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Hydrogen Storage

Chemical and Physical Solutions for Hydrogen Storage

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Hydrogen is a promising energy carrier in future energy systems. However, storage of hydrogen is a substantial challenge, especially for applications in vehicles with fuel cells that use proton-exchange membranes (PEMs). Different methods for hydrogen storage are discussed, including high-pressure and cryogenic-liquid storage, adsorptive storage on high-surface-area adsorbents, chemical storage in metal hydrides and complex hydrides, and storage in boranes. For the latter chemical solutions, reversible options and hydrolytic release of hydrogen with off-board regeneration are both possible. Reforming of liquid hydrogen-containing compounds is also a possible means of hydrogen generation. The advantages and disadvantages of the different systems are compared.

From the Contents

1. Introduction

Dwindling fossil fuel resources, and in particular especially oil and gas, means we are facing tremendous challenges over the next decades concerning our energy systems. The discussion is mostly focused on the development and use of new sources of energy. However, the fact that hydrocarbons are currently the major storage and transportation form of energy is largely neglected. Electricity, which is the other main energy carrier beside hydrocarbons, can not be stored efficiently, so production and consumption have to be maintained in a very delicate balance. The vulnerability of our current electricity infrastructure has been dramatically demonstrated in several blackouts over the last years in which relatively small causes resulted in large area breakdown of the electricity supply. In fact, the lack of a suitable storage and transportation form for energy after the era of hydrocarbons may even pose the most difficult challenge in the transformation of our energy systems, at least in a medium range. Therefore, we have to consider alternative means for storing and transporting energy.[**]

Upon analyzing the different options, those other than in the form of high-energy compounds seem unpractical. Mechanical energy storage is able to bridge short imbalances of electricity supply and demand, but such buffers are depleted very rapidly. Storage in batteries also fails to reach the required energy storage densities and levels needed for the creation of energy reservoirs for whole economies. Therefore, storage in the form of energy-rich compounds is currently the preferred method.

Although this Review focuses on the possibilities for storing hydrogen, other options that are being discussed as energy storage and transportation forms shall also be briefly mentioned. Hydrocarbons are such a class of compounds that has served for this purpose in the form of fossil fuels for almost a century. In principle, hydrocarbons could continue to be used as energy storage compounds, as they can be generated from hydrogen and CO_2 by the water-gas shift reaction to produce synthesis gas. The synthesis gas can then be converted into methanol with a subsequent MTG (methanol-to-gasoline) process, or directly by the Fischer–Tropsch process into hydrocarbons. Synthesis gas produced from coal or biomass could also serve this purpose; however, the overall energetics and the economics of such processes do not appear very attractive, because CO_2 is the deepest energy sink. Methanol or the related compound dimethyl ether have also been proposed as suitable material storage compounds.[1] The production technology for methanol is very well developed, methanol is only moderately hazardous as a liquid, it can be easily handled, and the energy stored in methanol is easily released, either in a combustion process or in the form of hydrogen, which can then be fed to a polymer electrolyte membrane fuel cell (PEMFC) or to a direct methanol fuel cell (DMFC). However, for the production of methanol, hydrogen is first needed, and it therefore seems highly attractive to use the hydrogen itself as a high-energy-content storage and transportation medium for energy. But as we will see in this Review, the storage of hydrogen poses tremendous challenges; therefore, methanol may be used to store the hydrogen, whilst methanol steam reforming would be used to release it again at the point of use.

In Section 2, the different methods to store hydrogen will be discussed in more detail. Various aspects of hydrogen storage have been covered in a number of reviews,[2] but to our knowledge, the various technology options have not been discussed as comprehensively as herein. It would be impossible to cover completely all the literature on the different hydrogen storage options, but we will try to give an introduction to the field and provide easy access to the more specialized literature.

The major application of hydrocarbons today is in transportation; that is, as a fuel for cars and trucks. This is also the application for which the highest demands regarding storage of alternative fuels, that is, hydrogen, have to be met (Figure 1).

If the difficulties with hydrogen storage on board of a car can be solved, then the other problems with a hydrogen

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[**] In this Review, temperatures are given in °C, pressures in MPa, and volumetric storage density in $kg\,m^{-3}$ for consistency.

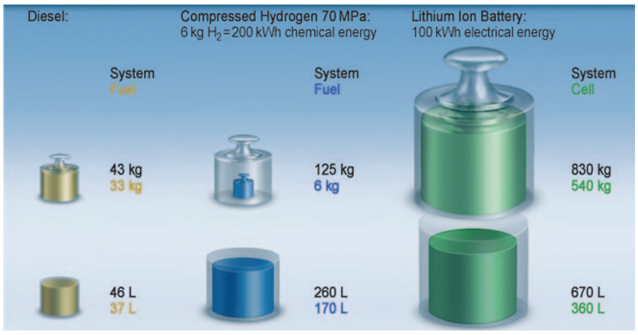

Figure 1. The weight and volume of various fuels and tank systems required for a 500 km range vehicle.

infrastructure appear to be manageable. A pathway to a hydrogen economy will proceed probably via hydrogen for portable applications first, then for stationary applications, and finally for transportation purposes. Table 1 illustrates the demands placed on a storage system for use in the most challenging application area: fuel-cell electric vehicles running on hydrogen. There are many more boundary conditions, but the ones listed seem to be most difficult to meet. Targets are only listed as approximate, as higher or lower values may be necessary or acceptable depending on other properties. The packaging problems which cylindrical high-pressure vessels cause should also be considered. If the shape can be chosen at will, a lower volumetric storage capacity may be acceptable, because space is then saved in packaging.

