

The energy efficiency of onboard hydrogen storage

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Abstract

A number of the most common ways of storing hydrogen are reviewed in terms of energy efficiency. Distinction is made between energy losses during regeneration and during hydrogen liberation. In the latter case, the energy might have to be provided by part of the released hydrogen, and the true storage density is then equivalently smaller. Systems covered include compressed and liquid hydrogen, reversible and irreversible metal hydrides, and methanol and ammonia.

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1. Introduction

The vision of a hydrogen-based energy system faces several technical challenges that will act as show stoppers if not dealt with. One key issue is hydrogen storage, and in particular, onboard hydrogen storage in vehicles. Generally speaking, 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 biofuels 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).

The publications and discussions on possible storage techniques often focus solely on the storage density, and the question of round trip energy efficiency is then forgotten. The round trip is in this relation the full circle from primary hydrogen through storage, transfer, and re-extraction of hydrogen. The different steps in the chain are associated with different energy balances that must be taken into account when storage systems are evaluated. 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.

Numerous techniques for storing hydrogen have been suggested, and they can be roughly 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.

The following comprises the different ways being considered for hydrogen storage: (1) compressed hydrogen is kept in a dense state by external physical forces only. (2) 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 be taken from the surroundings or any waste heat. (3) Adsorbed hydrogen is also bound weakly (van der Waals) to a substrate either through a high pressure or at low temperatures. Release is comparable to either compressed or liquid hydrogen or a combination. (4) 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. (5) In the true chemical systems, real chemical bonds ranging from ionic to covalent are formed between hydrogen and the carrier atoms. The hydrogen release reactions in these cases typically

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require a significant energy input and also elevated temperatures. This group comprises numerous solids, liquids, and gases, such as hydrocarbons, alcohols, ammonia, and chemical hydrides. Most of these are not reversible hydrogen carriers, but are manufactured through chemical synthesis. All of these techniques have their own energy balances for both storage and release of hydrogen and this is the focal point of the present work.

2. The approach

The aim of this study is first of all to compare the fundamental limitations and advantages of the different hydrogen storage techniques in terms of energy efficiency and capacity really available. 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.

3. Compressed hydrogen

3.1. Energy for storage

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

$$dw = V dp \quad (1)$$

where V is the tank volume and p is the pressure. Assuming ideal gas behaviour, integration of Eq. (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 non-ideality become significant in this connection, and the 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 [1]. 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 $k_{z,300} = 0.000631$, and p° is the standard pressure. Integration including Eqs. (3) and (4) gives

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

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

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

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 are plotted in Fig. 1 as a function of the final pressure. Isothermal compression is the absolute minimum theoretically possible, and in reality, due to the discussed heat effect and losses in the compressor, the work of compression lies somewhere between the two curves.

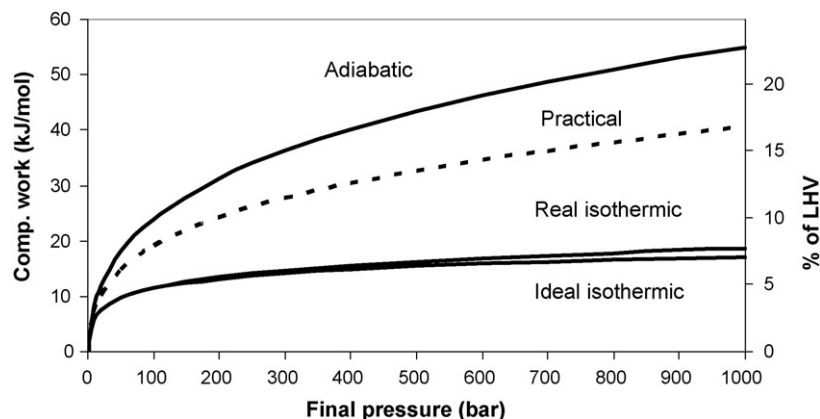


Fig. 1. The energy required to compress hydrogen from 1 bar to the final pressure specified on the primary axis.

