

The energy efficiency of onboard hydrogen storage

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1. Introduction

Hydrogen is often suggested as a versatile energy carrier in future energy systems. Hydrogen can be extracted from water by electrical energy through electrolysis and later when the energy is needed hydrogen can recombine with oxygen from the air and release the same amount of energy. The end product is water and the cycle is closed. Hydrogen as an energy carrier is typically associated with renewable energy technologies because it provides a way to store energy. The need for energy storage is tremendous if wind turbines, wave energy devices or photovoltaics are to be implemented on a large scale. This is because of the fluctuating nature of the electricity production by these means and moreover, because the energy might be meant for application in the transport sector. Batteries store electrical energy efficiently, but they are not economic for large scale storage and for transportation they are only practical in smaller vehicles with a limited driving range and certainly not in trucks, ships or airplanes. The alternative is to store energy as hydrogen and hydrogen is an ideal fuel in many aspects. It is easily combusted in an engine or converted back to electricity in a fuel cell. It is not poisonous and the raw material for its production (water) is practically unlimited.

Hydrogen is often said to have the highest energy content per unit mass, but since it is a low density gas at ambient conditions it needs a storage tank that adds so much to the weight and volume that the whole system ends up being both heavier and bulkier than a gasoline tank with the same energy content. Therefore, hydrogen storage is a key issue, and in particular, onboard hydrogen storage in vehicles. As a matter of fact, the production of hydrogen from renewable sources only makes sense if hydrogen is stored for later use or for use elsewhere. Otherwise, one might as well use the extracted electricity directly (one exception could be the use of bio fuels in a fuel cell through a stage where hydrogen is liberated by reforming for immediate use, but this is not really within the idea of hydrogen as an energy carrier). Two recent monographs each provide a detailed introduction to all the aspects of hydrogen energy with several chapters dealing with storage techniques (Leon, 2008), (Züttel et al., 2008).

Many different techniques have been developed to solve this fundamental problem, and any one of them has its own energy balance to consider. Storage of hydrogen can be quite energy consuming and so can the subsequent liberation of hydrogen. In some cases both processes are energy intensive. The literature on hydrogen storage often focuses on the storage

density, and the question of round trip energy efficiency of the storage process may then be forgotten. In small systems, such energy losses might, although significant, be of less importance, but for vehicular applications, they cannot be neglected. After all, improved efficiency is one of the arguments when future fuel cell vehicles are compared with conventional ones. This work will review the most common hydrogen storage techniques with the focus on energy efficiency for charging and discharging the system, i.e. the round trip efficiency. It is an elaborated version of a previous study (Jensen et al., 2007).

2. Overview of storage techniques

Hydrogen is a volatile gas at ambient conditions, and the storage challenge is to fight the kinetic energy of the hydrogen molecules. Basically there are three ways to go. (1) The gas can be confined at high pressure by external physical forces. (2) The energy of the molecules can be withdrawn by cooling and ultimately the gas condenses into a liquid. (3) The molecules can be bound to a surface or inside a solid material. This way hydrogen is more or less immobilized and like in the case of liquid hydrogen, most of its kinetic energy is removed. The three fundamental storage techniques are visualised in the corners of the triangle in figure 1. Between the corners combined techniques that utilize more than one of the principles are plotted.

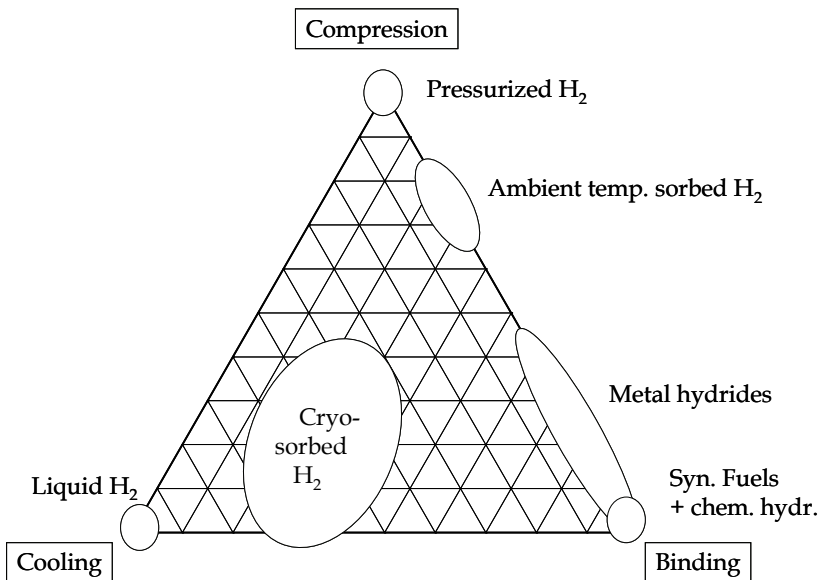


Fig. 1. The different storage techniques arranged qualitatively after degree of cooling, binding and pressurization.

