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Large-scale storage of hydrogen

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ABSTRACT

The large-scale storage of hydrogen plays a fundamental role in a potential future hydrogen economy. Although the storage of gaseous hydrogen in salt caverns already is used on a full industrial scale, the approach is not applicable in all regions due to varying geological conditions. Therefore, other storage methods are necessary. In this article, options for the large-scale storage of hydrogen are reviewed and compared based on fundamental thermodynamic and engineering aspects. The application of certain storage technologies, such as liquid hydrogen, methanol, ammonia, and dibenzyltoluene, is found to be advantageous in terms of storage density, cost of storage, and safety. The variable costs for these high-density storage technologies are largely associated with a high electricity demand for the storage process or with a high heat demand for the hydrogen release process. If hydrogen is produced via electrolysis and stored during times of low electricity prices in an industrial setting, these variable costs may be tolerable.

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Introduction

With a continuing transition to renewable, intermittent energy sources, such as solar and wind power, it is becoming increasingly clear that new methods to store electrical energy to balance the supply and demand are needed [1]. In addition, several major industries are currently looking to reduce their dependence on fossil fuels [2–4]. In the pursuit to find solutions in both these cases, hydrogen – and as part of that, the storage of hydrogen – may play a crucial role. Indeed, the storage of hydrogen is already receiving attention in the ongoing development of hydrogen as a transportation fuel. In the case of vehicular applications, it is necessary to store hydrogen in several links of the chain from production to use: in the vehicles themselves, in hydrogen fueling stations, and in connection to centralized locations for hydrogen production and distribution.

The storage of hydrogen is challenging. Being the lightest molecule, hydrogen gas has a very low density: 1 kg of hydrogen gas occupies over 11 m³ at room temperature and atmospheric pressure [5]. Thus, for the storage of hydrogen to be economically viable, its storage density must be increased. Several methods to store hydrogen at increased density exist. However, all these methods require some input of energy in the form of work, heat, or, in some cases, hydrogen-binding materials.

The goal of the stationary storage of hydrogen is generally either to minimize the cost of delivered hydrogen through the balancing of supply and demand or to use it for backup purposes. The demands of a particular application may have a substantial influence on the capital and operating costs of the storage [6,7]. For instance, some applications might have high demands on the response time of hydrogen release, while some hydrogen storages may only be emptied or filled up a couple of times per year at controlled rates. In some applications the purity of delivered hydrogen is of outmost importance, for instance when the hydrogen is to be delivered to a proton-exchange membrane (PEM) fuel cell; in other applications it is less critical, for instance if the hydrogen is to be combusted with air. Due to the different constraints, there is room for more than one technological option for large-scale hydrogen storage [8].

The lion's share of research related to the storage of hydrogen in recent years has focused on the storage of

hydrogen onboard fuel cell vehicles (FCVs). This research has been reviewed extensively [9–12]. The primary challenge of vehicular applications is to identify a storage method with sufficient hydrogen storage density that can release hydrogen under onboard conditions, most notably within the appropriate temperature interval to facilitate heat integration with the onboard PEM fuel cell. Such strict demands on the hydrogen storage density and hydrogen release temperature do not exist for most larger stationary applications of hydrogen storage.

Previous work related to the storage of hydrogen on a large scale (here meaning storage of tens to thousands of tonnes of hydrogen) is relatively scarce and is, with a few exceptions [13–15], mainly focused on the storage of hydrogen underground [16–18]. Therefore, a broader discussion of the available large-scale hydrogen storage options is due. This paper aims to review and compare the available options for large-scale hydrogen storage qualitatively and, to the extent currently possible, also quantitatively. The goal is to provide a wide overview of all the available options and the advantages and disadvantages of these with regard to different applications. However, a comprehensive listing and discussion of all hydrogen storage materials is not attempted here. Rather than aiming at comprehensiveness, the focus of this paper is to highlight and assess the most developed hydrogen storage technologies within the various categories, in particular with regard to their technical maturity and feasibility on large scales. Therefore, most novel or experimental materials have been excluded, not necessarily due to a lack of potential, but due to a lack of thorough characterization and investigation of their hydrogen storage properties. Review articles focusing on fundamental research on more cutting-edge hydrogen storage technologies can be found elsewhere [10,19–21].

Technologies for the storage of hydrogen

Due to the vast multitude of possible hydrogen storage options, it makes sense to organize these into categories. However, finding an optimal categorization system is not trivial, and most authors appear to use slightly different systems [22]. The categorization that will be applied here is based on the nature of the interaction between the stored hydrogen and the storage vessel or material and is graphically represented in

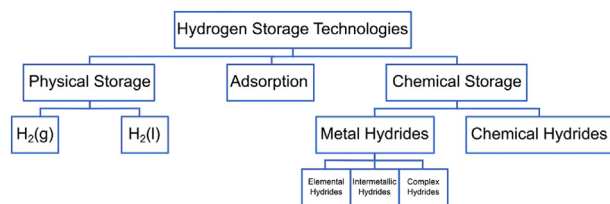


Fig. 1 – The applied categorization of hydrogen storage technologies.

Fig. 1 below. This divides hydrogen storage technologies into three main categories: (1) hydrogen may be stored as gas or a liquid in pure, molecular form without any significant physical or chemical bonding to other materials; (2) molecular hydrogen may be adsorbed onto or into a material, held by relatively weak physical van der Waals bonds; (3) atomic hydrogen may be chemically bonded (absorbed). Further, it is useful to divide the storage technologies based on chemical bonding into two subcategories: the metal hydrides and the chemical hydrides. This division makes sense due to the fundamentally different hydrogen storage properties of these materials. As implied by their designation, metal hydrides contain metal atoms. Hydrogen may either be directly bonded to the metal atom (elemental metal hydrides and intermetallic hydrides) or be part of some complex ion that is bonded to a metal atom (complex metal hydrides). In contrast, the chemical hydrides only consist of non-metallic elements, generally some combination of carbon, nitrogen, boron, oxygen, and hydrogen.

Storage of pure hydrogen

The storage of hydrogen in pure, molecular form can be achieved in the gas or liquid phase. These are the only types of hydrogen storage that are currently employed on any significant scale [23,24]. The storage of liquid hydrogen in the space industry and the large salt cavity storages in Texas, USA, and Teeside, UK, are notable examples [18,23].

Storage of compressed hydrogen gas

A compressed hydrogen gas storage system has two main components: the storage compartment(s) and the compressors needed to achieve the storage pressure. A detailed review of hydrogen compressors is considered to be beyond the scope of this article.

Due to reasons of material properties and operating costs, large amounts of gaseous hydrogen are usually not stored at pressures exceeding 100 bar in aboveground vessels and 200 bar in underground storages [17]. As the storage pressures are limited, so are the achievable hydrogen storage densities: at 100 bar and 20 °C, the density of hydrogen gas is approximately 7.8 kg/m³. The low hydrogen density leads to large storage specific volumes, and, thus, high investment costs. However, a lower storage pressure demands less compression work and, thus, operating costs [25,26]. The first FCVs to be made commercially available have utilized an onboard storage pressure of 700 bar, but storage tanks capable of storing hydrogen at such pressures are expensive

due to the need for advanced vessel materials, e.g., carbon fiber [27]. Therefore, such tanks are not considered viable for large stationary applications.

The storage of compressed hydrogen can be situated either above or below ground level. Investment costs are significantly higher for aboveground options on larger scales, as is generally the case for the storage of gases, and is, therefore, usually not preferred [28]. Large amounts of hydrogen are already stored underground: the already mentioned salt cavity storages in Teeside, UK, and Texas, USA, have proven the applicability of the approach [17]. While other types of underground storages of hydrogen have been suggested, salt cavities are the most suitable for a number of reasons, including low construction costs, low leakage rates, fast withdrawal and injection rates, relatively low cushion gas requirements, and minimal risks of hydrogen contamination [16]. However, not all regions have the proper geological prerequisites for salt cavity storage, or even less preferred underground storage options, such as depleted oil or gas fields, and aquifers [16]. Naturally, alternative solutions for the large-scale storage of hydrogen, underground or aboveground, have to be sought in such regions.

One such alternative solution is to contain the stored gas in a metal container. While a metal container increases investment costs, it ensures the stability of the storage, the purity of stored hydrogen, and it can be applied independently of location. If the vessel material and construction determine the structural integrity and the maximum allowable storage pressure, there is little advantage in burying the vessels more than a couple of meters below the surface level, but placement of larger vessels underground may still be advantageous for several reasons: it saves space, it protects against physical impact and weather, and it has an insulating effect. On the other hand, inspection of the storage system becomes much more cumbersome when it is underground, and special care must be taken to protect against corrosion, for example via the use of external coatings [16]. While there is little experience with the large-scale storage of hydrogen in metallic vessels, it is relatively common practice for natural gas, and the same types of vessels could be applied for the storage of hydrogen [28]. Three main types of metallic vessels are currently used for the storage of larger amounts of natural gas [23]:

- Gas holders, with storage pressures slightly above atmospheric pressure.
- Spherical pressure vessels, with maximum storage pressures up to approximately 20 bar.
- Pipe storages, with maximum storage pressures of approximately 100 bar.