3.2. 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.

3.3. Discussion

The work of compression in real systems is estimated by Bossel et al. [2] and Weindorf et al. [3]. 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 Fig. 1 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 energy) for reducing hydrogen at high pressure is close to the theoretical value because the reaction kinetics are very fast.

It is evident from Eq. (2) that the minimum ideal work of compression of 1 mol 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 electrolyzers working at 32 bar are commercially available today [4].

4. Liquefied hydrogen

4.1. Energy for storage

A simple theoretical pathway for liquid hydrogen is to cool it from room temperature 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 [5]. Based on this, the minimum energy required is 8.81 kJ/mol H₂ or 3.7% of LHV. However, liquefaction is carried out via a series of different techniques and according to an energy analysis for that, the theoretical energy demand is 28.4 kJ/mol H₂ [2] or 11.8% of LHV.

4.2. 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.

4.3. 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 et al. [2], 35% and to Weindorf et al. [3], 21% of LHV should be possible in very large liquefaction plants.

5. Adsorbed hydrogen

It is the general experience that sorption capacities of over 1% are only possible in cryogenic systems at, say 77 K (liquid N₂). This, as well as the fact that the sorption properties of different materials differ a lot, makes calculation of the energy balance quite complex. 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.

6. Reversible metal hydrides

The term “reversible hydride” refers to both interstitial and complex or chemical hydrides as long as they can be charged as well as discharged by direct solid/gas reactions (or liquid/gas).

6.1. 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 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 absorption is then around –30 kJ/mol H₂ or 12% of LHV. During charge, 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.

When hydrogen is liberated, the hydride cools and the plateau pressure must still be above ambient pressure to avoid subsequent compression. This implies that the plateau pressure will be correspondingly higher when the hydride is heating up during charge 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.

6.2. 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.

Table 1
Desorption properties of selected reversible metal hydrides

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

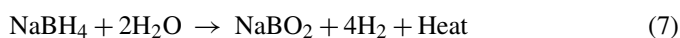
Examples of other reversible metal hydrides are MgH₂, Mg₂NiH₄, and NaAlH₄. The two magnesium-based hosts are both characterized by one flat plateau, while NaAlH₄ desorbs hydrogen in two steps with different stabilities. The first step is NaAlH₄ ↔ (1/3)Na₃AlH₆ + (2/3)Al + H₂, and the second step is (1/3)Na₃AlH₆ + (2/3)Al + H₂ ↔ NaH + Al + (3/2)H₂ [6].

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, NaAlH₄ 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.

7. Irreversible hydrides

7.1. 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 [7].

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. Methanol and ammonia

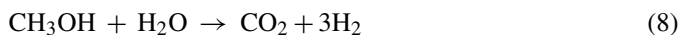
In this group, the hydrogen evolution reactions are characterized by equilibria with both reactants and products in the gas phase. There is no such thing as a desorption temperature

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 content increases, and this dilution effect can lead to local starvation of the electrode and poor performance. 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 overstoichiometry 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.

8.1. Methanol (CH₃OH)

Methanol can be steam reformed according to



The hydrogen storage capacity is 18.8 wt.% disregarding 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, +19.6 kJ/mol H₂ or 8.1% of LHV of the hydrogen. Prior to reforming, methanol and water must be evaporated and this takes another +75.8 kJ/mol methanol or 10.5% of LHV of the hydrogen. The total minimum requirement is then 18.6% of LHV of the hydrogen. 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 8.1% of LHV is needed for fuel processing. This should be easily obtained from the excess stoichiometry assuming $\lambda = 1.2$.