Compressed hydrogen is kept in a dense state by external physical forces only. This is what happens in a pressure vessel. It takes mechanical energy to compress the gas, but the release is free of charge. Liquid hydrogen is kept together by weak chemical forces (van der Waals)

at very low temperature but at ambient pressure. Heat must be supplied to release hydrogen through boiling, but due to the low boiling point of 20 K, the heat can in principle be taken from the surroundings or any waste heat. Liquefaction of hydrogen by pressurization alone is not possible since the critical point is as low as 33 K (and 13 bar).

Hydrogen can bind to matter in many ways. It can be via adsorption on a large surface with some affinity for hydrogen molecules. In order to obtain a reasonable storage capacity this is always done in combination with either cooling (to reduce the energy of the hydrogen molecules), pressurization or both. The binding forces are the weak van der Waals forces like in liquid hydrogen, but the interaction is stronger due to the substrate. Release is comparable to a combination of compressed and liquid hydrogen. Absorption of hydrogen takes place in specialized solid materials into which hydrogen can diffuse and bind by metallic, ionic or covalent bonds. These forces are much stronger than the van der Waals forces and consequently, it takes more energy to release hydrogen afterwards. Examples are interstitial metal hydrides and complex hydrides. Finally it is possible to store hydrogen by making synthetic fuels like hydrocarbons, alcohols and ammonia. In this case the bonds are mostly covalent and require a significant amount of energy for hydrogen release. Moreover, in many cases, addition of water is needed too like for steam reforming. Synthetic fuels cannot be recharged onboard. Instead they are manufactured through chemical synthesis in a plant.

Another way to arrange the storage techniques is shown in figure 2, where they are ordered in a line ranging from pure physical storage to a gradually more chemical technique. A tendency that goes with this is that the more chemical the technique, the less easily available is the hydrogen. This less easy availability of hydrogen is seen as higher energy demands for hydrogen release and/or higher release temperatures.

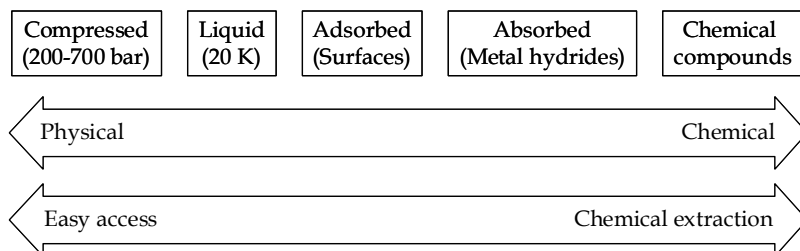


Fig. 2. The sequence of hydrogen storage techniques from physical to increasingly chemical.

3. The approach

The different storage techniques are in the following treated in the same order as in figure 2 from left to right. Although hydrogen storage does in principle not depend on the application, onboard storage, e.g. on a vehicle, is assumed since here we have the most demanding situation that may justify sophisticated and possibly expensive storage techniques. The aim of the study is first of all to compare the minimum energies required for storing hydrogen and releasing hydrogen. When energy is needed for the release, typically heat, it can in some cases be supplied by otherwise wasted heat from an engine or a fuel cell, but it depends on the temperature of that heat whether it is possible. Alternatively, the heat for release can be supplied by part of the hydrogen via a burner. In the latter case the available hydrogen for the main purpose (e.g.

propulsion) will be reduced comparatively and the effective storage capacity is thus lower than predicted from the amount of hydrogen stored.

A true comparison would involve a detailed analysis of whole systems. Such analyses are truly relevant but also complicated with numerous assumptions on which the outcome will strongly depend. Instead, transparency is aimed at with the hope that the conclusions are less questionable, although they do not tell the whole story. Throughout, the lower heating value (LHV) of the fuel is used instead of the higher heating value (HHV). This is because in several of the systems, heat for hydrogen liberation must be supplied at temperatures above 100°C likely by combustion of hydrogen. It is also assumed that hydrogen or a hydrogen mixture is released at no less than ambient pressure. The LHV used is 242.8 kJ/mol H₂.