Due to the higher storage pressure and, thus, compactness, the most promising option among these for the large-scale storage of hydrogen is pipe storage. Pipe storages have been applied for the storage of natural gas since the 1980s, mainly to manage peaks in demand for storage facilities with limited access to a natural gas grid [16]. The construction of a pipe storage is relatively simple: a series of relatively short pipelines are laid down with sealed ends and diameters ranging up to around 1.4 m. The total length of pipeline may be several

kilometers, usually positioned a couple of meters below the surface level [23]. Using the pressures and pipe diameter of existing pipe storages of natural gas, approximately 12 t of hydrogen could be stored per km of pipeline [16]. It appears that there are few technical obstacles to the construction of hydrogen pipe storages as the construction of hydrogen pipelines is well-established [29,30]. However, the construction of hydrogen pipelines is more expensive than that of those for natural gas, mainly due to the phenomenon known as hydrogen embrittlement negatively affecting the mechanical properties of steel materials over time, necessitating increased safety margins [31].

In addition to the three options of storage vessels listed above, there also exists one large underground natural gas storage vessel in the form of a lined rock cavern located in Skallen, Sweden. The lining is a steel cylinder, 35 m in diameter and 51 m in height, allowing for a maximum storage pressure of 200 bar [32]. This means that approximately 740 t of hydrogen could be stored under similar conditions. In this case, it is the surrounding rock formation which carries the main structural load, while the steel lining merely acts as a permeability barrier; the space between the inner steel lining and surrounding rock is filled with concrete [32]. It is thought that this type of storage facility may also be applicable for the storage of hydrogen, although further research is needed [18,32].

Liquid hydrogen

In addition to compression, the density of pure hydrogen may also be increased via its liquefaction (condensation). Liquefaction has the advantage that very high hydrogen storage densities can be attained already at atmospheric pressure: the density of saturated liquid hydrogen at 1 bar is 70 kg/m³ [33]. Liquid hydrogen has mainly been evaluated as a hydrogen distribution medium, where its high density is a substantial advantage [34].

The primary concern for the storage of liquid hydrogen is the energy-intensive liquefaction process. There are two main fundamental reasons as to why the liquefaction of hydrogen requires a substantial input of energy: the extremely low boiling point of hydrogen (−253 °C at 1 bar) and the fact that hydrogen gas does not cool down during throttling processes (adiabatic, isenthalpic expansion) for temperatures above around −73 °C. The latter problem necessitates precooling in the liquefaction process, most often by the evaporation of liquid nitrogen [35].

Nevertheless, hydrogen liquefaction is reasonably well-established: the global installed hydrogen liquefaction capacity is around 355 tonnes per day (tpd); the largest plant currently in operation has a capacity of 34 tpd [36]. The all-time largest hydrogen liquefaction plants were constructed for NASA during the 1950s–1970s; most more recently constructed plants are small in comparison (1–10 tpd) [36]. The most modern hydrogen liquefaction plants have a specific energy demand of approximately 10 kWh_{el}/kg, but it is thought that values approaching, or possibly even below, 6 kWh_{el}/kg can be achieved in larger plants with various process improvements (minimum theoretical work for 25 bar feed is 2.7 kWh/kg) [34,37,38]. Nonetheless, even if the specific energy demand of liquefaction can be significantly lowered, the

capital costs of a liquefaction plant are still a significant part of the overall costs of liquefaction, even for larger plants [34]. For instance, it has been estimated that the capital investment constitutes around 40–50% of the specific liquefaction costs for a new 100 tpd liquefaction plant [39].

After the hydrogen has been liquefied, it is essential that it can be stored so that evaporation is minimized. The evaporation of liquid hydrogen constitutes not only a loss of the energy spent liquefying the hydrogen but also, eventually, a loss of hydrogen as the evaporated gas must be vented due to the pressure build-up inside the storage vessel. This loss of stored hydrogen over time is known as boil-off and is often presented as the percentage of stored hydrogen lost per day: the boil-off rate. The heat transfer from the environment to the stored liquid hydrogen and, thus, the boil-off rate is reduced via minimizing the surface-to-volume ratio of tanks by making them spherical and via advanced insulation to minimize heat transfer through the tank walls.

Liquid hydrogen storage vessels are most commonly double-walled with a high vacuum applied between the walls. The vacuum minimizes heat transfer via conduction and convection [40]. The space between the vessel walls also contains additional materials such as alumina-coated polyester sheets; alternating layers of aluminum foil and glass fiber; or aluminum, silica, or perlite particles. The purpose of these materials is to shield against heat transfer via radiation [23,28,33,41]. As a result of the high degree of insulation and the low surface-to-volume ratio, boil-off rates are very low for larger spherical tanks, commonly below 0.1% per day [42]. NASA operates the largest current storage vessels for liquid hydrogen at Cape Canaveral, USA; the amount of hydrogen stored in these vessels is 230–270 t [23]. Construction of even larger spherical liquid hydrogen storage vessels should be possible with available technology, perhaps reaching storage capacities above 900 t [42]. Despite the relative complexity of their construction, there are indications that liquid hydrogen storage tanks are less costly per weight of hydrogen stored than vessels for pressurized gaseous hydrogen on larger scales [23,28].

It should be noted that boil-off is of less concern in applications where the liquefaction plant and the liquid hydrogen storage are in close proximity. In such cases, cold boil-off gas from the storage vessel(s) may be injected back into a late stage of the liquefaction process using an ejector [43]. As the boil-off gas from the storage is already close to its boiling point, reliquefaction is achieved at low additional cost. Alternatively, if reliquefaction is not a viable option, boil-off gas may be utilized in downstream applications.

Adsorption of hydrogen

The storage of hydrogen via adsorption exploits physical van der Waals bonding between molecular hydrogen and a material with a large specific surface area. Due to the weakness of the van der Waals bonding, low temperatures and elevated pressures must typically be applied to achieve significant hydrogen storage densities using adsorption. The by far most common refrigerant used for hydrogen adsorption is liquid nitrogen (boiling point: −196 °C) [44]. The applied hydrogen pressure is typically 10–100 bar but varies depending on the

adsorbent and the intended application [44]. Using higher pressures is not advantageous beyond a certain threshold as the presence of the adsorbent may then no longer improve the hydrogen storage capacity compared to if pressurized gas was stored in the same vessel, the reason being the space occupied by the adsorbent [45].

Many adsorbents have been suggested for hydrogen storage: porous carbon-based materials [46], metal-organic frameworks (MOFs) [47], porous polymeric materials [48], and zeolites [49], just to name some of the most prominent examples. In contrast to the storage of compressed gaseous or liquid hydrogen, there is relatively little experience with the application of adsorbent-based hydrogen storage; most developed adsorption-based storage vessels have yet only been on the laboratory scale. The most successful adsorbents, certain activated carbons and MOFs, have achieved an excess hydrogen adsorption of 8–10% (wt) hydrogen at $-196\text{ }^{\circ}\text{C}$ [50–52]. However, due to the low density of most applied adsorbents and the need for additives to improve the effective heat conductivity, the volumetric hydrogen storage density tends to suffer and achieving a vessel-level deliverable hydrogen storage capacity of much higher than $40\text{--}50\text{ kg/m}^3$ at $-196\text{ }^{\circ}\text{C}$ is likely challenging using currently available adsorbents [53,54].

Still, one of the most significant challenges of an adsorption-based hydrogen storage system will be heat management. While the interaction between the adsorbent and the adsorbed hydrogen is weak, typically $3\text{--}10\text{ kJ/mol}$ (hydrogen), the adsorption process is still exothermic. This produced heat must be removed efficiently to ensure that an adequate degree of adsorption can be reached. As mentioned earlier, the most commonly suggested refrigerant is liquid nitrogen, which has a heat of evaporation of approximately 0.056 kWh/kg nitrogen. If one considers an adsorbent which has a hydrogen adsorption enthalpy of 4 kJ/mol , or 0.56 kWh/kg , this means that at least 10 kg of liquid nitrogen need to be evaporated to remove the heat of adsorption of 1 kg of hydrogen. Large air separation plants have an energy demand of approximately $0.5\text{ kWh}_{\text{el}}/\text{kg}$ nitrogen [55]. Consequently, to produce the liquid nitrogen necessary to remove just the enthalpy of adsorption would require $5\text{ kWh}_{\text{el}}/\text{kg}$ hydrogen in this case. In addition, one must also consider heat transfer from the environment, even if very well-insulated containers are used. If temperature swing operation of the storage system is also applied, the cooling demands will increase further as the entire storage vessel must be cooled back to the storage temperature after desorption. Therefore, overall hydrogen-to-hydrogen efficiencies much higher than 80% ($<6.7\text{ kWh}_{\text{el}}/\text{kg}$) are not expected even for large adsorption-based storages and short storage times [56].

Metal hydrides

Hydrogen is chemically bonded in the metal hydrides. These bonds are much stronger than the physical bonds involved in the adsorption of hydrogen. Consequently, more energy is needed to release the chemically bonded hydrogen. On the other hand, the stronger bonding allows hydrogen to be stored at high density even at ambient conditions [57].

Hydrogen release from metal hydrides can be achieved in two main ways: via heating (thermolysis) or reaction with

water (hydrolysis). These approaches are radically different: thermolysis is endothermic while hydrolysis is exothermic; thermolysis is reversible in some cases while hydrolysis is irreversible; thermolysis occurs in the solid phase while hydrolysis generally occurs in solution; and thermolysis requires elevated temperatures while hydrolysis may be spontaneous at room temperature [45]. Although a vast array of metal hydrides have been developed and investigated for thermolysis-based storage, relatively few have been applied for hydrolysis with any significant success. The most notable and promising metal hydride for hydrolysis is sodium borohydride (NaBH_4), and this will be the only one covered in this section [58].