Table 1: Key properties of a hydrogen storage system for fuel-cell electric vehicles.[a]

Property	Benchmark	Target	Comments
gravimetric storage density	0.048 $kg\,kg^{-1}$	higher than benchmark	system capacity is decisive
volumetric storage density	23 $kg\,m^{-3}$	45 $kg\,m^{-3}$	system capacity is decisive
refueling time	3 min	3 min	slightly longer may be acceptable
maximum extraction rate	$>2\,g\,H_2\,s^{-1}$	$>2\,g\,H_2\,s^{-1}$	
start-up time	0 s	0 s	around 10 s may be acceptable
production cost (large volumes)		ca. €400 per kg^{-1} H_2	
heat exchanger capacity	0 kW	0 kW	some hundred kW may be acceptable, but compromises storage density
losses	0	0	

[a] The benchmark is 70 MPa high-pressure storage in carbon-fiber vessels.

As can be seen from the Table 1, these demands are very stringent, and thus no fully satisfactory solution has been developed to date. In some cases, stationary applications have more stringent requirements, especially with respect to cycle stability and memory effects, but overall, transportation applications pose the most severe challenge.

Before the different available technologies are discussed, the energetics of hydrogen storage will be briefly addressed, as this poses both a fundamental problem and an engineering problem for many storage technologies. If the storage of hydrogen is brought about by a phase change, be it by condensation, adsorption, or chemical reaction, the hydrogen pressure in the gas phase at a certain temperature is governed

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by the free enthalpy of the phase-change reaction. This allows a rough estimate of the enthalpy changes required for a certain pressure at a given temperature. If a hydride is formed, the entropy change is dominated by the entropy of gaseous hydrogen; that is, to a first approximation the entropy change is about 15*R*, where *R* is the ideal gas constant. Thus, the enthalpy of hydrogenation has to be about −40 kJ per mol of H_2 to achieve a hydrogen pressure of 0.1 MPa at room temperature. For physisorption of hydrogen on high-surface-area materials, the entropy change is lower, because the adsorbed hydrogen retains some degrees of freedom. It has been estimated from a Langmuir analysis of the isotherms of hydrogen on different adsorbents that the phase change entropy in this case is around 8*R*. This value is fairly independent of pore size and the nature of the adsorbent, with the exception of very small pore sizes, for which the hydrogen essentially behaves as a one-dimensional fluid.[3] Therefore, a pressure of 0.1 MPa at −196 °C would be reached at an adsorption enthalpy of about −5 kJ per mol of H_2, which is a typical value observed for hydrogen adsorption on high surface area adsorbents. These fundamental correlations will be difficult to overcome for a storage material; therefore, the heat that develops during the refueling of a hydrogen storage system somehow has to be dealt with, which is a formidable engineering challenge. For a cryoadsorption system, this would lead to excessive evaporation of nitrogen used for cooling (see Section 2.1.3); for a solid-state storage system, a heat exchanger in the megawatt range would be required for a typical tank size and refueling times on the order of minutes!

2. Available Technologies

2.1. Physical Storage

Under the term "physical storage" of hydrogen, three sub-technologies (Figure 2) are generally categorized:

a) CGH2 (compressed gaseous hydrogen), 35–70 MPa, room temperature
b) LH2 (liquid hydrogen), 0.1–1 MPa, circa −253 °C
c) Cryoadsorption on high-surface-area materials, 0.2–0.5 MPa, circa −193 °C

In all of these cases, no strong chemicals bonds (covalent or ionic interactions) between hydrogen and a host compound are involved. Sometimes, interstitial metal hydrides are also referred to this category. However, in this Review, the authors the properties of such interstitial compounds will be treated as chemical storage in Section 2.2, because the binding energies of 20–30 kJ mol^{-1} H_2 are quite significant.

Currently, the physical storage technologies, and in particular CGH2[4] and LH2,[5] are most mature; most prototypes of fuel-cell-powered cars use one of these storage systems. 70 MPa CGH2 is considered to be the state-of-the art technology. In this Section, the advantages and drawbacks of the various physical tank systems shall be discussed and evaluated for their viability in automobiles under special consideration of thermodynamic, engineering, and technology maturity issues.[6]

2.1.1. Compressed Gaseous Hydrogen

As the density of hydrogen at ambient conditions is far from any technological significance as an energy carrier (considering its net calorific value or lower heating value of 120 MJ per kg of H_2), it is obvious that the pressure level has to be increased to obtain a viable tank system (Figure 3).

To achieve vehicles with a range of about 500 km, it is necessary to store about 5–6 kg of hydrogen on board the car. As that available space is limited, working at pressure levels of 35–70 MPa is unavoidable. Lower levels do not make sense because of the insufficient energy content; for pressures greater than 70 MPa, the deviations from the ideal gas behavior are too large, so that the increased demands on the pressure container are not justified by the relatively small increase in energy content.