8.2. 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

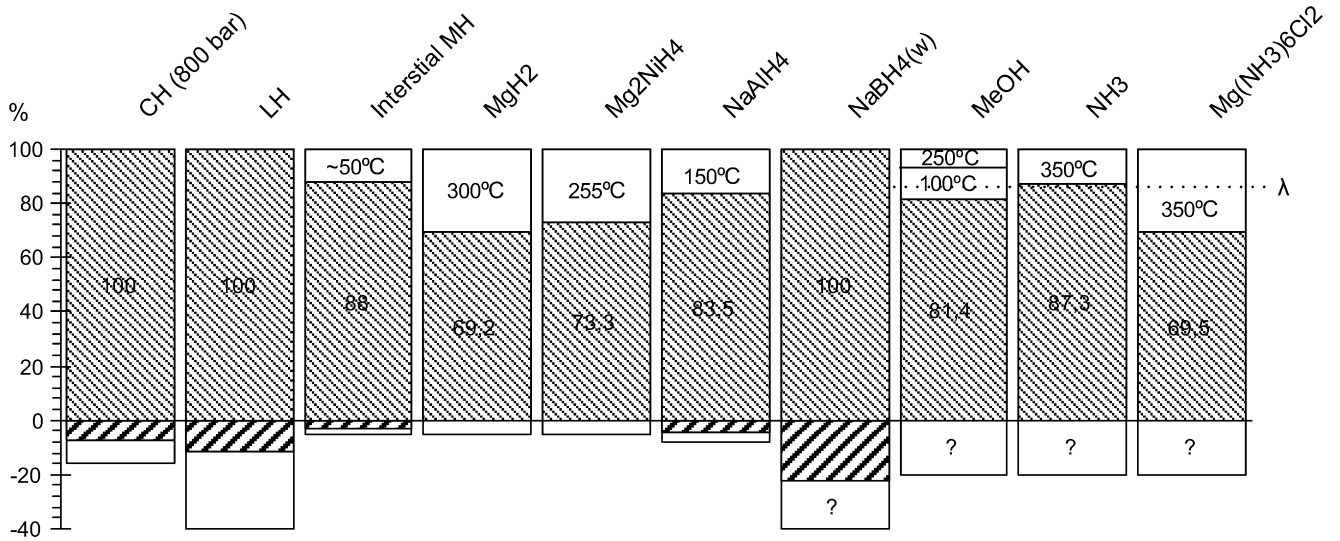


Fig. 2. Maximum hydrogen storage efficiencies of the storage systems. Onboard hydrogen is set to 100%. Negative columns represent energy to charge the system. White fractions in the positive columns are the heats for hydrogen liberation. White parts in the negative columns are the practical energy demands exceeding the theoretical minimum for charging the system.

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 perfluorosulfonic acid membrane even at levels of 10 ppm [8]. Solid oxide fuel cells are claimed to be able to run on ammonia.

The process of ammonia splitting is endothermic:

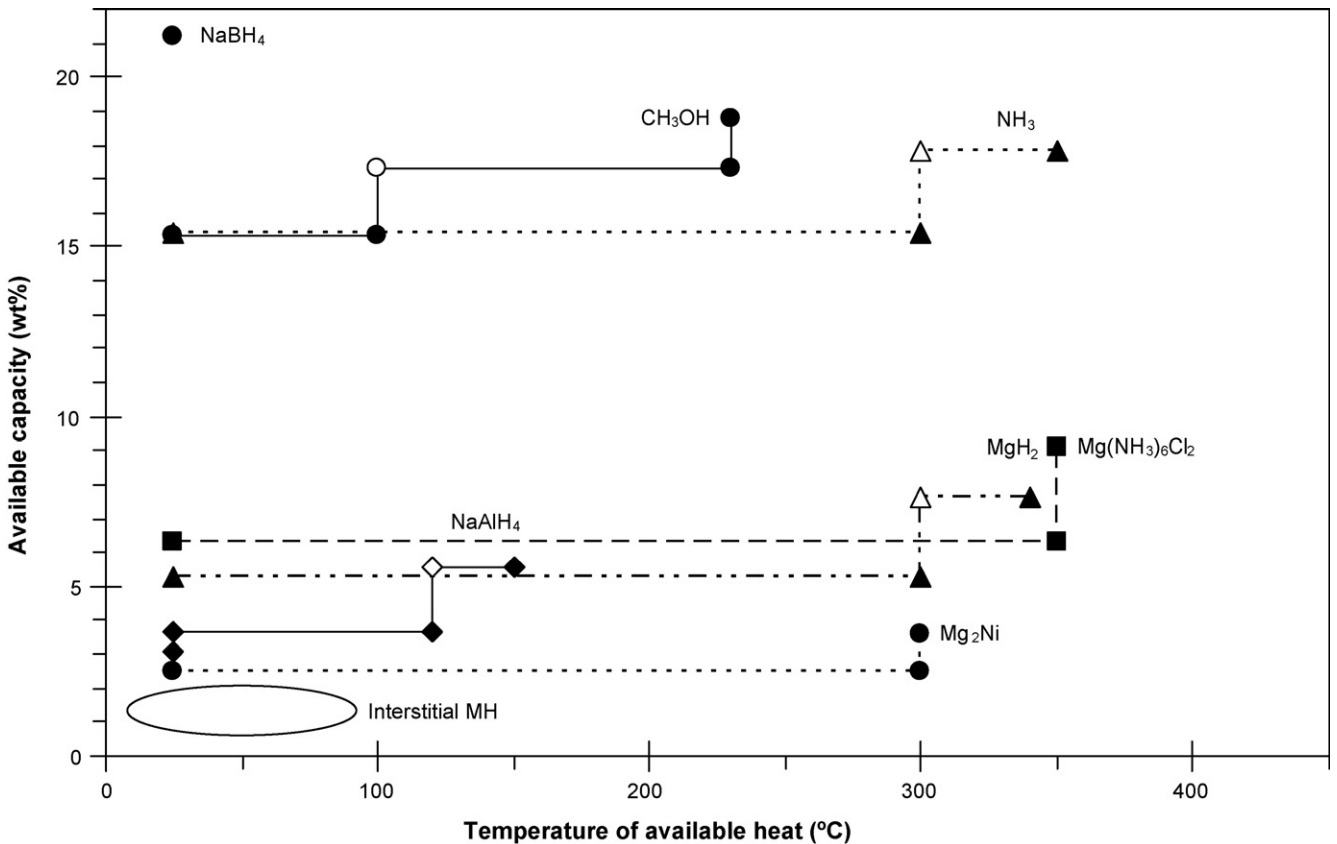
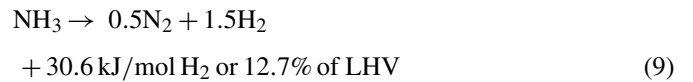


Fig. 3. The maximum available hydrogen from different storage techniques as a function of temperature of available heat. Only the host material is considered, not the tank. Open markers represent thermodynamic values and filled markers represent values assumed kinetically realistic.

and thus, high temperature and low pressure favours hydrogen formation.

If the pressure is set to 1 bar and only a few percent of 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 cannot 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.

One approach addressing the safety issue is to store ammonia as a complex with a salt, e.g., MgCl_2 . This idea was recently presented as hydrogen storage in tablet form [9]. Dry MgCl_2 can reversibly take up six 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 H_2 [9] or 17.8% of LHV. When the enthalpy for ammonia splitting is added, the overall minimum energy is +75 kJ/mol H_2 or 30.5% of LHV. Liberation of all NH_3 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.

9. 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 H_2 (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 [10].

10. Conclusion/comparison

In Fig. 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%. A top fraction is kept white, representing the energy that must be supplied as heat for hydrogen liberation. This part can be reclaimed if waste heat is available at the temperature indicated. If heat is not available, fuel must be burned to provide it, thus limiting the practical storage capacity. The negative columns represent the energy consumption offboard, i.e., for charging the hydrogen. The striped parts are the theoretical minima and the white parts are the excess necessary in reality. These values are relevant to the overall energy efficiency, but they do not reduce the practical storage capacity onboard.

In Fig. 3, the available storage capacities are plotted as a function of temperature of the waste heat available (e.g., from a fuel cell).

Acknowledgements

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