Elemental metal hydrides

Most metallic elements can form binary compounds with hydrogen, i.e., elemental hydrides. However, most of these are not suitable for hydrogen storage due to thermodynamics, hydrogen storage capacity, or both [59]. The elemental metal hydrides considered most promising for the large-scale storage of hydrogen are magnesium hydride (MgH_2) and aluminum hydride (AlH_3).

Magnesium hydride. Magnesium hydride (MgH_2) is an attractive hydrogen storage material for two main reasons: it has a high theoretical hydrogen storage capacity of 7.6% (wt), and magnesium metal is widely available at low cost [60,61]. Unfortunately, the bond between magnesium and hydrogen is strong – the enthalpy of dehydrogenation is approximately 75 kJ/mol – and, in addition, the kinetics of both hydrogenation and dehydrogenation reactions are sluggish, primarily due to the slow dissociation of molecular hydrogen on the magnesium surface and the slow diffusion of hydrogen through the hydride phase [61–63]. As a result of these thermodynamic and kinetic restrictions, temperatures of over $300\text{ }^{\circ}\text{C}$ must be applied to dehydrogenate pure MgH_2 at a reasonable rate [64]. A wide range of strategies have been applied aiming to improve the kinetics of the dehydrogenation and hydrogenation reactions [60–62,64–66]. While more sophisticated strategies, such as nanoconfinement [67], have been applied with some success on the laboratory scale, the most promising pilot-scale storage systems have generally been based on particle size reduction via ball milling, alloying, addition of transition metal additives, and compaction with ENG to improve the thermal conductivity of the material [65,68,69]. By using combinations of these strategies, it is possible to produce magnesium-based hydrogen storage materials with excellent long-term stability, rapid kinetics, and adequate heat transfer properties. Still, the temperature needed for dehydrogenation and hydrogenation is typically high; this is the most significant disadvantage of magnesium hydride as a hydrogen storage material. The long-term gravimetric hydrogen storage capacity which appears achievable is around 6% (wt) [65,69]. Compacted MgH_2 pellets can have volumetric hydrogen storage densities of 86 kg/m^3 [70].

Aluminum hydride. The other promising elemental metal hydride, aluminum hydride (AlH_3), has vastly different hydrogen storage properties than MgH_2 : hydrogen is bonded

relatively weakly – the enthalpy of dehydrogenation is just 7 kJ/mol – and release of the theoretical 10.1% (wt) of hydrogen proceeds rapidly already at 100 °C. However, this reaction is practically irreversible in the sense that aluminum hydride cannot be formed by the direct reaction of aluminum metal and gaseous hydrogen at anything but extreme pressures [71]. Thus, the key to the application of aluminum hydride as a hydrogen storage material is to identify a reasonable route to regenerate it from aluminum [72].

While electrochemical regeneration routes have demonstrated some promise [72], the most well-investigated aluminum hydride regeneration routes are based on thermochemical processes [26]. Although no version of such a process has yet been applied on a large scale, there are seemingly few technical barriers [73]. The most encouraging of these chemical aluminum hydride regeneration routes are based upon the initial formation of an aluminum hydride-tertiary amine adduct via the hydrogenation of a mixture of aluminum and a tertiary amine in the presence of a titanium catalyst in a solvent, commonly diethylether or THF [71]. The tertiary amine adducts which readily form at mild conditions are, however, too stable to be thermally decomposed without also dehydrogenating the formed aluminum hydride at the same time. The solution to this problem is to substitute the initially formed stable amine adduct for a less stable amine adduct (via so-called transamination), which can be achieved at relatively mild conditions (50–75 °C). The formed less stable amine adduct can then be decomposed under low pressures (around 0.2 bar) to yield aluminum hydride. Typical choices of the amines forming stable amine aluminum hydride adducts are trimethylamine (TMA) and dimethylethylamine (DMEA), while the product of the transamination of these adducts is usually a trimethylamine (TEA) adduct. While the temperatures applied in the various steps of these processes are relatively moderate, the need for low pressures during the final adduct decomposition step still means that the overall energy demand is relatively high. A recent study estimated the energy demand of the process to be 13.32 kWh_{el}/kg and 48.5 kWh_{heat}/kg when based on TMA, and 10.03 kWh_{el}/kg and 53.8 kWh_{heat}/kg when based on DMEA. The most significant share of the electricity demand (>60%) is for the operation of the vacuum pumps necessary for the decomposition of the TEA adduct in both cases [26].

Intermetallic hydrides

As mentioned, relatively few elemental metal hydrides have properties suitable for the storage of hydrogen. The idea of using intermetallic hydrides is that an alloy A_xB_yH_z consisting of one element A, which binds hydrogen strongly, and one element B, which binds hydrogen weakly, will have hydrogen storage properties intermediate to those of its constituent elements [59]. As might be expected, since both the choice of elements A and B as well as their ratio in the alloy (x/y) can vary, many different intermetallic hydrides are possible. In practice, variants of a relatively limited number of intermetallic metal hydride structures are utilized in hydrogen storage applications, namely those of crystal structures AB₅, AB₂, and AB [74]. While it is seemingly generally agreed upon that the intermetallic hydrides store too little hydrogen gravimetrically – often less than 2% (wt) – to be considered viable for

FCV applications, they might still be applicable in certain stationary applications [9,75]. It should also be noted that while their gravimetric hydrogen storage densities are low, the volumetrically storage capacities of the intermetallic hydrides are not necessarily lower than those of other metal hydrides when factors such as of packing porosity and density are taken into account [57,76]. For instance, compacted AB₂-type intermetallic hydrides can achieve volumetric hydrogen storage densities as high as 65 kg/m³ [77].

A commonly stated problem with the intermetallic hydrides is that they are expensive [78]. For instance, the raw material cost of TiFe, considered to be one of the least costly intermetallic hydrides, can be estimated at around \$6.9/kg [79]. Considering the reversible hydrogen storage capacity of TiFe of approximately 1.9% (wt), the cost of storing hydrogen in TiFe is consequently around \$367/kg just in terms of raw material costs. In practice, there will also be additional costs for melting, annealing, and various other metallurgical processes, which may increase the cost of the material by over 100% [59]. However, the long-term stability and hydrogen capacity retention have proved to be excellent for several intermetallic hydrides (loss of approximately 5% of capacity over 1300 cycles, for instance Ref. [80]), helping the business case somewhat [59].

Despite their high cost, intermetallic hydrides have been successfully applied for hydrogen storage in a number of applications since the 1970s [78,80,81]. The most successful of these applications, such as in forklifts and mining vehicles, have essentially two elements in common: the stored hydrogen is used to power some type of relatively low-temperature fuel cell, and the lightness of the hydrogen storage system is not of utmost importance; it might even be advantageous to increase the weight when used as a counterbalance in forklifts. Indeed, there appears to be few insurmountable technical barriers to the implementation of intermetallic hydrides for the large-scale storage of hydrogen [82].

Complex metal hydrides

In the complex metal hydrides, hydrogen is present as a part of a complex anion that is in turn bonded to a metallic cation. The main groups of complex hydrides considered of interest for hydrogen storage are the alanates (based on the [AlH₄][−] anion), the borohydrides (based on the [BH₄][−] anion), and the amides (based on the [NH₂][−] anion) [83]. In contrast to the intermetallic hydrides, the complex metal hydrides mainly consist of fairly light elements. This enables the complex metal hydrides to have quite high gravimetric hydrogen storage capacities, a fact that has spurred much interest regarding the use of these materials in FCV applications [84]. Unfortunately, most of the complex hydrides require rather high temperatures for their dehydrogenation via thermolysis, and only a handful can be reversibly dehydrogenated, then generally only in the presence of suitable catalysts or additives [85].

Alanates. The first and most thoroughly investigated complex hydride material for the storage of hydrogen is sodium tetrahydridoalanate (NaAlH₄), most often referred to as sodium alanate [9,86]. In the presence of 2–4% (mol) Ti-based catalyst, it is possible to hydrogenate the products of

dehydrogenation – sodium hydride (NaH) and aluminum – at temperatures slightly over 100 °C, but relatively high pressures, typically around 100 bar, are needed to achieve suitable kinetics [87]. While Ti-based catalysts, such as TiCl_3 , are the most common choice in the literature, use of Sc- or Ce-based catalysts has been found to be advantageous, especially at lower hydrogenation pressures [88]. In practice, the achievable, long-term, reversible hydrogen storage capacity of Ti-doped NaAlH_4 is 3.5–4% (wt), markedly higher than for the intermetallic hydrides, but lower than what is considered necessary for FCV applications [83,84,89]. The volumetric hydrogen storage density attainable via the compaction of Ti-doped NaAlH_4 is around 54 kg/m³ [90].