Apart from the chemical energy content of hydrogen (compared to the net calorific or lower heating value), the mechanical energy content of a CGH2 system is also of great interest because this energy is related to the energy required to compress the gas from ambient conditions to 35 or 70 MPa, with respect to the lower heating value.

The mechanical energy ΔW can be simply calculated using the assumption of an ideal gas and isothermal compression [Equation (1), where p_i = initial pressure, p_f = final pressure]. This equation leads to a mechanical energy content of about 8 MJ per kg of H_2 for 70 MPa, and 7 MJ per kg of

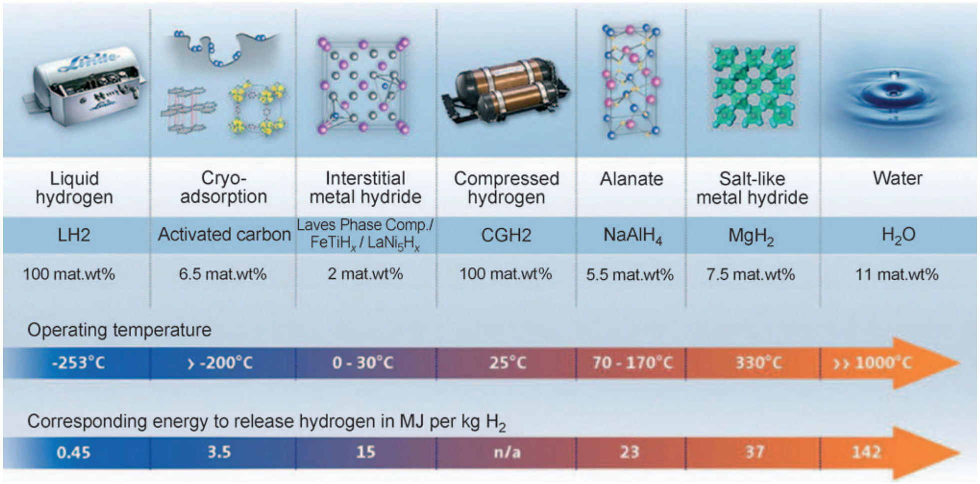

Figure 2. Several hydrogen storage technologies and their operating conditions. (Reproduced with kind permission from Ref. [6]).

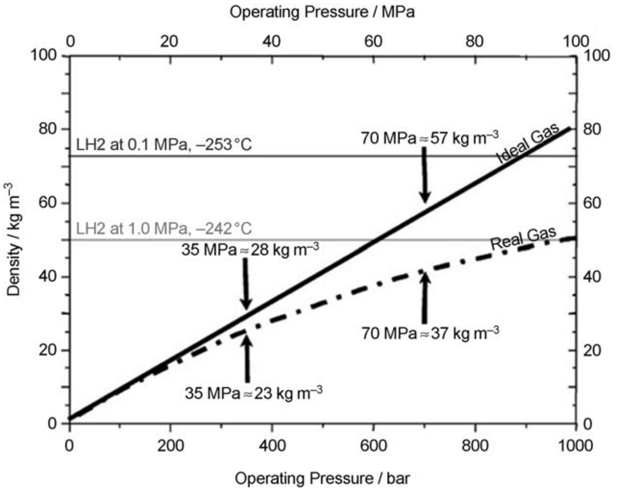

Figure 3. The density of hydrogen in LH2 systems under various conditions. (Reproduced by permission of the PCCP Owner Societies).

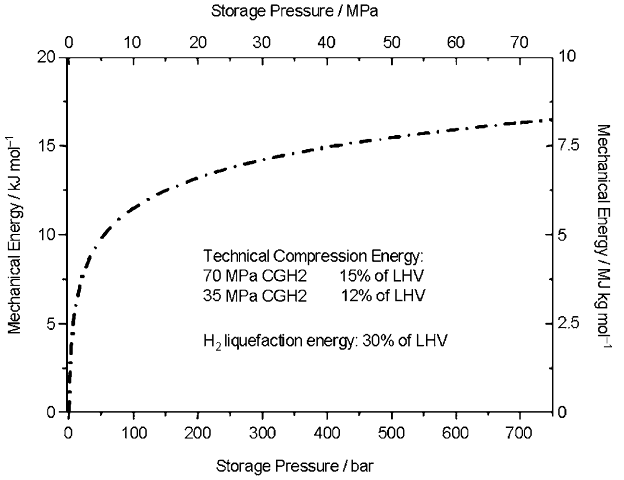

Figure 4. Mechanical energy content of hydrogen, using the assumptions of an ideal gas and isothermal compression at 27 °C and constant mass. For comparison, technical compression and liquefaction energies are shown.[2c] (Reproduced by permission of the PCCP Owner Societies).

H_2 for 35 MPa tank systems. This fact sometimes causes surprise, but is a consequence of integrating over the ideal gas law. In a real-world environment, the compression process is of course far from isothermal, and thus a polytropic description should be used to estimate the ideal compression energy [Equation (2), where n = polytropic coefficient].

$$\Delta W = \int p dV = RT \ln \frac{p_f}{p_i} \tag{1}$$

$$\Delta W = \frac{n}{n-1} RT \left[\left(\frac{p_f}{p_i} \right)^{\frac{n-1}{n}} - 1 \right] \tag{2}$$

With $n = 1.36$, in the case of a 70 MPa system, an ideal value of 10.2 MJ per kg of H_2 can be determined. In contrast, a real-world compressor device undergoes additional mechanical losses, and thus the engineering value to compress hydrogen is approximately 18 MJ per kg of H_2 at 70 MPa, or 14.5 MJ per kg of H_2 at 35 MPa.

