,81]. Addition of MgH_2 to $LiBH_4$ (1:2 M ratio) releases the hydrogen at much lower temperature. The rehydrogenation occurs at $230\text{--}250^\circ C$ and 100 bar, thus makes $LiBH_4$ reversible [62]. Total H_2 capacity of $LiBH_4\text{--}MgH_2$ is 11.4 wt%, however, 8 wt% can be released reversibly [62,77].

Another important borohydride is $NaBH_4$. It contains 10.8 wt% of H_2 , but it requires high temperature of $400^\circ C$ for the decomposition to NaH and B [77]. Alkali metal amidoboranes, $LiNH_2BH_3$ and $NaNH_2BH_3$, are also worth mentioning. They offer 10.9 wt% and 7.5 wt% H_2 capacity, respectively, with H_2 release temperature as low as $\sim 90^\circ C$ [82], and they also do not give any harmful products. However, they are not reversible [82]. A borohydride that is liquid at room temperature and pressure conditions is $Al(BH_4)_3$ [45]. It has high hydrogen content of 17 wt% [45], however, it is not widely studied and additional research is needed in this direction.

2.5.3. Amides-imides

Amides and imides are complex hydrides containing nitrogen atom. The general formula for amides and imides can be written, respectively, as $M(NH_2)_x$ and $M(NH)_x$. Examples of amides and imides are lithium, magnesium, and calcium amides and imides. Both amides and imides offer high hydrogen storage content and low hydrogen release temperature [3]. However, they have substantially low rates of hydrogen hydriding/dehydriding and therefore in the absence of a catalyst or additive they are not suitable for the practical purpose. Moreover, ammonia is formed during the dehydrogenation reaction of amides and imides [2,9,38,39]. The produced ammonia can damage the fuel cell assembly and especially the catalyst and the membrane [2]. The ammonia also consumes a bit of H_2 [38,39] and decreases the cycling ability [39] of the hydride due to the loss of nitrogen. Additionally, they are sensitive to the atmospheric exposure and affected by the presence of water [9].

The most common and widely recognized amide is lithium amide, $LiNH_2$. $LiNH_2\text{--}LiH$ contains total of 10.4 wt% H_2 [38]. The hydrogen is released according to the following stoichiometry:



$LiNH_2$ is decomposed to produce lithium imide, Li_2NH , and hydrogen is released. In the second reaction Li_2NH is dehydrogenated and additional hydrogen is evolved. The first reaction is only reversible [18] and 5.5 wt% H_2 is released [64] with 44 kJ/mol H_2 enthalpy change [58]. The desorption commences at $180^\circ C$ [83], but the kinetics of the reaction is unacceptably slow [58]. For total absorbed H_2 to

release, greater than $400^\circ C$ temperature is required [39].

Substituting $Mg(NH_2)_2$ in place of $LiNH_2$ or MgH_2 in place of LiH can improve the original hydride properties. $Mg(NH_2)_2\text{--}LiH$ reversibly releases 5.6 wt% H_2 (enthalpy of reaction equals to 54 kJ/mol H_2) and desorption takes place at $150\text{--}250^\circ C$ [79]. Moreover, the ammonia formed readily reacts with LiH and extinguished [64]. On the other hand, $LiNH_2\text{--}MgH_2$ contains 4.5 wt% H_2 , but the enthalpy of desorption is only 40 kJ/mol [67]. KH and RbH doping effectively catalyzes the kinetics and the reversibility of the $Mg(NH_2)_2\text{--}LiH$. Furthermore, the addition of $LiBH_4$ in $LiNH_2\text{--}MgH_2$ to produce ternary hydride composite, $LiNH_2\text{--}MgH_2\text{--}LiBH_4$, enhances the kinetics and the enthalpy of desorption decreases to 24 kJ/mol.