Unlike for the previously considered metal hydrides, the dehydrogenation of NaAlH_4 is a discrete multi-step process. First, 3.7% (wt) of hydrogen is released upon the formation of elemental aluminum and sodium aluminum hexahydride (Na_3AlH_6), which in turn is dehydrogenated to NaH and more elemental aluminum, releasing a further 1.8% (wt) hydrogen in the process. The first dehydrogenation reaction has an enthalpy of reaction of 37 kJ/mol, while the corresponding value for the second dehydrogenation reaction is higher at 47 kJ/mol [91]. As these two reactions are separate, and – in the presence of a Ti-catalyst – reversible, it is entirely possible to utilize just one of the reactions to store hydrogen. In this case, it is most sensible to consider the cycling between Na_3AlH_6 and NaH, despite this step having the lower reversible hydrogen storage capacity. The main reason for considering the storage of hydrogen in Na_3AlH_6 is that the hydrogenation pressure can be reduced drastically compared to when using NaAlH_4 . Pressures of around only 25 bar are necessary for the former, four times lower than what is typically needed to yield NaAlH_4 [92]. This lower hydrogenation pressure is advantageous as less expensive tank materials may be used and the costs of compression of hydrogen are reduced. Nevertheless, the hydrogen storage density of a Na_3AlH_6 -based storage system is likely to be very low; compaction of Na_3AlH_6 leads to a volumetric hydrogen storage density of 11.1 kg/m³ on the material level if the theoretical maximum of 1.8% (wt) hydrogen can be stored [93].

Borohydrides. The borohydrides have the highest theoretical gravimetric hydrogen storage capacities of the complex hydrides; up to 18.5% (wt) for lithium borohydride (LiBH_4) [94]. However, there is a predisposition for very stable elemental hydrides (such as LiH) to form upon the dehydrogenation of borohydrides, reducing the useable storage capacity [95]. The borohydrides tend to bind hydrogen stronger than the alanes, an example is LiBH_4 for which the average dehydrogenation enthalpy is approximately 75 kJ/mol; hence, higher temperatures are needed to release hydrogen, generally above 300 °C [95]. As a result, direct application of the borohydrides for hydrogen storage is not viable. Therefore, several strategies aiming to increase the accessibility of the hydrogen in borohydrides have been developed. The two most promising approaches so far are the use of mixtures of borohydrides with other metal hydrides, so-called reactive hydride composites (RHCs), and hydrolysis-based dehydrogenation [58,95,96].

The so far most investigated RHC is the mixture of LiBH_4 with MgH_2 [97,98]. The advantage of mixing these hydrides is that the product of complete dehydrogenation is then not elemental boron, as when pure LiBH_4 is dehydrogenated, but instead magnesium diboride (MgB_2). The formation of MgB_2 from magnesium and boron is exothermic, thus reducing the endothermicity of the overall dehydrogenation process to 46 kJ/mol [99]. MgB_2 and LiH can then be hydrogenated at pressures around 50 bar at 350–400 °C to yield LiBH_4 and MgH_2 [100]. However, the kinetics of hydrogenation and dehydrogenation are very slow for the pure RHC. Therefore, additives with catalytic effect such as Nb_2O_5 , yielding a reversible hydrogen storage capacity of 7.0% (wt), or more costly TiCl_3 , yielding a reversible hydrogen storage capacity of 9.1% (wt), are used [100,101]. Depending on the type and concentration of additives, volumetric hydrogen storage densities of up to 68 kg/m³ have been reported for compacted pellets of the LiBH_4 – MgH_2 RHC [102].

As mentioned in section **Metal hydrides**, the by far most well-investigated metal hydride for the release of hydrogen via hydrolysis is sodium borohydride (NaBH_4) [58]. In hydrolysis, NaBH_4 is typically dissolved in an alkaline solution, often sodium hydroxide (NaOH), which is then sent to a catalytic bed reactor to induce hydrogen release. A typical solution consists of 20% (wt) NaBH_4 , 10% (wt) NaOH, 70% (wt) water, achieving gravimetric and volumetric hydrogen storage capacities of 4.2% (wt) and 42.3 kg/m³, respectively [103]. The concentration of NaBH_4 must be kept relatively low so that the precipitation of the products of hydrolysis, hydrated borates, can be avoided to prevent the poisoning of catalysts via the blocking of active sites [104]. Catalysts for the hydrolysis of NaBH_4 are most commonly based on cobalt (Co), mainly due to their relatively low cost; catalysts based on Ru are generally more active, but also expensive [105].

The advantages of hydrolysis-based dehydrogenation are compelling: fast kinetics at room temperature, high exothermicity (240 kJ/mol), straight-forward control of hydrogen release, and cold start possibilities [103]. Unfortunately, the widespread use of NaBH_4 hydrolysis is being held back by several problems. Most critically, the products of the hydrolysis reaction, hydrated borates, are very stable, rendering regeneration to NaBH_4 challenging [106]. A number of regeneration routes have been suggested, but most are energy intensive [107]. Recently, regeneration routes based upon the direct ball milling of sodium borate hydrates with metallic magnesium or MgH_2 have been investigated, showing promise regarding reducing costs and energy demand of NaBH_4 regeneration, although the economic viability of these routes remains unclear [108].

Amides. Like the RHCs discussed above, the amide-based storage systems also consist of mixtures of two compounds: a metal amide ($[\text{M}][\text{NH}_2]_x$, M usually being Li ($x = 1$), Na ($x = 1$), or Mg ($x = 2$)) and an elemental hydride. The addition of the elemental hydride is crucial as the amide would otherwise release ammonia rather than hydrogen upon its thermolysis [109]. Still, most of the amide-based materials will release trace amounts of ammonia during thermolysis, which reduces reversibility through the loss of active material. The

release of ammonia is also a problem in PEM fuel cell applications, where the ammonia acts as a poison.

While the original amide-based hydrogen storage material consisted of a mixture of lithium amide (LiNH_2) with LiH [110], the so far most promising variant is the mixture of LiNH_2 with MgH_2 . Replacing LiH with MgH_2 reduces the reaction enthalpy of dehydrogenation from 51 kJ/mol to 34 kJ/mol [111]. The dehydrogenation and re-hydrogenation properties of the LiNH_2 – MgH_2 mixture, mainly the high temperature needed for dehydrogenation, may be improved further via incorporation of small amounts of various additives, such as other alkali metal hydrides, alkali metal hydroxides, borohydrides, or lithium halides [112]. A mixture consisting of 2.0 LiNH_2 - 1.1 MgH_2 - 0.1 LiBH_4 together with 3% (wt) ZrCoH_3 can reversibly store 4.5–5.2% (wt) hydrogen, be dehydrogenated at 1 bar and 150 °C, and be hydrogenated at 150 °C and 70 bar [113]. Compaction of 2 LiNH_2 - MgH_2 into pellets can achieve volumetric hydrogen storage densities of 54 kg/m³ [90].

Chemical hydrides

Like the metal hydrides, the chemical hydrides chemically bond hydrogen. However, since the chemical hydrides consist of lighter elements, their properties are radically different from those of the metal hydrides. The most significant difference is, perhaps, that the chemical hydrides are generally liquids at normal conditions, thereby simplifying their transport and storage as well as heat and mass transfer during dehydrogenation and hydrogenation processes.

Several of the chemical hydrides suggested for hydrogen storage, such as methanol, ammonia, and formic acid, are currently bulk chemicals commonly synthesized from natural gas. In other words, the utility of these chemicals goes beyond the storage of hydrogen. The fact that these chemicals are already widely produced is advantageous in the sense that much of the necessary infrastructure required for their production, handling, and transport is already in place. Also, producing these bulk chemicals using hydrogen sourced from the electrolysis of water, rather than from the reforming of natural gas, is therefore not only useful for storing hydrogen but is also a way of reducing fossil fuel use in the production of bulk chemicals. It should also be noted that some of the chemical hydrides have also been suggested as alternatives to hydrogen, rather than as hydrogen storage materials. It is not within the scope of this article to compare such fundamentally different routes.

Methanol

Methanol (CH_3OH) is the simplest alcohol with gravimetric and volumetric hydrogen storage capacities of 12.5% (wt) and 99 kg/m³, respectively. The most discussed route to produce renewable methanol is through the hydrogenation of carbon dioxide (CO_2) [114]. Hydrogen release from methanol can be realized in multiple ways: via the reaction with water in steam reforming, via the reaction with oxygen in partial oxidation, or through methanol thermolysis (decomposition) [115,116]. Steam reforming has the critical advantage of being the only one of these three reactions that causes the release of three, rather than two, moles of hydrogen per mole of methanol [115,117]. This is possible because water provides one mol of hydrogen in

the steam reforming reaction. The steam reforming of methanol requires temperatures around 230–330 °C; as the reaction and evaporation of water and methanol is endothermic (16.3 kJ/mol), external heating must be applied [115]. Typically, a $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ catalyst is used [115,118].

The synthesis of methanol from CO_2 and hydrogen, while far less widespread than the traditional natural gas-based process, is commercialized technology: the world's first plant, the “George Olah Renewable Methanol Plant”, operated by Carbon Recycling International (CRI), was put into operation in 2011 on Iceland and multiple similar plants are planned [114]. Indeed, the CO_2 -based process is not radically different from the process based on natural gas: for instance, the same type of catalyst based on $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ or $\text{Cu}/\text{Zn}/\text{SiO}_2$ can be used in both processes [114,119,120]. Temperatures around 220–280 °C and pressures in the range of 10–80 bar are normal reactor conditions. Note that the CO_2 hydrogenation reaction to form methanol is exothermic: the overall reaction-distillation process to yield high purity methanol (and water) from CO_2 and hydrogen will have a small excess of heat if internal heat exchange is efficiently implemented [121,122]. Even so, if methanol is to be used solely as a hydrogen storage material it is in principle not necessary to go through the energy-intensive separation of produced methanol and water via distillation since the methanol-water mixture may be used to yield hydrogen release via the steam reforming reaction directly [123]. In that case, it is likely that there will be a relatively large excess of heat during methanol synthesis and also that the overall process can be simplified due to the absence of the distillation unit and related equipment [124].