Therefore, from a normalized compression-energy point of view, there is no relevant drawback to work with considerably larger operating pressures than 35 MPa. Rather, the upper end of the viable range is given by the drastic flattening of the mass energy density for pressure values greater than 70 MPa (Figure 4).

When working with such high pressures, special vessel designs are required. Obviously, a sphere would be the preferred geometry, but owing to space availability in vehicles, cylinders are used, which embody the second best geometry, in which longitudinal stress is the decisive parameter governing the required wall thickness. From an analysis of the stresses, it follows that raising operating pressure or the vessel diameter leads to an at least proportional increase in wall thickness. Therefore, when anticipating increasing the volume stored inside a pressure vessel, extending the vessel length and not the diameter is preferable, and high-strength materials, such as carbon composites, should be used. Other options would lead to a correspondingly thicker wall. Thus, small- to mid-scale pressure vessels make the most sense; for example, a three-vessel carbon composite unit to store 4.2 kg of hydrogen at 70 MPa weighs 135 kg (the weight of a similar steel system would be 600 kg). An drawing of a typical vessel design can be found in reference [6].

The energy densities for the optimal hydrogen tank comprising a single vessel correspond to values of about 0.048 kg H_2 per kg tank weight and 0.023 kg H_2 per liter tank volume. Together with the requirement of a cylindrical design (caused by the large operating pressures of about 35–70 MPa), the integration of such a tank into existing car architectures remains an important challenge. But despite all volumetric limitations of the CGH2 technology, this option yields the best overall technical performance to date and shows the highest maturity for automotive applications. Furthermore, it is feasible to refill an empty CGH2 system completely within three minutes. For this reason this technology is established as the benchmark for all competing conventional and alternative storage systems. CGH2 is the state-of-the art technology for fuel-cell vehicles for nearly all car manufacturers.

2.1.2. *Liquid Hydrogen*

Until very recently, liquid hydrogen was evaluated as a viable on-board storage option for the automotive industry. A potential advantage of LH2 systems is the high mass density of hydrogen at –253 °C and 0.1 MPa (see Figure 3) in comparison to 70 MPa CGH2 systems. On the other hand, heat flowing from the environment into the tank vessel leads to an evaporation of the hydrogen. As a consequence, the pressure inside the vessel increases, and after a certain maximum pressure is reached (in the order of 1 MPa), hydrogen has to be vented. The period of time from putting a vehicle into an idle or parking mode and the venting of hydrogen is known as dormancy: In an ideal case, this period is several days long. The hydrogen lost to the environment after that point is called boil-off gas. These losses are significant and have to be suppressed as much as possible. Unfortunately, owing to the very low phase-change enthalpy of about 0.45 MJ per kg of H_2 between the liquid and gaseous state (see Figure 1), even advanced engineering concepts have so far not been able to address the challenges of minimizing the heat input into the system adequately.

Heat input into the system occurs a) via thermal conduction though pipes, cables, and mountings, b) via convection, and c) via thermal radiation, with effects (a) and (c) being dominant. As a very good (that is, very low) surface-to-volume ratio S/V is needed, low overall values of heat flows can only be achieved when utilizing cylindrical tank structures. Schematic drawings of such systems can be found in reference [6].

The scaling behavior of a LH2 system is different to that of a CGH2 system: Larger tanks have an implicitly better thermal behavior than small ones owing to their improved S/V ratios. In contrast, tanks with more complex shapes (often called "conformable") show an inherently worse thermal performance because of their higher S/V ratios.

For any cryogenic tank system, the use of a very efficient multilayer vacuum superinsulation is required, consisting of approximately 40 layers of a foil used as radiation shields. This optimum number of about 40 layers results when the heat conduction effects are also considered.[7] The wrapping of these foils around the cylindrical and in particular the dome parts (as well as around the inlets and outlets for H_2 and the mountings) is highly demanding.

Another important point are the cooling-down losses during refilling of hydrogen at the station. The complete transfer line between the stationary LH2 reservoir and the vehicle tank system has to be cooled down to about −253 °C and therefore additional evaporation occurs. Despite large efforts of the technology providers of the infrastructure technology, these losses cannot be neglected and remain significant.

Both effects, on-board- and infrastructure-related, lead to unacceptable hydrogen losses. In addition, because of the complexity of LH2 tanks (and in particular, if using higher operating pressures to reduce boil-off gas and/or if boil-off capture systems are implemented), the system costs of LH2 systems are at least as high as those of CGH2 systems.

Despite the fact that the usable volumetric storage density is slightly higher compared to CGH2 systems, most car manufacturers do not see strong advantages in liquid hydrogen tanks that could compensate the drawbacks mentioned above. Additionally, the energy required to liquefy hydrogen already consumes 30 % of the chemical energy stored based on the net calorific value or lower heating value (LHV) of 120 MJ per kg of H_2. For this reason, virtually all of the world's large car manufacturers concentrate their efforts in the field of conventional hydrogen storage on 70 MPa.