4. Compressed hydrogen

Despite many attempts to develop advanced techniques for compact, practical and safe hydrogen storage, pressurization is still the dominating technique. This is a fact for onboard hydrogen as well as for hydrogen storage in general. The standard pressure for steel cylinders is 200 bar, but high pressure fibre composite tanks rated for up to 7-800 bar have been developed. The gravimetric storage capacity ranges from 1-2 wt.% for 200 bar steel tanks to 5-10 wt.% for high pressure fibre tanks. Fibre tanks are more expensive than steel tanks.

4.1 Energy for storage

The theoretical minimum work needed for gas compression can be calculated based on integration of the infinitesimal pressure-volume work, dw

$$dw = Vdp \quad (1)$$

where V is the tank volume and p the pressure. Assuming ideal gas behaviour integration of (1) from p_0 to p_1 results in the expression of the work, W , of ideal isothermal compression

$$W = p_0 V \ln\left(\frac{p_1}{p_0}\right) \quad (2)$$

where p_0 and p_1 are initial and final pressures. At hydrogen pressures over 100 bar, deviations from ideality become significant in this connection, and the dimensionless compression factor, Z , shall compensate for the non-ideality. The real gas equation is then

$$pV = ZnRT \quad (3)$$

Z depends on both pressure and temperature and is tabulated elsewhere (Perry et al., 1984). At 300 K and pressures up to 1000 bar, the compression factor is modelled well as

$$Z = 1 + k_{z,300} \left(\frac{p}{p^\circ}\right) \quad (4)$$

where $k_{z,300} = 0.000631$. Integration including (3) and (4) gives

$$W = p_0 V_0 \left[k_{z,300} (p_1 - p_0) + \ln \left(\frac{p_1}{p_0} \right) \right] \quad (5)$$

However, the compression is never isothermal, as heat is formed during the process. If the compression is very slow, most heat will dissipate to the surroundings, but in practical high pressure systems, a significant amount of heat is formed. The other extreme is adiabatic compression in which all heat produced is kept in the gas by ideal insulation. The work of adiabatic compression is

$$W = \frac{\gamma}{\gamma - 1} p_0 V \left[\left(\frac{p_1}{p_0} \right)^{\frac{\gamma - 1}{\gamma}} - 1 \right] \quad (6)$$

where γ is the ratio of specific heats (C_p/C_v). $\gamma = 1.41$ for hydrogen. The work of adiabatic compression to a fixed final density is much larger than the work of isothermal compression because the heat accumulated creates a higher pressure for the compressor to work against. Both isothermal and adiabatic compression is plotted in figure 3 as a function of the final pressure. Isothermal compression is the absolute minimum theoretically possible, and in reality, due to the discussed heat effect compression is performed in multiple stages with inter-cooling of the gas. Consequently, the work of compression lies somewhere between the two curves. The efficiency of a compressor system varies a lot and the curve in figure 3 is assuming a satisfactory compressor technology (Bossel et al., 2003).

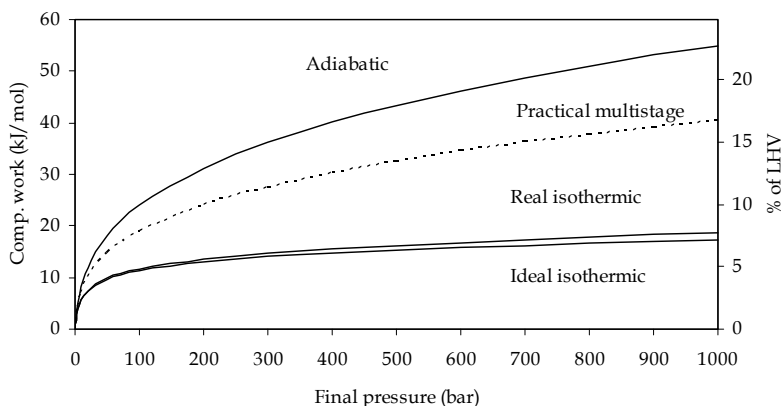


Fig. 3. The energy required to compress hydrogen from 1 bar to the final pressure specified on the primary axis. Re-plotted from (Jensen et al., 2007)

4.2 Energy for release

One strong advantage of compressed hydrogen is that it is easily available at a pressure high enough for fast transport through tubes. Even though the pressure vessel will cool during

release, the pressure will in most cases still be way above ambient pressure. Therefore, no energy is needed for the release. In principle, part of the compression energy can even be reclaimed via an expander, but as it adds to complexity and cost it can be argued whether or not it is feasible.