Interestingly, the methanol-water mixture acts as a storage for not only hydrogen but also for CO_2 as the latter is released upon steam reforming. Capturing, storing, and recycling this released CO_2 is likely to be relatively straightforward, compared to e.g., direct air capture (DAC), due to its high concentration in the steam reforming product gas [124,125]. Nevertheless, the separation of released CO_2 and hydrogen will inevitably require a certain input of energy. The most well-established such separation processes are based on the absorption of CO_2 in amine solutions; such processes require an input of up to 1.1 kWh/kg CO_2 (4.0 GJ/t CO_2) of heat for the regeneration of the amine solution [126].

Ammonia

Ammonia (NH_3) is an attractive hydrogen storage medium in several regards: it has a very high hydrogen storage density, 17.7% (wt) gravimetrically and 123 kg/m³ volumetrically for liquid ammonia at 10 bar, and its synthesis, handling, and transportation is very mature [127]. One difference compared to methanol when transferring from natural gas-based ammonia production to one based on the electrolysis of water is that the ammonia synthesis loop can be unchanged as the reactants, nitrogen (N_2) and hydrogen, are unchanged. This means that existing ammonia plants may in principle be retrofitted to utilize hydrogen from electrolysis relatively easily [128]. Moreover, the synthesis of ammonia based on electrolysis is a well-known process: the majority of European fertilizer production was based on the production of ammonia using water electrolysis up until the 60s [129].

The dominating ammonia synthesis route is the Haber-Bosch process [130]. While no heat must be supplied to the reactors during the process due to the exothermicity of the ammonia synthesis reaction (-30.7 kJ/mol), high pressures are necessary to achieve favorable thermodynamics; reaction conditions of 300 – 550 °C and 200 – 350 bar are typical [127]. However, on larger process scales the heat of reaction can be used to generate enough steam to cover the energy needs for compression, enabling a very energy-efficient process despite the high pressure [128,131]. Modern natural gas-based ammonia plants export steam, which is often used in nearby urea production [132].

Given that the ammonia production process remains virtually unchanged, the most challenging technical aspect of applying ammonia as a large-scale hydrogen storage medium is likely to be the dehydrogenation process. The most common way to convert ammonia to hydrogen is its thermolysis, the exact reverse reaction of ammonia synthesis. While ammonia starts to decompose spontaneously at temperatures exceeding 200 °C, heat at high temperatures, typically above 650 °C, must be supplied to achieve complete conversion [133,134]. The most active catalysts for ammonia decomposition are based on ruthenium (Ru) that unfortunately is likely to be too expensive for large-scale use, leading to catalysts based on cobalt, nickel, or iron being explored [134]. As these alternative catalysts are less active, higher reaction temperatures are necessary to reach a complete conversion of ammonia – over 900 °C for the case of nickel [135]. These high temperatures are not only detrimental to operating costs, more expensive reactor materials must be used as well [136]. Recently, new catalysts based on light metal amides or imides have been suggested, which, while less costly than catalysts based on transition metals, still require high temperatures (>500 °C) to reach close to full conversion of ammonia [137]. Although early results using these amide or imide catalysts are encouraging, there are still technical problems to be solved regarding their industrial application [138].

Formic acid

Among the chemical hydrides covered so far, formic acid (HCO_2H) has the lowest hydrogen storage capacity, 4.4% (wt) gravimetrically and 53 kg/m³ volumetrically. The significant advantage of formic acid over ammonia and methanol as a hydrogen storage material is that its dehydrogenation can be performed at very mild conditions, in some cases at room temperature [139].

The currently dominating formic acid production process is based on the hydrolysis of methyl formate, but large amounts of formic acid are also produced as a side product of acetic acid production [140]. Producing formic acid via direct CO_2 hydrogenation, using the products of its dehydrogenation reaction (CO_2 and H_2), appears much more attractive if formic acid is to be used as a hydrogen storage medium. Unfortunately, the direct gas-phase reaction between CO_2 and hydrogen is thermodynamically inhibited. The most common solution to this problem is to perform the reaction in a basic solution. The base, which is generally an amine, reacts with the produced formic acid as it is formed to yield a formate salt, thus driving the equilibrium towards formic acid production.

In terms of catalysts, a wide range of highly active homogeneous catalysts are available for this process, although the most efficient are expensive due to the presence of noble metals [141,142]. While the use of a basic solution is efficient from a reaction standpoint, the subsequent separation is difficult: the isolation of pure formic acid and recycling of catalysts from the attained solution are energy-intensive procedures [142,143]. However, as for methanol, concentrating formic acid might not be necessary for certain hydrogen storage applications as the formic acid-amine adduct or formate salt solutions may be directly applied to release hydrogen. Still, the hydrogen storage density of such solutions is low, and the low concentration also affects the energy efficiency of dehydrogenation negatively due to the heat capacity of the added water [143].

In 2010, BASF patented a formic acid production process based upon the hydrogenation of CO_2 in a basic medium, the layout of which is seen in Fig. 2 below [123,144]. The basic idea of the BASF process is to drive the equilibrium towards formic acid production via the formation of a trihexylamine formic acid salt ($\text{NHEx}_3 \cdot \text{FA}$) which is both easily thermally decomposed and, critically, soluble in diols while the lone amine, NHEx_3 , is not [144]. Using a hydrophobic catalyst, it is then possible to design a two-liquid phase system where one phase contains the free amine and most of the catalyst, while the other phase contains the diol, into which the amine formic acid salt is dissolved as it is formed. The diol phase is then sent to a distillation process, yielding three streams: relatively pure formic acid (high-boiling), diol (low-boiling) for recycling back to the reactor, and the amine (medium-boiling), which is used to extract trace amounts of catalyst from the diol stream entering the distillation process to be recycled to the reactor. The extraction of the catalyst from the diol stream ensures that no catalyst is lost due to thermal decomposition in the distillation process. Subsequent patents by BASF have refined the process slightly: simple alcohols such as methanol or ethanol are used in place of the diol and the phase containing the amine formic acid salt being sent to the distillation column is subjected to a treatment of CO to deactivate any remaining traces of catalyst, preventing any catalysis of the decomposition of formic acid back into CO_2 and hydrogen [123].

As mentioned above, the relatively easy decomposition of formic acid and its derivatives to yield hydrogen and CO_2 is the foremost reason for the interest in its application as a hydrogen storage medium. The primary challenge is not reactivity but rather selectivity: formic acid has a tendency to decompose to CO and water rather than CO_2 and hydrogen upon heating. Selectivity may be improved via catalysis. The use of homogeneous catalysts has been the most successful, for instance in a series of small pilot-scale hydrogen generators [139,145].

Due to the favorable thermodynamics of the formic acid decomposition reaction, high hydrogen pressures are relatively easily attained; pressures as high as 1200 bar with minimal production of CO (<6 ppm) have been reported [146,147]. This ability to release hydrogen at high pressure is unique for formic acid among the chemical hydrides described here. However, high-pressure CO_2 is also formed in such a dehydrogenation process. For the setup to be

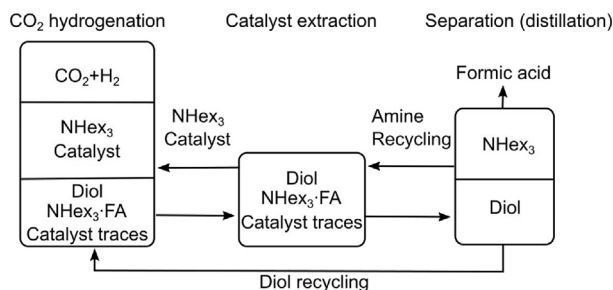


Fig. 2 – Process for formic acid production via the hydrogenation of CO₂ in a basic solution.

sensible, separation of CO₂ and hydrogen should preferably also be performed at high pressure so that the recompression of hydrogen can be avoided. The most attractive separation option appears to be to the condensation of CO₂ as the critical point of CO₂ is 73.8 bar and 31.2 °C, indicating cooling the mixture at high pressure could be a viable separation method [146]. If the problem of high-pressure CO₂ separation can be solved in an economically viable fashion, the possibility of the release of high-pressure hydrogen without the need for mechanical compressors is attractive in several applications, most notably for FCV fueling stations [146,147].

Liquid organic hydrogen carriers

Liquid organic hydrogen carriers (LOHCs) are different materials characterized by their reversible dehydrogenation and hydrogenation and their liquid state in both hydrogenated and dehydrogenated forms. Note that while methanol and formic acid are both organic and liquid, they are not considered LOHCs by this definition as their dehydrogenation results in only gaseous products [148]. The fact that both the hydrogenated and dehydrogenated forms of LOHCs are liquid at ambient conditions is advantageous in several regards. For instance, there is no need to produce, capture, or store CO₂ or N₂, and the hydrogen obtained upon dehydrogenation is relatively pure. Although LOHCs are liquids at ambient conditions, they may still be gaseous at reaction conditions, but separation to yield a pure hydrogen stream is relatively easily achieved via condensation of the LOHC. Nevertheless, if the LOHC must be evaporated the heating demand increases, at least if the heat of condensation cannot be efficiently utilized after the reactor [149].