2.1.3. *(Cryo-)Adsorption*

Adsorption is a borderline situation between physical and chemical storage. However, because most of the adsorbents discussed only have relatively weak interactions with hydrogen and the hydrogen is molecularly adsorbed and not dissociated, it is mostly categorized as a physical storage technology. The difference between cryoadsorption and chemical storage in a hydride is shown in Figure 5. As there is highly interesting chemistry involved in adsorptive hydrogen storage, relatively more space will be devoted to these technologies in this Review. At room temperature and atmospheric pressure, none of the currently-known adsorbents has as storage capacity which would come even close to target values; adsorptive storage solutions will therefore necessarily be cryogenic and/or pressure systems. Thus, general considerations of such systems will be presented first before different adsorbents are addressed.

2.1.3.1. *General Considerations*

Typical adsorption enthalpies for hydrogen on adsorbents such as carbon or metal–organic frameworks are in the order of 2–5 kJ per mol of H_2, so significant adsorptive storage

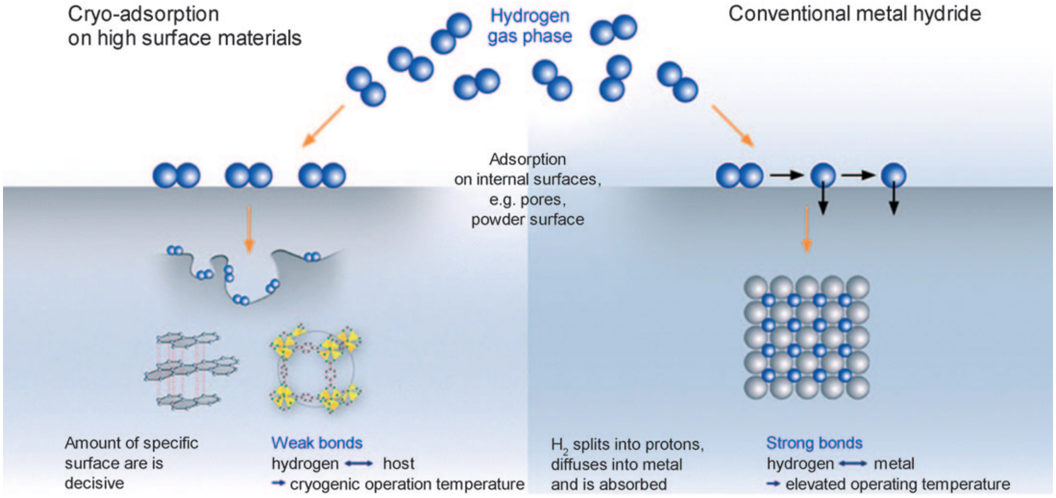

Figure 5. Representation of cryoadsorption and chemical storage in a hydride. (Reproduced by permission of the PCCP Owner Societies).

capacities can be reached at liquid-nitrogen temperatures and pressures of several MPa. Generally, the hydrogen uptake appears to be limited by the specific surface area (SSA) and by the pore structure and the pore sizes of the adsorbents. Ideal materials have a high surface area and pores in the micropore range; that is, with diameters below 2 nm, and ideally below 1 nm. The adsorption potentials in front of opposite pore walls then overlap to a significant extent, resulting in relatively high adsorption energies. On the other hand, materials with extremely large pore volumes also typically have rather large pore diameters, and thus do not adsorb much hydrogen, as the adsorption enthalpies of adsorbed hydrogen molecules beyond the monolayer approach the evaporation enthalpy of hydrogen. There are several comparative studies on the dependence of the storage capacity of various adsorbents on their specific surface area.[8–11] These studies typically agree on a roughly linear scaling of the storage capacity with specific surface area (mostly as BET equivalent surface area), with a proportionality constant of 1.9×10^{-3} wt% g m^{-2}[9] calculated for −196 °C and the saturation value of the Langmuir equation; that is, at pressures of several MPa. For 0.1 MPa and −196 °C, the proportionality constant for several plots appears to be about 1.3×10^{-3} wt% g m^{-2}, although the scatter is substantial.

For materials having very small micropores, the SSA measured with N_2 is misleading, as these compounds, which might be optimal for hydrogen, are not accessible to N_2 molecules. To prevent premature conclusions on the viability of cryoadsorption materials, the hydrogen capacity should be measured up to pressures of at least 2 MPa, and preferably to 10 MPa. It is also very important that only the "excess hydrogen material capacity" according to the IUPAC definitions should be used to compare the storage properties of different high-surface materials (see Figure 7).