4.3 Discussion

The work of compression in real systems is estimated by Bossel et al (Bossel et al., 2003) and Weindorf et al (Weindorf et al., 2003). According to these studies, compression to 800 bar is possible using 18 % (Bossel) or 13 % (Weindorf) of LHV. The estimated curve for a real system added to figure 3 is between these values. Compression to a final pressure of 800 bar then costs 15.5 % of LHV.

One way to minimize the work of compression is to produce hydrogen by high-pressure electrolysis. The extra voltage (corresponding to extra energy) for reducing hydrogen at high pressure is close to the theoretical value because the reaction kinetics is very fast.

It is evident from equation (2) that the minimum ideal work of compression of one mole hydrogen from 100 to 1000 bar is the same as from 1 to 10 bar. This means that there is a significant benefit even if the electrolyser is operated at just 10-50 bar. Industrial electrolysers working at 32 bar are commercially available today from Statoil (former Norsk Hydro) and IHT.

There may be additional sources for spending energy during filling of the tank. Filling stations often store the gas to higher pressure than used onboard in order to facilitate fast transfer. This "over compression" will naturally lead to some losses. Moreover, cooling may be applied during the transfer to the vehicle and that costs energy too. These effects are not considered in the above calculations.

5. Liquefied hydrogen

Liquid hydrogen has the advantages that it is quite dense and that fuelling is fast and in principle as easy as for gasoline. The main drawbacks are that liquefaction is very energy intensive and that hydrogen continuously evaporates due to influx of heat. The latter can be reduced to a few percent per day or less by advanced thermal insulation, but it will always have to be dealt with. Liquid hydrogen tanks are high cost items and at present liquid hydrogen are only available in selected countries.

5.1 Energy for storage

Some gasses like propane and butane can be liquefied at room temperature by compression to moderate pressures. Unfortunately this is not the case for hydrogen (as well as for oxygen and nitrogen). The reason is that the critical point is situated at a temperature lower than ambient temperature. The critical point of hydrogen is at 33 K and 13 bar. At this point in the phase diagram the gas-liquid equilibrium line ends and above the critical temperature the substance will never liquefy, but will act as a compressed gas even at extreme pressure (eventually hydrogen will form a solid, but at room temperature it requires several thousand bar). This means that for the liquefaction of hydrogen cooling at minimum to 33 K is mandatory.

A simple theoretical pathway for liquid hydrogen is to cool it from room temperature (298 K) to the boiling point at 20 K and then condense it. The average heat capacity in the interval

is 28.48 J/mol K, and the heat of vaporization at 20 K is 892 J/mol H₂ (Values by Air Liquide). Based on this, the minimum energy required is 8.81 kJ/mol H₂. To this value 1.06 kJ/mol H₂ should be added for ortho-para conversion of the hydrogen (see below) and the total theoretical enthalpy change is then 9.87 kJ/mol H₂ or 4 % of LHV. In reality the process is quite complicated and much more energy intensive.

Pressurized nitrogen can be liquefied by Joule-Thomson expansion through a valve. The case of hydrogen is more complicated since the Joule-Thomson coefficient [$\mu_{JT} = (\partial T/\partial p)_H$] for hydrogen is negative at room temperature. This means that the gas would heat up instead of cooling. The final complication is that molecular hydrogen exists in two forms called *ortho* and *para*-hydrogen depending on the nuclear spin being parallel (ortho-H₂) or anti-parallel (para-H₂). At room temperature hydrogen contains 75% ortho and 25% para-H₂ and at 20 K the stable form is para-H₂. Hydrogen converts slowly between the two forms and this process is exothermic in the direction ortho-para (-1.06 kJ/mol H₂ at 20 K). Over time the equilibrium composition will be reached, but this takes a time orders of magnitude longer than the liquefaction process. Consequently, heat will be produced in the liquid hydrogen if this is not dealt with in the liquefaction process. The ortho-para conversion can be accelerated by a catalyst, but the heat produced adds to the amount of heat that has to be removed in the liquefaction process.