Most commonly, reversibility is achieved in LOHCs via the saturation and unsaturation of carbon-carbon bonds. The suitability of a LOHC for hydrogen storage then depends on the strength and density of these bonds, the long-term stability of the compounds during repeated hydrogenation and dehydrogenation, and the cost of synthesizing the compounds. In addition, the toxicity should be low, and it is advantageous if both forms of the LOHC have high boiling points and low freezing points: high boiling point for easier separation from produced hydrogen during dehydrogenation and low freezing point to prevent clogging of equipment and to maintain pumpability at low temperatures.

The most well-investigated LOHCs are (hydrogenated and dehydrogenated forms) methylcyclohexane and toluene (MCH-TOL); dibenzyltoluene and perhydro-dibenzyltoluene (DBT-PDBT); and N-ethylcarbazole and dodecahydro-N-ethylcarbazole (NEC-DNEC), although many others have been suggested [150]. All of these compounds are aromatic in their dehydrogenated form; the resulting gravimetric hydrogen storage densities are 6.1% (wt) for MCH-T, 6.2% (wt) for DBT-PDBT, and 5.8% (wt) for NEC-DNEC, while the volumetric hydrogen storage densities are 47 kg/m³ for MCH-TOL, 64 kg/m³ for DBT-PDBT, and 54 kg/m³ for NEC-DNEC. The dehydrogenation of cyclic hydrocarbons to produce unsaturated or aromatic compounds is a relatively well-established procedure, especially in the petroleum industry [151]. Supported noble metal catalysts, most often based on platinum (Pt), but also palladium (Pd), ruthenium (Ru), or rhodium (Rh), can be used for the dehydrogenation of LOHCs [149]. The reaction is endothermic, and high-temperature heat must be provided to the process, the necessary temperature depending on the LOHC. MCH is relatively stable (enthalpy of dehydrogenation: 68 kJ/mol) and requires temperatures as high as 350 °C for its dehydrogenation. The presence of a nitrogen atom in the structure of DNEC has a destabilizing effect that reduces the enthalpy of dehydrogenation to 55 kJ/mol and the dehydrogenation temperature to 200–230 °C [152,153]. The stability of PDT is intermediate to those of MCH and DNEC (65 kJ/mol), and dehydrogenation temperatures are normally 270–290 °C [154]. Due to the high temperatures, coking, dealkylation, and catalyst deactivation must be taken into account, although these effects can be controlled via periodic oxidation using steam or air [155,156].

Like for dehydrogenation, the hydrogenation of LOHCs also generally involves a noble metal catalyst – supported Ru is a common choice for the hydrogenation of TOL, DBT, and NEC. Hydrogen pressures in the range of 10–50 bar and temperatures around 130–200 °C are typically applied [155]. Recently, the use of a single reactor filled with a Pt-based catalyst for both the hydrogenation of DBT and subsequent dehydrogenation of PDBT by merely varying the temperature and pressure has been demonstrated, thus possibly allowing for a more straightforward hydrogen storage facility design and maybe even a prolonged catalyst lifetime due to the periodic variation between reducing and oxidative atmospheres in the reactor [157].

Discussion

As seen in the previous chapter, there currently exists no hydrogen storage technology without shortcomings, i.e., there is presently no “perfect” hydrogen storage technology. There exist relatively few purely technical barriers for several of the considered technologies; nevertheless, the added cost of the storage technologies is a concern. The cost of hydrogen storage is, as mentioned in the introduction chapter, made up of three main parts: the costs of constructing the storage facility, the costs of the utilities needed to operate the facility, and the costs to maintain the facility. Let us first focus on and compare the achievable hydrogen storage densities of the various

storage technologies and how these factors affect the cost of hydrogen storage.

Storage density

While a high hydrogen storage density is essentially always beneficial for the storage of hydrogen, its relative importance compared to other factors varies depending on the hydrogen storage application. The hydrogen storage density mainly affects the investment costs: the volumetric hydrogen storage density determines the size of the storage, and the gravimetric hydrogen storage density determines how much storage material is needed per unit weight of hydrogen stored (for materials-based storages). The volumetric and gravimetric hydrogen storage densities of the considered storage technologies are seen in Fig. 3 below. Note that the values in the figure neither include the weight nor the volume of the storage vessels. In the case of the metal hydrides, the values below are for single pellets; packing these into a column will achieve lower storage densities.

As can be seen, the storage of gaseous hydrogen has the lowest volumetric hydrogen storage density of all considered storage technologies, even for a high storage pressure of 700 bar. The highest storage densities are achieved by methanol and ammonia, which, along with MgH_2 and AlH_3 , have higher volumetric storage densities than liquid hydrogen. Most storage technologies have storage densities intermediate to those of gaseous and liquid hydrogen storage. The general trend is that a higher volumetric storage density is correlated with a higher gravimetric storage density. The notable exception to this rule in Fig. 3 is the AB_2 -type intermetallic hydride, which has a very low gravimetric hydrogen storage density. This means that in order to store the same amount of hydrogen, one needs at

least two to three times the amount (in weight) of this type of intermetallic hydride compared to when utilizing other materials-based storage technologies. Considering the generally high cost of the intermetallic hydrides, the material investment costs of a storage system based on these might very well be a limiting factor for their large-scale use.

Energy demand of storing hydrogen

To begin to estimate the operating costs of a hydrogen storage facility, one must first consider the energy demands of the different processes for storing and releasing hydrogen for the various technologies discussed in the previous chapter. For the first three storage options discussed, storage of compressed gas, liquid hydrogen, and adsorption, it is clear that the main part of the operating costs is related to the mechanical energy needed to fill the storages, while releasing hydrogen from these is relatively straightforward. These technologies will therefore not be analyzed further in this section. In contrast, when hydrogen is chemically bound to the storage material, as in the metal and chemical hydrides, a considerable amount of energy in the form of heat must usually be supplied to release hydrogen. In addition, the released hydrogen must generally be purified if released from a chemical hydride, which generally requires an input of energy.

Metal hydrides

For most of the metal hydrides covered in this article, with the exceptions of AlH_3 and the hydrolysis of NaBH_4 , the processes of storing and releasing hydrogen are relatively simple. During hydrogenation, hydrogen is compressed and undergoes an exothermic reaction to form the metal hydride, while during dehydrogenation, the metal hydride undergoes an

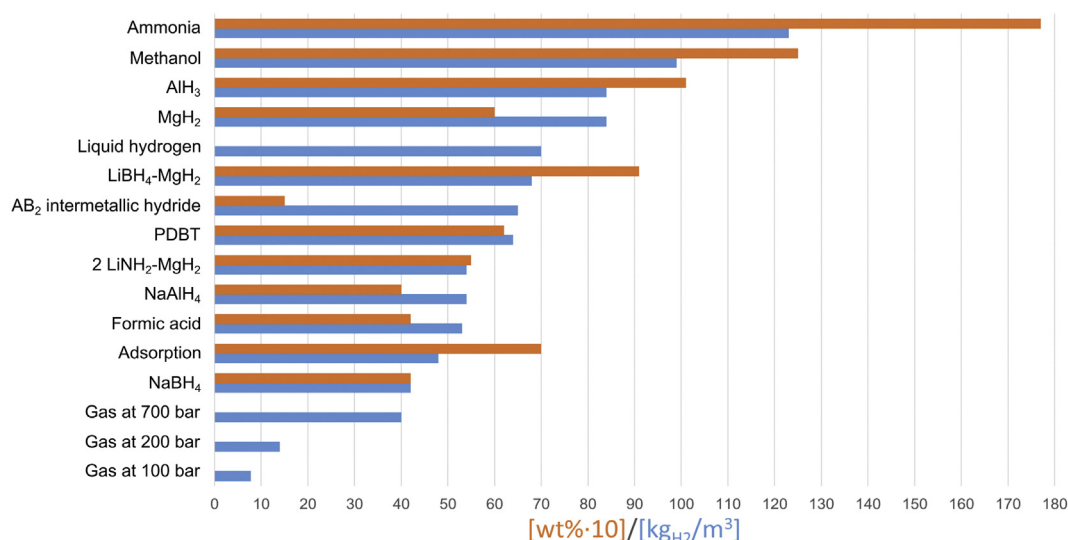


Fig. 3 – Volumetric (kg/m^3 , in blue) and gravimetric ($\text{wt}\% \cdot 10$, in orange) hydrogen storage densities of considered technologies. For the metal hydrides, the values in the graph indicate volumetric and gravimetric hydrogen storage densities that have been achieved in practice. The AB_2 intermetallic hydride is Hydralloy C5_2 compacted with ENG [77]. For NaBH_4 a 20% solution in 10% NaOH is assumed. Adsorption refers to values by Mokaya et al. (2017) for cellulose acetate-derived activated carbons at 30 bar and -196°C [50].

endothermic reaction at an elevated temperature and relatively low pressure to release the hydrogen again. The majority of the energy demand of such thermolysis-based storage is generally the heat that must be provided for the dehydrogenation reaction, and the most critical parameter is, thus, the enthalpy of dehydrogenation [158]. The compression of hydrogen for the hydrogenation reaction also plays a role, but the applied pressures during the hydrogenation of metal hydrides are usually modest (the highest needed pressure is for NaAlH_4 at around 100 bar). As can be seen in Table 1 below, it is clear that the intermetallic hydrides are at an advantage over the complex hydrides and MgH_2 by the measure enthalpy of dehydrogenation.