Although such cryoadsorption systems appear to be simple principle if cooled with liquid nitrogen, the practical challenges should not be underestimated. The heat of adsorption is in the range between 2–5 MJ per kg of H_2. If a storage tank is filled with about 6 kg of H_2, heat in the order of 12–30 MJ is produced. This enormous amount of heat could only be compensated by the evaporation of liquid nitrogen. For nitrogen, the heat of vaporization is 5.6 kJ per mol of N_2. Considering a heat of adsorption of 2 MJ per kg of H_2 material (a reasonable number for many MOF materials), 2200 moles of N_2 corresponding to 80 kg liquid nitrogen would be needed. About 200 kg of liquid nitrogen would be necessary if the heat of adsorption would be close to the higher values of 5 MJ per kg of H_2.[2c]

This extremely large quantity of liquid nitrogen required for cooling purposes causes severe engineering challenges for automotive applications; furthermore, it creates additional costs (prices depend on quantity, but €0.25 per kg of liquid nitrogen is probably a good estimate), which make this solution highly unattractive. Therefore, more sophisticated and advanced heat management technologies and tank operating strategies (compared to a conventional steady-state LN2 Dewar) are required to provide a technically convenient way for storing acceptable amounts of hydrogen.

2.1.3.2. *Adsorbents*

2.1.3.2.1. *Zeolites*

Zeolites and related compounds are crystalline microporous materials, and are in the strict sense of the definition alumosilicates, but nowadays other compositions, such as aluminophosphates, are also included in the definition. Their microporous framework appears in principle to be highly suitable for hydrogen adsorption, as the adsorption energies in the narrow pores are very low; furthermore, materials are known in which the pore size is almost equal to the size of the hydrogen molecule, so that thermal cycling can be used to absorb or release hydrogen. The first studies on this topic were published by Weitkamp et al.,[12–15] but the storage capacities reported in materials with the sodalite structure were very low, being on the order of 10 cm^3 (STP) g^{-1} at room temperature (STP = standard conditions for temperature and pressure). Storage capacities substantially increase at −196 °C. For faujasite, a capacity of 172 cm^3 (STP) g^{-1}, corresponding the about 1.5 wt%, has been reported,[16] but even these capacities fall short of technically relevant values. A low Si/Al ratio and smaller pores is beneficial for high loading in such compounds,[16] but even if such considerations are taken into account, technically relevant capacities cannot be expected using zeolites. The zeolitic material with the highest micropore volume to date is ITQ-33,[17] for which a pore system of 0.37 cm^3 g^{-1} has been predicted for the pure silica polymorph. If this system was filled with hydrogen at liquid hydrogen density, the storage capacity would only amount to about 2.5 wt%. It can thus be expected that zeolite-based storage materials will be not suitable for hydrogen storage in technical applications.

2.1.3.2.2. *Carbon Materials*

There have been numerous studies on the use of different carbon materials as media for hydrogen storage. Various different forms of carbons were used, such as activated carbons of different origin, single- and multi-walled carbon nanotubes, nanohorns, and carbon cloth. Although extremely high sorption capacities over carbon nanotubes were reported in some of the first reports, it is now widely accepted that these results were erroneous, and more consistent data have been published in the last few years, suggesting that the adsorption on carbon nanotubes and nanohorns also roughly obeys the same scaling behavior as observed for other carbon samples. A compilation of results from many different groups has been given by Thomas.[8] For storage capacities plotted over the specific surface area, proportionality constants of around 1.3 wt% $\times10^{-3}$ g m^{-2} are typically obtained. The adsorption capacity of isolated graphene sheets for adsorption on both sides can be estimated at 2630 m^2 g^{-1}, which seems to be roughly the limiting value for the surface area one may maximally achieve with carbons. This calculation would suggest that carbon materials will not reach technically relevant adsorption capacities for hydrogen storage.

However, plots of limiting sorption capacities (saturation value of the Langmuir equation) versus micropore volume, as determined by different methods from different groups, give somewhat more reason to be optimistic (Figure 6). The proportionality constant for this plot is roughly 7 wt% $cm^{-3}g^{-1}$. Taking again graphene sheets as the limiting case and a spacing of these sheets of 0.7 nm (pores below this size seem to be most suitable for hydrogen storage),[8] an upper threshold of about 0.92 cm^3g^{-1} can be determined for the micropore volume of carbon materials. Thus it appears highly unlikely that carbon-based materials will be developed with a storage capacity reaching technically relevant values. Even carbon materials approaching the limit will probably not be accessible from natural raw materials as used in the synthesis of activated carbon, but will be tailored solids synthesized by complex procedures.

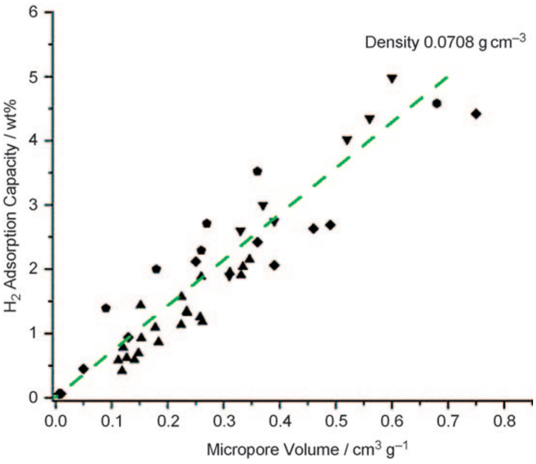

Figure 6. Hydrogen adsorption capacity (from Langmuir analysis) for different carbon samples versus micropore volume. The dashed line is the expected capacity for liquid hydrogen at the same volume. (Reproduced with kind permission from Ref. [8]).