Practical hydrogen liquefaction plants provide the initial cooling of moderately compressed hydrogen by a conventional cooling system. Further cooling is done by liquid nitrogen followed by a mechanical expander and finally a Joule-Thomson valve. At low temperature the Joule-Thomson coefficient becomes positive and hydrogen cools and liquefies. Along this pathway ortho-para conversion catalysts are inserted at selected locations.

Bossel et al. (Bossel et al., 2003) refer to a detailed analysis concluding that the theoretical energy demand is 14.2 MJ/kg H₂. This equals 28.4 kJ/mol H₂ or 11.7 % of LHV.

In addition, hydrogen needs to be purified to high purity prior to liquefaction because all gaseous impurities will solidify at the low temperature and possibly block the Joule-Thomson valve.

5.2 Energy for release

Because the temperature is very low compared to the surroundings, all heat for hydrogen evaporation should be available. Nevertheless, in practical systems, a built-in electrical heater is often used because heat transfer fluids freeze if passed through heat exchange tubes in the tank. In this study it is assumed that heat from the surroundings is used. However, if electrical heating is used the latent heat of 892 J/mol H₂ should be sufficient to liberate hydrogen gas. Further heating can take place in the external tubing.

5.3 Discussion

The practical energy demand for liquefaction is significantly larger and depends on the size of the plant. Today, the energy demand in a modern plant is on the order of 40-45 % of LHV, but according to Bossel (Bossel et al., 2003), 25 % and to Weindorf (Weindorf et al., 2003), 21% of LHV should be possible in very large liquefaction plants.

6. Adsorbed hydrogen

Like any gas, hydrogen can adsorb on surfaces. The molecules are held by the weak van der Waals forces which are much smaller than those of real chemical bonds. Equilibrium is established between adsorbed and free molecules and the surface coverage increases with the gas pressure and with decreasing temperature. Materials like active carbon, carbon nano-tubes, zeolites and metal-organic frameworks have been studied for sorption capacities. The binding energy is 1-10 kJ/mol H₂. It is the general experience that at room temperature and pressures in the range 50-100 bar only up to 1 wt.% hydrogen storage is possible. At liquid nitrogen temperature (77 K) 4-6 wt.% has been reported by different groups. These values refer to the high surface area material only and do not take into account a pressure tank or the insulation in case of cryogenic sorption.

The heat for adsorption is limited compared to the hydrides (treated below). This is an advantage when filling the tank since only 1-10 kJ/mol H₂ is released (0.4-4 % of LHV). However, in the cryogenic case this heat must be removed at 77 K and that requires more energy than for cooling at room temperature or at elevated temperature.

A detailed calculation of the energies for storage and release is very complex. The sorption energy and the storage pressure can both vary by an order of magnitude and if liquid nitrogen is applied it requires an additional energy contribution that too depends on the conditions. When, on top of that, hydrogen storage by adsorption has not yet shown advantages over the other techniques discussed here, the calculation was not attempted.

7. Reversible metal hydrides

The term "reversible hydride" refers to both interstitial and complex hydrides as long as they can be charged as well as discharged by direct solid/gas reactions (or liquid/gas). "Reversible" should not be understood in a thermodynamic sense in this context, it only means "capable of reversing".

Hydrogen stored in interstitial metal hydrides is bound into interstitial positions in a host metal alloy in a more or less metallic way. This bond is stronger than the van der Waals forces mentioned before and a significant amount of heat is required to release hydrogen.

In the complex hydrides or other real chemical systems chemical bonds ranging from ionic to covalent are formed between hydrogen and the carrier atoms. The hydrogen release reactions in these cases typically require a significant energy input and also elevated temperatures to overcome the activation energy.

7.1 Interstitial hydrides

Interstitial hydrides are the most studied metal hydride systems for hydrogen storage. Examples are plentiful such as LaNi₅H₆, TiFeH₋₂, and LaNi₅-based alloys for nickel metal hydride batteries. They are considered very safe and easy to operate, and their main drawback apart from the price in some cases is the fact that the hydrogen storage capacity (with a few exceptions) is below 2 wt.%. One convenient characteristic is that the alloys can be tailored to a moderate equilibrium pressure of a few bars at ambient temperature. The heat of desorption is then around 30 kJ/mol H₂ or 12 % of LHV. During charging, this heat is liberated. In small canisters, the heat can be exchanged with the surroundings, but in larger systems like in a vehicle, active cooling by water

is necessary. The energy balance of such a cooling system depends highly on the charging rate aimed at. Consequently, only the sorption energy is considered.