2.6. Physical adsorption

In the physically adsorbed form hydrogen is adsorbed at the surface of the solids and the adsorption follows van der Waals interactions or dispersive forces. Unlike hydrogen stored in many metal hydrides and complex metal hydrides, the hydrogen is stored reversibly in physically adsorbed form [18,45]. Physically adsorbed hydrogen offers high rates of adsorption (loading) and desorption (unloading) [10,18,82] and the refueling time is not an issue [7]. The enthalpy of adsorption/desorption is only 1–10 kJ/mol [9] and due to these low values involved in the adsorption/desorption of hydrogen, the heat transfer problems are far easier to be managed [13]. Moreover, there are no losses of hydrogen due to byproduct formation [18]. The materials which are candidates for the hydrogen storage by physical adsorption include microporous carbon structures, metal organic frameworks, and zeolites. These adsorbent materials are mostly well developed and have high surface area. As adsorption is a surface phenomenon, high surface area is undoubtedly a requirement.

Carbon based materials can be prepared in a manner that provides high surface area. Zhou et al. [84] determined that activated carbons contain 5 wt% H_2 at 77 K and 30–60 bar. Recently, Zhao et al. [82,85] has reported the hydrogen capacity in single walled carbon nano tubes (SWCNTs) as 1.73 wt% at 77 K and 10 MPa. Liu et al. [86] used various types of CNTs (inclusive SWCNTs and MWCNTs) with and without post modifications and found the H_2 storage capacity at room temperature and 12 MPa is less than 1.7 wt%. Reader is referred to Yürüm et al. [87] for a detailed review of hydrogen uptake on carbonaceous materials.

Zeolites are microporous ordered aluminosilicates with appreciable surface area. CaX zeolite has shown the H_2 capacity of 2.19 wt% at 15 bar and 77 K [88]. Du and Wu [89] have measured hydrogen capacity of 2.55 wt% at 77 K and 40 bar over NaX ($565\text{ m}^2/\text{g}$) and observed that at $20^\circ C$ and 40 MPa the value dropped to 0.4 wt% only. Chung [90] studied various kinds of zeolites for hydrogen storage at $30^\circ C$ and found that USY has shown the maximum hydrogen capacity of 0.4 wt% at a pressure of 50 bar.

Metal organic frameworks are versatile and can be modified in a number of different ways. They offer the highest surface area of all H_2 storage materials, e.g., MOF-210 has shown $6240\text{ m}^2/\text{g}$ surface area [91], the highest experimentally measured surface area. MOF-210 has shown hydrogen capacity of 7.9 wt% at 77 K and 80 bar [92]. Li et al. [93] used MOF-5 and found that MOF-5 has the capacity of 4.5 wt% H_2 storage at 77 K near ambient pressure and only 1.0 wt% at 20 bar and room temperature. Farha et al. [94] reported hydrogen capacities over NU-100 ($6143\text{ m}^2/\text{g}$) as 9.0 wt% at 56 bar and 77 K. Langmi et al. [92] comprehensively reviewed the hydrogen storage capacities of MOFs and concluded that at room temperature hydrogen capacities of MOFs are generally less than 1 wt%. Additionally, MOFs have low thermal conductivity of the order of $0.3\text{ W}/(\text{m}\cdot\text{K})$ [95] which can create thermal management issues [7].

Physical adsorbents of hydrogen show quite low room temperature capacity. It is reasonable only at cryogenic temperatures and/or higher pressures. It is important to mention here that there will be desorption losses similar to the boil-off losses, discussed in the case of liquid

hydrogen storage, if hydrogen will be physically adsorbed at cryogenic temperatures. We limit our discussion about physical adsorbents as the physical adsorbents exhibit no potential to be used for the hydrogen storage applications.

2.7. Liquid organic hydrogen carriers

In a liquid organic hydrogen carrier (LOHC) or liquid organic hydride, hydrogen is stored chemically by reacting with a hydrogen deficient organic molecule. The organic hydride is dehydrogenated in the reactor and the necessary hydrogen is released for the power production either in a stationary power plant or in an on-vehicle application. The dehydrogenated product is removed at the filling station and the organic hydride is recharged. The dehydrogenated organic hydride is transported to an off-site hydrogenation facility and hydrogenated and the organic hydride is finally conveyed to the filling station. During the whole cycle, the carbon atom remains in the cycle and does not leave into the atmosphere. Fig. 2 shows the concept of organic hydride cycle for on-board and stationary applications.