2.1.3.2.3. Metal–Organic Frameworks (MOFs)

Metal–organic framework materials are among the youngest in the class of porous materials. They consist of metal ions as vertices that are connected by organic molecules, which are often polyvalent carboxylic acids, but also nitrogen donor linkers and others are known.[18] A remarkable feature of these materials is their exceedingly high surface areas. Although the meaning of surface area, be it Langmuir or BET equivalent surface area, is questionable for materials with such small pores, these values, which can exceed 5000 m^2g^{-1}, are spectacular, even if the numbers should not be taken at face value.

There is still substantial scatter in the reports on hydrogen storage of different MOF materials, which is partly due to the different conditions under which the storage properties have been evaluated. For a series of samples studied by Yaghi et al., saturation adsorption of hydrogen on various MOFs was found to scale best with Langmuir surface area,[19] with a proportionality constant of about 1.1×10^{-3} wt% gm^{-2}. There is an offset of roughly +1 wt%, so that the material MOF-177, with a surface area of 5900 m^2g^{-1}, was observed to have a saturation uptake of 7.5 wt% at −196 °C. However, results of other groups do not necessarily fall on this line, which is partly due to the fact that the pressure dependency of the adsorption on these materials varies greatly. Whereas a number of materials reach saturation close to atmospheric pressure, MOF-177 has a sorption capacity of only 1.62 wt% at 0.1 MPa and −196 °C (in the publication, a surface area of 4500 m^2g^{-1} was quoted).[20] Thus, although adsorption at one pressure will give an initial indication of the suitability of a material for hydrogen storage, for a thorough assessment, recording of a full isotherm up to higher pressure is necessary so that at least sufficient data points for fitting to an isotherm are available. This has not been done in any of the cases reported in the literature, which is one reason for deviating data. Furthermore, surface area may not be the only influential factor in determining sorption capacity; micropore volume could also be relevant. Another factor is that hydrogen sorption was observed to be site-specific to some extent, both experimentally and by theoretical methods.

There is an interesting feature of MOFs which may be exploited for hydrogen storage, namely gated adsorption.[21,22] This form of adsorption relies on the flexibility of the framework of some MOFs; that is, the structure expands upon adsorption of guest species, and shrinks again upon desorption. This typically leads to a rather pronounced hysteresis, which can be used to load the materials at high pressures and still capture the hydrogen at lower pressure or at somewhat higher temperature. Whether such an effect is useful under the conditions present in an automobile is questionable, as the mechanical stability of the pressure container is governed by the peak pressure; as long as loading at high pressure is required, the weight of the container is not reduced. Thermal cycling is also a problem, because cooling down the whole system for loading the storage material with hydrogen is very energy-intensive, even if the hydrogen would then be stored at room temperature. Moreover, if the void space beyond monolayer coverage is to be used in such porous materials, the filling density would not be expected to exceed the density of hydrogen at peak pressure, which places another limitation upon this method.

2.1.3.2.4. Polymers with Intrinsic Microporosity

Polymers with intrinsic microporosity (PIMs) have been studied as potential hydrogen storage materials. The polymer with the highest storage capacity is based on a triptycene monomer and takes up 2.7 wt% H_2 at a pressure of 1 MPa at −196 °C.[23] With BET surface areas in the range of 400–1050 m^2g^{-1} and the high diversity of polymer synthesis, increasing storage capacities of PIMs can be expected.

2.1.3.2.5. Volumetric Storage Density in Cryoadsorption

One severe disadvantage remains with MOFs and other adsorbents as cryoadsorption hydrogen storage materials: whilst the gravimetric storage density is one key requirement, volumetric storage densities also need to be sufficiently high. The United State Department of Energy (DOE) has set a target value of 45 kgm^{-3} for 2010,[24] a value which is based more on atmospheric pressure and non-cryogenic conditions. The volumetric storage capacities of MOFs, however, are only slightly higher than 30 kg m^{-3}; for example, 32 kg m^{-3} for MOF-177, which has the highest gravimetric capacity[19] reported to date, and other adsorbents have much lower values. The combination of a cryotank and a pressure tank results in additional weight and volume, so it can be estimated that on a materials basis, about 10 wt % excess hydrogen capacity (at −196 °C and 2–3 MPa) and a volumetric hydrogen density of about 50 kg m^{-3} are needed for cryoadsorption to become a viable technology. That leaves a substantial gap that still needs to be closed.

Nevertheless, cryoadsorption is a very promising method, because it shows a way of tackling the drawbacks of LH2 systems as the respective phase-change energy is an order of magnitude greater than that of liquid hydrogen. It can also be concluded that the dormancy periods are therefore also an order of magnitude larger, and the boil-off gas losses an order of magnitude lower than for a conventional LH2 tank.

It must be noted that cryoadsorption is still in the development phase, and significantly improved hydrogen adsorber materials are needed. Only early upscaling of the synthesis processes and the tank designs have been initiated. Although cryoadsorption shows significant potential, the maturity of the technology is not comparable to either an automotive LH2 or a CGH2 tank system (Figure 7).