When hydrogen is liberated, the hydride cools and the plateau pressure must still be above ambient pressure to avoid subsequent compression of the released hydrogen. This implies that the plateau pressure will be correspondingly higher when the hydride is heating up during charging and the charging pressure must match that. A 20-50 bar charging pressure can be suggested. Based on the discussion above, compression to 20 bar is set to 4-5 % of LHV (or 3 % with isothermal compression).

The amount of heat for desorption is the same as for absorption. It can be taken from the excess heat of the fuel cell or combustion engine provided that the temperature is high enough. The interstitial hydride can be designed for that.

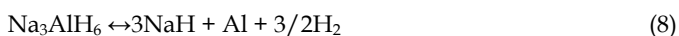
7.2 Other reversible hydrides

Other reversible hydrides obey the same thermodynamic laws but possibly with other pressure-temperature characteristics. They are not as easily tailored, and the reaction enthalpy is generally more or less fixed.

Examples of other reversible metal hydrides are MgH_2 , Mg_2NiH_4 and $NaAlH_4$. The two magnesium-based hosts are both characterized by one flat plateau, while $NaAlH_4$ desorbs hydrogen in two steps with different stabilities (Bogdanovic, 2000). The first step is:



and the second step is



The key desorption properties of the mentioned hydrides are listed in table 1. The column "Temperature for 1 bar" is based on thermodynamics. For kinetic reasons, $NaAlH_4$ needs temperatures of around 150°C even when Ti-doped. This means that the charging hydrogen pressure must be on the order of 100 bar which, assuming isothermal compression, takes 4.8 % of LHV or practically 7-8 % of LHV in reality. The other systems can be charged at low pressures like the interstitial hydrides.

Hydride	Rev. capacity	Heat of desorption	Temperature for 1 bar
Interstitial MH	1-2 wt. %	~ 30 kJ/mol H ₂ (~12.4 % of LHV)	Near room temperature
MgH ₂	7.6 wt. %	74.5 kJ/mol H ₂ (30.8 % of LHV)	300°C
Mg ₂ NiH ₄	3.6 wt. %	64.5 kJ/mol H ₂ (26.7 % of LHV)	255°C
NaAlH ₄ (one step)	3.7 wt. %	37 kJ/mol H ₂ (15.3 % of LHV)	35°C
Na ₃ AlH ₆	1.9 wt. %	47 kJ/mol H ₂ (19.4 % of LHV)	110°C
NaAlH ₄ (two steps)	5.6 wt. %	40 kJ/mol H ₂ (16.5 % of LHV)	110°C

Table 1. Selected metal hydrides and their hydrogen storage properties.

7.3 Energy for storage

The energy for storage is basically the energy for pressurizing hydrogen to the charging pressure, i.e. 10-50 bar for interstitial metal hydrides and 100 bar for NaAlH₄ as explained above. Energy for active cooling is not estimated, but will be relevant, especially in case of fast charging.

7.4 Energy for release

The energy for hydrogen release is the heat of desorption as listed in Table 1.

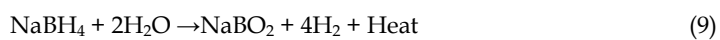
7.5 Discussion

The significant amount of heat liberated during charging will practically need to be removed actively in a vehicle size tank for an acceptable filling rate. There is a separate energy balance for this, but since it can be done in many different ways and at different rates it has been omitted in this context.

8. Irreversible hydrides

8.1 NaBH₄

NaBH₄ does not easily liberate hydrogen like the hydrides discussed so far, but it reacts with water over a catalyst. NaBH₄ is stored in an alkaline aqueous solution in which it is stable. When passed over a catalyst the following reaction takes place



The reaction is exothermic with the enthalpy -212 kJ/mol NaBH₄ or -53 kJ/mol H₂ (22% of LHV). The hydrogen storage capacity is 21.2 wt.% disregarding the water, but the practical capacity is much lower due to the water. Besides the role as a reactive solvent the water also acts as a heat sink for the heat liberated during the process. The system is commercialized by Millennium Cell®, and several demo cars have been fitted with such a system. The concept can also be used directly in alkaline fuel cells with the catalyst being the anode catalyst (Li et al., 2003).