Beyond determining how much heat that must be supplied for the dehydrogenation process, the enthalpy of dehydrogenation of the metal hydrides also determines the position of the chemical equilibrium between its hydrogenated and dehydrogenated forms. The equilibrium is described by the Van't Hoff equation – a lower enthalpy of dehydrogenation means that lower temperature heat must be supplied to deliver hydrogen of a certain pressure, at least thermodynamically. This effect can be seen in Table 1, although there is also a slightly varying entropic contribution to the position of the equilibrium. In practice, kinetic effects also play a role, particularly for the complex hydrides, leading to temperatures higher than the equilibrium temperature being necessary for reasonable dehydrogenation rates to be attained [160]. From Table 1, it is clear that the intermetallic hydrides not only may be dehydrogenated at low temperatures using waste heat or even heat exchange with the environment in some cases, some intermetallic hydrides may even be used to generate high-pressure hydrogen if slightly elevated temperatures are applied. This is referred to as the thermal compression of hydrogen [161].

So far, only the amount and temperature of the heat that needs to be supplied for the dehydrogenation process has been considered. In practice, it must also be ensured that the supplied heat is efficiently transferred to and throughout the metal hydride material. As the metal hydrides are solids, this is no trivial engineering challenge, especially if large flows of hydrogen are required. As an example, if a hydrogen flow of 10 t/h is demanded from a

MgH_2 dehydrogenation unit, a heat flow of at least around 100 MW at a temperature above 300 °C must be transferred to the solid hydride material. Different methods of supplying such heat will be discussed in section [Generating the heat for dehydrogenation processes](#), but the best way to actually transfer the heat on an industrial scale remains a problem to be solved for the metal hydrides.

For AlH_3 and the hydrolysis of NaBH_4 , the situation is entirely different compared to the other metal hydrides in that their dehydrogenation is not directly reversible. In these cases, one has to estimate the energy demand of the regeneration processes. Detailed techno-economic evaluations of various possible regeneration processes on a large scale are currently not available. However, considering the stability of the byproducts of the hydrolysis of AlH_3 and NaBH_4 , the regeneration processes are inherently energy-intensive, and the discovery of an energy-efficient regeneration process seems unlikely.

Chemical hydrides

Liquefaction of hydrogen is considered to be an energy-intensive process. To put the energy demand of liquefaction into context, it is useful to compare it to the corresponding values for hydrogen storage in other liquid hydrogen carriers, i.e., the chemical hydrides. As mentioned in section [Liquid hydrogen](#), the best currently existing liquefaction plants have specific energy demands of around 10 $\text{kWh}_{\text{el}}/\text{kg}$, and the goal is to lower this to around 6 $\text{kWh}_{\text{el}}/\text{kg}$ in future larger and improved plants [36].

It has been estimated that ammonia can be produced via the electrolysis of water at a total electricity demand of approximately 10–12 $\text{kWh}_{\text{el}}/\text{kg}$ of ammonia [135]. Subtracting the electricity for water electrolysis, the resulting electricity demand of ammonia-based hydrogen storage is approximately 2–4 $\text{kWh}_{\text{el}}/\text{kg}$ [125,128]. The specific electricity demand of the methanol synthesis process based on CO_2 hydrogenation is 1.3–1.8 $\text{kWh}_{\text{el}}/\text{kg}$, according to recent estimates (again, excluding electricity for water electrolysis) [122,162]. Formic acid production based on the previously mentioned BASF process has been estimated to have an electricity demand of approximately 6.7 $\text{kWh}_{\text{el}}/\text{kg}$, in addition to which around 3.7 kg of high-pressure and 2.0 kg of medium-pressure steam is needed per kg of formic acid produced [142]. Despite the exothermic nature of the formic acid synthesis reaction, additional heat must be provided to the process due to the energy-intensive separation process [142]. For the LOHCs, the situation is different compared to the other chemical hydrides, mainly due to the liquid state of the dehydrogenated form. As the dehydrogenated form of the LOHC can be pumped to the hydrogenation reactor pressure, rather than compressed, significant energy savings are possible compared to the other chemical hydrides, the synthesis of which requires the compression of both N_2 or CO_2 and hydrogen. Thus, the LOHCs most likely have the lowest electricity cost of hydrogenation among the chemical hydrides. It can be concluded that all chemical hydrides considered here compare favorably to liquefaction when it comes to the filling of the storage with hydrogen but the energy costs of the dehydrogenation step must also be considered.

Table 1 – Enthalpies of dehydrogenation and equilibrium temperatures for 1.0 bar hydrogen pressure of select metal hydrides.

Metal hydride	Enthalpy of dehydrogenation [$\text{kWh}/\text{kg H}_2$]	Equilibrium temperature for 1 bar H_2 [°C]	Source
MgH_2	10.3	278	[64]
MmNi_5 (AB_5)	2.9	−56	[59]
LaNi_5 (AB_5)	4.3	12	
$\text{TiCr}_{1.8}$ (AB_2)	2.8	−91	
TiFe (AB)	3.9	−8	
$\text{TiFe}_{0.8}\text{Ni}_{0.2}$ (AB)	5.7	73	
$\text{LiBH}_4\text{--MgH}_2$	6.4	169	[97]
2 $\text{Li}(\text{NH}_2)\text{--MgH}_2$	5.6	90	[159]
NaAlH_4	5.1	18	[85]
Na_3AlH_6	6.5	103	

Generally, the necessary amount of heat that must be supplied for the dehydrogenation process at steady state can be approximated with the sum of the enthalpy of dehydrogenation and, if the dehydrogenation process takes place above the boiling point of the chemical hydride, the enthalpy of evaporation. In the case of the steam reforming of methanol, the evaporation of water must also be considered. The enthalpies of dehydrogenation and evaporation of the chemical hydrides, along with typically applied temperatures during dehydrogenation, are summarized in Table 2. For methanol and formic acid, it is assumed that only CO₂ and hydrogen is formed on their dehydrogenation.

As can be seen in Table 2, the LOHCs, especially MCH and PDBT, require more substantial inputs of high-temperature heat to release hydrogen than the other chemical hydrides. Ammonia and formic acid have the lowest values; it should also be noted that the boiling point of ammonia is very low and, thus, its evaporation is realized at a low cost or even negative costs if integrated with processes with a low-temperature cooling need. However, critically, the temperature level of the heat typically needed for formic acid decomposition is much lower than for the other chemical hydrides and this heat could, for instance, be sourced from the waste heat of a PEM fuel cell (80–90 °C) [164]. For methanol, the majority of the heat demand is for the evaporation of methanol and water, and the amount of high-temperature heat which must be added is relatively low. The possible sources of high-temperature heat will be discussed further in section [Generating the heat for dehydrogenation processes](#).

Comparison of energy demands

The energy demand of a hydrogen storage system includes the costs of supplying heat and electricity during both the storage and release of hydrogen. For certain storages, notably those that are “cold” (liquid hydrogen, adsorption), there will also be a cost associated with storage itself, either in the form of operating costs of continuous cooling or via the loss of hydrogen over time (boil-off, desorption). The theoretical energy demands for hydrogen storage using the methods considered here in terms of heat and electricity are summarized in Table 3, which is divided in the processes of filling and emptying the storage. Note that losses of hydrogen and heat during storage, as well as pump work has been neglected. For

the liquefaction of hydrogen, a future projected electricity demand of 6 kWh_{el}/kg has been used.

In conclusion, one can determine that all of the metal and chemical hydrides could potentially store hydrogen at volumetric densities comparable to that of liquid hydrogen and that the total operating costs for most also could be lower, given that the cost of supplied heat is below that of electricity. Liquefaction and adsorption have the by far highest electricity demands out of all technologies but require no high-temperature heat. The intermetallic hydrides are unusual in that they do not require large amounts of high-temperature heat nor electricity; hence, the operating costs of storage systems based on these materials could potentially be low.

It is notable that none of the considered hydrogen storage technologies require a considerable input of electricity for hydrogen to be released. This fact is essential if the intended purpose of the hydrogen storage is to minimize the cost of hydrogen produced via the electrolysis of water based on intermittent renewables. In such an application, hydrogen is generally produced and sent to storage during times of low electricity prices and released from the storage at times of high electricity prices. Thus, the electricity demand of the release process is weighted heavier due to the associated higher electricity price.

Generating the heat for dehydrogenation processes

Some of the metal and chemical hydrides require a substantial addition of high-temperature heat to release hydrogen. If large amounts of hydrogen must be released from the storage in a short time span, this heat must be transferred quickly and efficiently. The required heat flow may well be in the tens to hundreds of MW range in applications requiring large hydrogen flows.