The organic hydrides possess reasonably high reversible hydrogen capacity ranging between 1.7 and 7.3 wt% and are liquids at room temperature. The biggest advantage of using an organic hydride is that the current infrastructure of bulk storage and transportation of gasoline can be effectively utilized [96–98].

In earlier studies only cycloalkanes such as cyclohexane, methylcyclohexane (MCH), and decalin remained the main focus of attention. These cycloalkanes contain 6.2–7.3 wt% [99] reversible hydrogen storage capacity. The dehydrogenation product of cyclohexane is benzene and that of decalin is naphthalene. Benzene is carcinogenic while naphthalene is solid at room temperature. Toluene, the dehydrogenation product of methylcyclohexane dehydrogenation, on the other hand, is non-carcinogenic and liquid at ambient conditions. Moreover, toluene is widely handled at industrial scale. It is easier to start the hydrogen economy based on methylcyclohexane and toluene due to the bulk availability of toluene and that the bulk production of toluene is a well-established technology.

Under typical operating conditions, the equilibrium conversion is the highest for decalin, but the lowest for the cyclohexane [100]. The methyl group in methylcyclohexane renders relatively easy dehydrogenation of methylcyclohexane to toluene than cyclohexane to benzene

[100]. Keeping all this in consideration, methylcyclohexane can be regarded as a better selection than the other two hydrides discussed above. Additionally, methylcyclohexane has density and viscosity close to that of gasoline and has normal boiling point of 100.9 °C in the vicinity of the normal boiling point of water. At 38 °C (100 °F), the vapor pressures of methylcyclohexane and toluene are 11.2 kPa and 7.2 kPa, respectively (the vapor pressure of water at this temperature is 6.6 kPa). Table 4 shows the comparison among the three hydrides mentioned above.

Methylcyclohexane/toluene system, the so called MTH (Methylcyclohexane-Toluene-Hydrogen) system is a widely studied hydrogen storage system. The hydrogen capacity is 6.2 wt% corresponding to 5.5 MJ/L hydrogen [99]. The catalyst, Pt/Al₂O₃, is well developed reforming catalyst and the kinetics of the dehydrogenation required for the design of the dehydrogenation reactor is also available [101]. Moreover, the heat transfer problems associated with high endothermicity and diffusion in the catalyst bed are also addressed [102,103]. Usman and Cresswell [103] inspired by the Hrein Energy's [104] hybrid methylcyclohexane-gasoline concept has simulated a prototype MTH-gasoline system and found encouraging results applicable in the future on-vehicle applications. In a later study, Usman and Cresswell [99] proposed a storage tank design that can accommodate the liquid hydride and its product of dehydrogenation in a minimum volume.

The problem with cycloalkanes is that their dehydrogenation temperatures and the enthalpy of reaction (dehydrogenation/hydrogenation) are quite high. As an example, methylcyclohexane dehydrogenation is associated with 205 kJ/mol MCH or 68.3 kJ/mol H₂ [99] and the equilibrium conversion of ~100% is achieved at 325 °C and 1 bar. These problems to some extent can be addressed by introducing a heteroatom in the cycloalkane ring [105–107]. Pez et al. [105] proposed that if a nitrogen atom or to a lesser extent oxygen is introduced within the cycloalkane ring, the dehydrogenation enthalpy can be substantially reduced. Clot et al. [106] computationally developed additional nitrogen containing organic hydrides and proposed that the use of N atom substantially decreases the dehydrogenation temperature. They observed that for the five-membered cycloalkanes the effect is stronger than six-membered ring for reducing the enthalpy of reaction and the hydrogen release temperature. Moreover, they found that the position of N in the ring also affects the thermodynamic and kinetic properties. Experimentally Cui et al. [107] and He et al. [108] have confirmed the