8.2 Energy for storage

Being irreversible, NaBH₄ must be regenerated through other chemical pathways. As a minimum, the 212 kJ/mol must be supplied during that process, but the real number is significantly larger and depends on how regeneration is done.

8.3 Energy for release

No energy is needed for hydrogen liberation apart for pumping the liquid or for active heat management.

8.4 Discussion

The round trip energy efficiency of this hydrogen storage system will most likely exclude it from any application in which energy efficiency matters.

9. Methanol and ammonia

In this group, the hydrogen evolution reactions are characterized by equilibria with both reactants and products in the gas phase. There is no such thing as a desorption temperature at which the hydrogen pressure is 1 bar. The minimum hydrogen release temperature is therefore chosen as the temperature at which kinetics are reasonably fast and the equilibrium is strongly in favour of hydrogen formation.

The liberated hydrogen is in these cases mixed with either carbon dioxide or nitrogen. This fact affects the way a fuel cell is fuelled. As the fuel part of the mixture is consumed, the inert gas fraction increases, and this dilution effect can lead to local starvation of the electrode and poor performance (and lead to electrode degradation). To overcome this problem, fuel is fed in excess of at least 20 % (This problem can to some extent apply to any fuel cell operating below the boiling point of water because of water vapour accumulation followed by condensation. However, it can be solved by eventual purging without large losses). The over-stoichiometry is labelled λ . $\lambda = 1$ means strictly stoichiometric and $\lambda = 1.2$ means 20% excess. The 20 % excess fuel is normally combusted in a burner, and the resulting heat can then be used for fuel processing.

9.1 Methanol (CH₃OH)

In order to extract hydrogen from methanol it can be steam reformed according to



The hydrogen storage capacity is 18.8 wt.% disregarding the mass of the water. The process is fast at 230-250°C with a suitable catalyst, and the equilibrium is strongly in favour of hydrogen. The enthalpy of reaction at 250°C is +58.7 kJ/mol CH₃OH or +19.6 kJ/mol H₂ or 8.6 % of LHV of methanol. Prior to reforming, methanol and water must be evaporated and this takes another +75.8 kJ/mol H₂ or 11.1 % of LHV of methanol. The total minimum requirement is then 19.7 % of LHV of methanol.

However, the LHV of the produced hydrogen (725.4 kJ/mol 3H₂) is slightly higher than that of the methanol (685.5 kJ/mol CH₃OH). Taking this upgrading of 39.9 kJ into consideration, the expense for reforming is only 58.7 + 75.8 - 39.9 = 94.6 kJ/mol CH₃OH, which is only 13.8 % of LHV of CH₃OH. Moreover, the energy for evaporation can be taken from the waste heat of a fuel cell provided it is operated above 100°C. In that case, only 2.7 % of LHV is needed for fuel processing. This should be easily obtained from the excess stoichiometry assuming $\lambda = 1.2$.

9.2 Ammonia (NH₃)

Ammonia is sometimes considered as an attractive onboard hydrogen carrier because of its high hydrogen content of 16.6 wt.%, the absence of carbon, and the easy storage. At room temperature, its vapour pressure is less than 10 bar and consequently it can be stored as a liquid at moderate pressure. The major drawbacks are its chemical properties and its stability. It is corrosive and poisonous. As a base, it reacts with acids and it is therefore considered a poison to PEM fuel cells because it reacts with the perfluorosulphonic acid membrane even at levels of 10 ppm (Halseid et al., 2006). Solid oxide fuel cells are able to run on ammonia.

The process of ammonia splitting is endothermic:



and thus high temperatures and low pressure favours hydrogen formation.

If the pressure is set to 1 bar and only a few pct. ammonia are accepted for a subsequent clean-up process, then the temperature must be at least 300-400°C, and the reaction heat must be supplied at that temperature (practically the temperature can not be lower for kinetic reasons either).

Ammonia synthesis is exothermic, and in principle, the heat produced can be utilized. Today however, ammonia is manufactured from natural gas and nitrogen from the air, and the plants are consuming energy. A minimum energy required for synthesis is not estimated. Normally, it is manufactured from natural gas instead of primary hydrogen.