There are several possible sources of high-temperature heat for the hydrogen release process: 1) the combustion of a part of the storage material (only viable for the chemical hydrides); 2) the combustion of a part of the released hydrogen; 3) some heat storage technology utilizing the waste heat from the exothermic storage process or some other source; 4) the combustion of an external fuel; or 5) heat integration with some other heat-generating process. It is not useful to make general statements about the last two options as they are application-dependent, e.g., if a low-cost external

Table 2 – Enthalpies of dehydrogenation and, where relevant, evaporation for the chemical hydrides.

Storage medium	Enthalpy of dehydrogenation [kWh/kg H ₂]	Typical temperatures for hydrogen release [°C]	Boiling point of hydrogenated form [°C]	Enthalpy of evaporation (if gas phase during dehydrogenation) [kWh/kg H ₂]	Total heat which must be provided [kWh/kg H ₂]
Methanol	2.3	250	64.7 (100 for water)	4.4 ^a (1.8 for water)	6.7
Ammonia	4.2	>425	–33.3	2.1	6.3
Formic acid	4.3	<100	100.8	-	4.3
MCH	9.7	350	101	1.5	11.2
DNEC	7.6	220	>220	-	7.6
PDBT	9.0	300	390	-	9.0

^a For steam reforming of methanol, one must evaporate both methanol and water. In a real case, a stoichiometric excess of water of approximately 50% is typically used; this excess ratio is used to generate the value above [163].

Table 3 – Operating costs in terms of heat (amount and temperature) and electricity for considered hydrogen storage technologies. All values can be found in the relevant sections of the present article unless noted. If the process is thermoneutral or exothermal, no value for the required heat is specified in the table.

Storage technology	Storage process			Release process		
	Heat (kWh/kg H ₂)	Temperature (°C)	Pressure (bar)	Electricity (kWh/kg H ₂)	Heat (kWh/kg H ₂)	Temperature (°C)
Gas 100 bar	-	-	100	1 ^a	-	-
Gas 200 bar	-	-	200	1.2 ^a	-	-
Gas 700 bar	-	-	700	1.6 ^a	-	-
Liquid hydrogen	-	-253	-	6	-	-
Adsorption	-	-176	40	6.7	-	-
AlH ₃	54	<70	-	10	1	100
MgH ₂	-	300	30	0.7 ^a	10.3	350
Intermetallic hydride ^d	-	<80	50	0.8 ^a	≈2–6	<80
NaAlH ₄	-	125	100	1 ^a	5.7	160
LiBH ₄ –MgH ₂	-	350	50	0.8 ^a	6.4	350
2 Li(NH ₂)–MgH ₂	-	150	70	0.9 ^a	5.6	150
Methanol	-	250	50	1.3–1.8	6.7	250 ^c
Ammonia	-	400	250	2–4	4.2	>425
Formic Acid	64	100–180	105	6.7	4.3	<100
MCH-TOL	-	150	30	0.7	11.2	350 ^b
DBT-PDBT	-	150	30	0.7	9	300
NEC-DNEC	-	150	30	0.7	7.6	220

^a Estimated as the work of compressing hydrogen to the hydrogenation pressure with an isothermal efficiency of 0.7 [15].

^b Approximately 13% of heat can be supplied at a temperature of around 101 °C, the rest at 350 °C.

^c Approximately 66% of heat can be supplied at a temperature of around 100 °C, the rest at 250 °C.

^d Generic intermetallic hydride (low-temperature heat may be used).

fuel is available, using this is frequently advantageous; otherwise, it is not. Heat integration with another process, while attractive in theory, may be difficult to achieve as the dehydrogenation process will not be continuous and may require high-temperature heat – finding a process with matching heat excess may prove challenging. However, high-temperature excess heat may be provided if the hydrogen is delivered to a solid oxide fuel cell (SOFC) [165–167].

To utilize a heat storage is in principle an attractive solution, e.g., if the heat generated by the exothermic hydrogenation process could be stored and then used to subsequently drive the endothermic dehydrogenation process. However, it is presently unclear whether such a solution is technically feasible on a large scale. Even if the use of phase-change materials (PCMs) has been explored for metal hydride-based storages [168,169], the viability of this approach on larger scales has been questioned considering the massive amount of PCM that is needed and the complexity of the heat transfer system [158]. For the chemical hydrides, one must consider that some of the heat generated during the hydrogenation process may be of immediate use in post-reactor separation processes, such as distillation of water and methanol, and is thus not available for storage. Another option for large-scale storages is, of course, to export steam from the hydrogenation process to some other process or, possibly, to district heating. However, the intermittency of the available heat is a limiting factor in such cases.

The combustion of some of the storage material or released hydrogen is naturally not ideal from the viewpoint of efficiency. More hydrogen must be produced and stored to deliver the same amount of net hydrogen, and this will increase both

operating and investment costs. Combustion of part of the released hydrogen or the chemical hydride may, however, be the most practical and generally applicable options to provide high-temperature heat for the dehydrogenation process. The minimum share of the (chemical) hydride (X_{Hyd}) or hydrogen (X_{H_2}) which must be combusted to provide the necessary heat for dehydrogenation may readily be calculated using the following equations:

$$X_{\text{Hyd}} = \frac{\Delta h_{\text{R, Hyd}}}{\Delta h_{\text{R, Hyd}} + \text{LHV}_{\text{H}_2} / (\eta_{\text{burner}} \cdot \eta_{\text{HEX}})} [\%] \quad (1)$$

$$X_{\text{H}_2} = \frac{\Delta h_{\text{R, H}_2}}{\Delta h_{\text{R, H}_2} + \text{LHV}_{\text{H}_2} / (\eta_{\text{burner}} \cdot \eta_{\text{HEX}})} [\%] \quad (2)$$

In Eqs. (1) and (2), η_{burner} is the efficiency of burners, that may be taken as 80%, and η_{HEX} the efficiency of heat exchangers, that may be taken as 97.5% [170]. Note that the reaction enthalpy must be entered in units of kWh/(kg of hydride) in (Eq. (1)) and kWh/(kg of hydrogen) in (Eq. (2)). The lower heating value of hydrogen is 33.3 kWh/kg. The results of applying equations (Eq. (1)) and (Eq. (2)) for some of the considered hydrides are seen in Table 4 below.

Opting to combust released hydrogen carries with it advantages and disadvantages: the combustion will generally be clean, but cold start may not be easily achieved. To allow for cold start capabilities, a small reserve of gaseous hydrogen or some other fuel could be used until the proper reaction temperature has been reached. After that point, the hydrogen release starts, and part of it can be sent to a burner. In contrast, applying direct combustion of methanol or ammonia

Table 4 – The amount of released hydrogen or stored chemical hydride that must be combusted to provide the necessary heat of dehydrogenation for selected hydrides.

Hydride	Enthalpy of dehydrogenation [kWh/kg]	Lower heating value of hydride [kWh/kg _{Hyd}]	Share of released hydrogen which must be combusted [%]	Share of hydride which must be combusted [%]
MgH ₂	10.3	-	28	-
TiFe	3.9	-	13	-
NaAlH ₄	5.6 ^a	-	18	-
Methanol	2.3	5.5	8	9
Ammonia	4.2	5.2	14	16
PDBT	9.0	-	26	-

^a Average value of the two consecutive dehydrogenation reactions.

allows for cold start operation and circumvents the need for a buffer storage of gaseous hydrogen.

Conclusions

Hydrogen may be stored at elevated density in various ways but few of these have reached commercial maturity for large scale applications. The option currently considered most promising, salt cavity storage, is not universally applicable. Therefore, alternative options must be explored. As the available technologies differ fundamentally in approach, a common-ground evaluation of these is not without challenge.

In this paper, the current states of promising technologies for large-scale hydrogen storage were reviewed. The achievable hydrogen storage densities and the different processes for storing and releasing hydrogen were then compared. It is emphasized that several technologies may be viable, and that the most suitable option depends on the storage application and the specific context.

Most of the covered storage technologies are still being very actively researched, indicating that substantial advances are still to be made. What is also clear is that optimal layouts of large-scale hydrogen storage systems based on adsorption and chemical or metal hydrides have not yet been determined. Basic aspects, such as reactor designs, methods of heat supply for dehydrogenation, and acceptable load ranges are critical pieces of information still missing for several technologies. Due to these uncertainties, a detailed, accurate economic comparison of all hydrogen options including investment costs is presently not accomplishable.

While it is obvious that novel storage technologies, i.e., all but the storage of liquid or compressed gaseous hydrogen, are still at relatively early stages of development, it is also evident that some of these technologies are encouraging from the perspective of density of storage. It was also found that several chemical hydrogen storage technologies, specifically methanol, ammonia, and LOHCs, could possibly outmatch hydrogen liquefaction in terms of the electricity demand of the total storage process, although their thermal energy demands are substantially higher. However, in industrial applications it appears feasible that these thermal energy demands can be met without major technical challenges, either by the combustion of the hydrogen carrier, an external fuel, or part of the released hydrogen.

Beyond physical, thermodynamic, and economic arguments, it is also important to realize that the initial successful choice of a large-scale hydrogen storage technology is likely to significantly impact the further developments of a hydrogen infrastructure, since few full-size alternatives exists globally. The production and storage of large amounts of hydrogen for one application may well catalyze other actors to move in a similar direction due to reasons of economy of scale and availability. Therefore, possible synergies between applications or industries should be taken into account at an early stage, at least regionally. One example of such a synergy may be between an industrial application of large-scale hydrogen storage and a hydrogen distribution network for fuel cell vehicles.

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