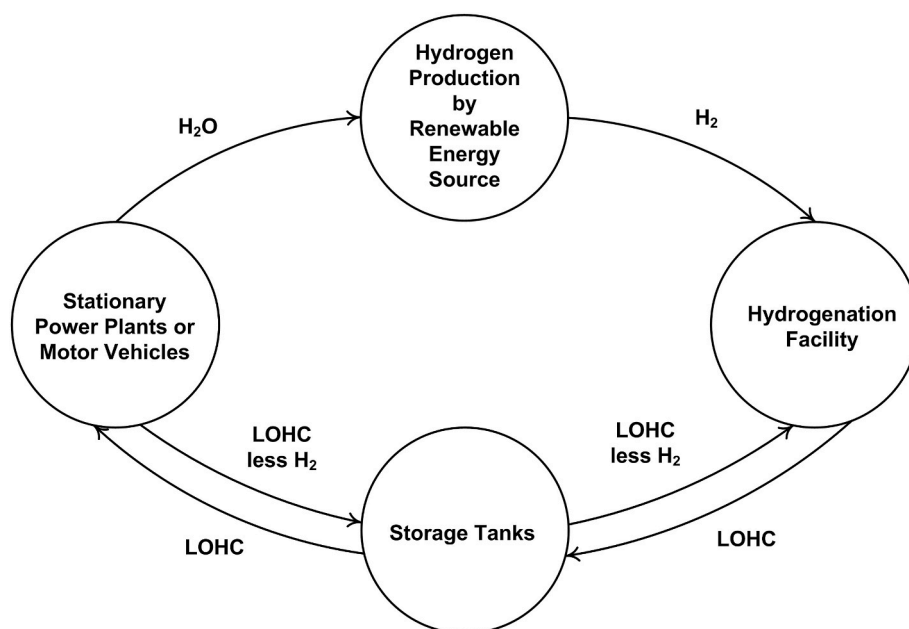


Fig. 2. Concept of an LOHC cycle.

Table 4

Hydrogen storage properties of liquid organic hydrogen carriers (LOHCs) [1, 97–99, 115, 116, 131].

Organic Hydride	Dehydrogenated product	H ₂ capacity (wt %)	Energy (MJ/L Hydride)	Dehydrogenation temperature (°C)	Dehydrogenation enthalpy (kJ/mol H ₂)
Cyclohexane	Benzene	7.2	6.67	325	68.8
Methylcyclohexane	Toluene	6.2	5.68	325	68.4
Decalin	Naphthalene ^a	7.3	7.57	325	66.5
Dodecahydrocarbazole	Carbazole ^a	6.7	10.4	170	51.1
Dodecahydro-N-ethylcarbazole	N-ethylcarbazole ^a	5.8	6.48	170	50.6
perhydro-benzyltoluene	Benzyltoluene	6.2	6.72	>270	71
perhydro-dibenzyltoluene	Dibenzyltoluene	6.2	6.96	>270	71
Indoline	Indole	1.7	2.17	110	51.9
1,2-BN-cyclohexane ^a	–	4.7	5.76	150	38.9
3-methyl-1,2-BN-cyclopentane	–	4.7	5.04	<80	–

^a Solid at room temperature.

above mentioned improvement in thermodynamics and kinetics of this type of hydride. However, it is found that N-based heterocyclic compounds are liable to decomposition and result in unwanted degradation products [109,110].

Recently, Verevkin [111] by both experimentally and computationally identified that oxygen containing cycloalkanes (diphenyl ether derivatives), due to their low vapor pressure and high hydrogen storage capacity, can also be considered as favorable candidates for the hydrogen storage applications.

Dodecahydro-N-ethylcarbazole is widely discussed liquid organic hydride [112]. The gravimetric hydrogen capacity is 5.8 wt% [110], somewhat lower than cyclohexanes, but it involves lower enthalpy of dehydrogenation equals to 51 kJ/mol [98] and decreased dehydrogenation temperature (170 °C) [113,114]. Moreover, as an ethyl group is attached to the N atom, the system is inherently less liable to catalyst deactivation [98] than the dodecahydrocarbazole/carbazole system shown in Table 2. However, although dodecahydro-N-ethylcarbazole is liquid, but its product of dehydrogenation N-ethylcarbazole, is solid at room temperature (68 °C melting point). Handling of solids especially for on-board systems is highly inconvenient. However, by restricting the conversion to a lower value (~20%) [115] or by using a solvent suitable for this purpose, this issue can be resolved though yielding lower energy densities. Moreover, the dehydrogenation temperature is not in the range of PEM cells exhaust temperature and that hydride has the tendency to deethylation above 270 °C [116]. Based on N-ethylcarbazole, it is difficult to start hydrogen economy as it is not abundantly available [116] and the associated cost is therefore high.