One approach addressing the safety issue is to store ammonia as a complex with a salt, e.g., MgCl₂. This idea was recently presented as hydrogen storage in tablet form (Christensen et al., 2005). Dry MgCl₂ can reversibly take up 6 molecules of ammonia, and the vapour pressure of ammonia becomes many orders of magnitude smaller. Moreover, in contrast to the hydrides, the complex can be stored in air with only a slow liberation of ammonia. The complex contains 9.1 wt.% hydrogen. Liberation of ammonia is endothermic and the enthalpy for the process is +43 kJ/mol H₂ (Christensen et al., 2005) or 17.8% of LHV. When the enthalpy for ammonia splitting is added, the overall minimum energy is +75 kJ/mol H₂ or 30.5 % of LHV. Liberation of all NH₃ requires a temperature of 350°C, although 2/3 of the ammonia is liberated at 200°C. The system is reversible with respect to ammonia storage, but not with respect to hydrogen storage. Ammonia can be charged onboard, but hydrogen cannot, and ammonia must be synthesized in a plant.

10. Heat available from fuel cells

Fuel cell systems operate with different efficiencies, but in most cases, at least 50 % of the fuel energy is liberated as heat due to different losses, mainly in the fuel cell. This corresponds to 120.9 kJ/mol H₂ (LHV) and is plentiful for any of the storage systems discussed here, even with large transfer losses. The determining factor is the working temperature of the fuel cell (or the exhaust temperature of the combustion engine) because the heat must be delivered at the working temperature of the storage device. Today the PEM fuel cell is almost exclusively considered for vehicles, due to, among other things, the low working temperature of around 80°C. This advantage becomes a disadvantage when heat is needed at higher temperatures, but today there are PEM fuel cells with working temperatures up to 200°C (Li et al., 2009).

11. Conclusion /Comparison

In Table 2, the maximum hydrogen storage efficiencies of the different storage systems are compared. For each system, the onboard hydrogen content is arbitrarily set to 100%.

The column "Energy available onboard" shall be understood as follows: The first percentage listed is the amount available when only heat at 25°C can be used for hydrogen liberation. The value in brackets (when relevant) is the percentage available if a heat source at higher temperature is available. If heat is required, but not available at the working temperature, fuel must be burned to provide it, thus limiting the practical storage capacity.

The column "Energy used for storage process" lists energy consumption for storing the hydrogen (e.g. for compression or charging a hydride). This is in principle an off board energy consumption that does not affect the amount of hydrogen stored. The two sub-columns contain minimum theoretical values and estimated practical values.

The column "Round trip efficiency" gives the overall efficiency for storing and liberating hydrogen.

In all cases energy consumptions due to thermal losses, pumping and the like are omitted.

System	Energy available onboard (% of stored H ₂)	Energy used for storage process (% of LHV of stored H ₂)		Round trip efficiency (based on the assumptions made)	
	At 25°C	Theoretical minimum	Practical	Theoretical minimum	Practical
Compressed 200 bar	100%	5.4%	10.0%	94.9%	91%
Compressed 800 bar	100%	7.3%	15.5%	93.2%	87%
Liquid hydrogen	~100%	11.8%	40%	89.4%	71%
Interstitial hydride	88% (100% @ ~50°C)	3%	5%	85.4% (97% at 50°C)	84% (95% at 50°C)
MgH ₂	69.2% (100% @ 300°C)	0%	5%	69.2% (100% @ 300°C)	66% (95% @ 300°C)
Mg ₂ NiH ₄	73.3% (100% @ 255°C)	0%	5%	73.3% (100% @ 255°C)	70% (95% @ 255°C)
NaAlH ₄ (3H available)	83.5% (100% @ 150°C)	4.8%	8%	79.7% (95% @ 150°C)	77% (93% @ 150°C)
NaBH ₄ + water	100%	22%	Very much	82%	Very low
Methanol	81.4% (92.5% @100°C) (100% @ 250°C)	-	-	-	-
Ammonia	87.3% (100% @ 350°C)	-	-	-	-
Mg(NH ₃) ₆ Cl ₂	69.5% (100% @ 350°C)	-	-	-	-

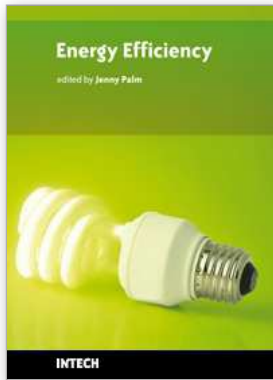
Table 2. A summary of the efficiencies for storage and release of hydrogen. Note that heat transfer losses and pumping might reduce the practical energy efficiency further.

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