Commercially available heat transfer oils such as benzyltoluene and dibenzyltoluene can be hydrogenated to store hydrogen [116–118]. Both ethylbenzene and diethylbenzene being commercially used are well studied chemicals and their properties and safety data are well documented. They are liquid at room temperature, thermally stable to a much higher temperature, and have low vapor pressure. The hydrogenated product of benzyltoluene is perhydro-benzyltoluene and that of dibenzyltoluene is perhydro-dibenzyltoluene, each of them is also a liquid at room temperature. Both of these hydrides contain 6.2 wt% H₂ [116], somewhat higher than dodecahydro-N-ethylcarbazole. Comparing the two, diethylbenzene is cheaper [118] and has lower vapor pressure due to which its liquid phase dehydrogenation is possible [119]. However, much higher viscosities of diethylbenzene and its hydrogenated product pose transportation problems and slow rates in the dehydrogenation and hydrogenation reactions [118]. A better solution is proposed by some researchers [115,118,120] while mixing the two hydrides to reduce the viscosity and to increase the reaction rates. The concept of reactive distillation introduced by Geißelbrecht et al. [121] can open the door for lower vapor pressure hydride systems, so the perhydro-benzyltoluene/benzyltoluene could become more important in the future. High enthalpy of the dehydrogenation reaction (71 kJ/mol H₂) of these hydrides close to methylcyclohexane and high

dehydrogenation temperatures not less than 270 °C [116] perhaps not suitable for their use for the on-board applications. Moreover, cyclic ability is reduced above 330 °C where byproducts formation is crucial [1]. The high viscosity of these hydrides is also needed to be analyzed when considering these heating oils for the practical hydrogen storage applications.

Other liquid organic hydrogen carriers of interest are indoline and BN (boron and nitrogen) based cycloalkanes. Indoline has low dehydrogenation enthalpy as well as low dehydrogenation temperature, 110 °C [122], but the gravimetric hydrogen capacity is only 1.7 wt% [98]. Introducing BN in a cycloalkane is a newer way of producing hydrogen storage material. 1,2-BN cyclohexane [123] and methyl BN cyclopentane [123] are the examples. These BN containing organic hydrides have reasonably high gravimetric densities and show fast kinetics [124]. For example, 1,2-BN cyclohexane has 4.7 wt% hydrogen capacity and dehydrogenates at 80 °C. However, the problems with regeneration of the BN based hydrides and the high costs [97] are the key issues for the practical applications [99]. Their low temperature dehydrogenation within the range of PEM cells operating conditions demands further research for improving the hydrogenation properties.

3. Conclusion and recommendations

Various hydrogen storage options are reviewed and their distinguishing characteristics are discussed. It is revealed that both liquefied hydrogen and cryocompressed hydrogen may not be able to find their way in the future hydrogen economy due to the extremely low temperature requirements for the liquefaction of hydrogen. Owing to the low room temperature hydrogen capacities, physical adsorbents are not practically suitable materials for hydrogen storage. Compressed hydrogen in cylinders is a well-established technology and it is the most practical storage method for the stationary purposes such as in hydrogen based power plants. With the development of sophisticated gas cylinders, compressed hydrogen in cylinders has also shown promise for the on-board hydrogen storage. A hybrid compressed hydrogen system is expected to find its clear role in the future hydrogen economy. Metal hydride such as MgH₂ and complex metal hydride such as LiBH₄ have shown the potential and additional research for improving their thermodynamics and kinetics is required. Among the liquid organic hydride carriers (LOHCs), during the interim period, owing to the gasoline like properties of methylcyclohexane and toluene where the current infrastructure of gasoline transportation, with the necessary modifications, can be used, the well-studied methylcyclohexane/toluene system (MTH system) is recommended for the on-board applications. Along with, a mixed hydride system of perhydro-benzyltoluene and perhydro-dibenzyltoluene is suggested suitable to the stationary applications. Some recently proposed LOHCs that have shown potential need further research before being considered for the practical applications.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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