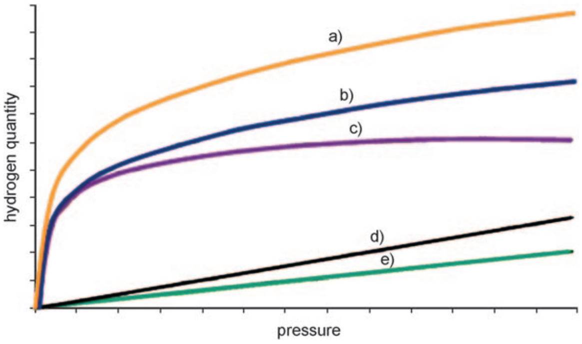

Figure 7. Cryoadsorption fundamentals and relevant hydrogen capacities: hydrogen quantity as a function of pressure a) Total amount of hydrogen stored, including dead volumes of the tank system; b) total amount of hydrogen stored by the high-surface-area material; c) quantity of hydrogen adsorbed on the adsorber (calculated using the skeletal density). d,e) For comparison: d) hydrogen quantity in the empty pressure vessel; e) hydrogen present in the macropores of the high-surface-area material (calculated using the skeletal density).

2.1.4. *Conclusions about Physical Hydrogen Storage*

CGH2 is the best system and is the state-of-the-art technology. 70 MPa tank systems are sufficient to ensure vehicle ranges greater than 480 km once purpose-built fuel-cell vehicles (that is, optimized for the hydrogen application) are considered. This has recently been shown by car manufacturers in 2007, for instance by General Motors in May 2007 with the Chevrolet Sequel. CGH2 tanks can be refilled with hydrogen in three to five minutes. The stored chemical energy in a 70 MPa CGH2 tank system with 5 kg H_2 (1600 Wh kg^{-1} tank weight) is more than one order of magnitude greater than that of an advanced automotive lithium ion battery system. The electric energy density (considering also the fuel-cell energy conversion efficiency) is still at least a factor of five greater than for the above-mentioned battery system. The technology maturity is high.

LH2 is also a quite mature hydrogen storage technology, but suffers from the fundamental problem of unavoidable hydrogen losses after the so-called dormancy period. These losses and the related losses during refilling are very significant, and led virtually all car manufacturers to the conclusion that LH2 is not viable for a mass-produced vehicle application.

Cryoadsorption is a very promising research path that could revolutionize hydrogen storage if adsorber materials are discovered in the near future with 10 wt % or more excess capacity at −196 °c and approximately 2–3 MPa. Additionally, the tank design and operating strategies have to be improved because a steady-state LN2 Dewar design is not sufficient. The energy density at the systems level is at least about 50 % less than the energy density at a materials level. The technological maturity is still at the basic research phase, but first steps for an up-scaling of this technology have been initiated.

2.2. *Chemical Storage*

2.2.1. *Hydrides*

2.2.1.1. *Hydrolytic Systems*

In general, any metal with a redox potential below that of the H^+/H_2 system at the corresponding pH could be considered a hydrogen storage system, as upon reaction with water, hydrogen is released and the metal hydroxide or oxide is formed. In practice it is better to use metal hydrides, because then not only the hydrogen liberated by oxidation of the metal is released, but also the hydride hydrogen, and thus rather high storage capacities could be achieved on a materials basis (for example, 8.4 wt % for the reaction of $LiBH_4$ with $4\,H_2O$). Reference [2b] gives a survey over some systems which appear to be attractive in this context. However, hydrolytic systems have a severe drawback: they can not be regenerated on-board, but instead need to be exchanged after the hydrogen has been released, shipped back to the plant, and regenerated by a cost- and energy-intensive industrial process. Furthermore, such hydrolytic processes are not easy to control, as one solid is consumed to form another solid, which could lead to crust formation with hindered reagent access and thus severe control problems. Moreover, the full capacity may not always be exploited for this reason.

However, for one case a solution for part of these problems has been found: $NaBH_4$ is reasonably stable in alkaline aqueous solution and can be stored under ambient conditions without additional precautions apart for the alkalinity. For hydrogen release, the solution can be brought into contact with a catalyst, a fact that has been known for more than 50 years.[25,26] This principle was used by the company Millennium Cell for the storage of hydrogen for cars running on fuel cells. They used a 25 wt% $NaBH_4$ solution in 2% NaOH, which was pumped over a ruthenium-based catalyst to release the hydrogen.[27], Based on the stoichiometric reaction in Equation (3), the storage capacity would theoretically result in an amount of 7.3 wt%.

$$NaBH_4 + 4\,H_2O \rightarrow NaOH + H_3BO_3 + 4\,H_2 \qquad (3)$$

If only a 25% solution of $NaBF_4$ is used, the practical storage capacity is reduced to about 5.3 wt% (the reduction of storage capacity does not scale linearly with the content, as water is a reagent and also releases hydrogen). This storage capacity is however amongst the highest that has been achieved. Furthermore, the aqueous $NaBH_4$ system has the advantage that the fuel is liquid, as is conventional gasoline or diesel fuel. However, in contrast to those fuels, the product from $NaBH_4$ decomposition is not gaseous, but a slurry of $NaBO_2$, which has to be removed from the vehicle and recycled.

Such a system in combination with a fuel cell has been used in a prototype vehicle in a Chrysler Voyager, but the practical experience was not sufficiently convincing to perform a second prototype test, and the development for use in cars has been discontinued. For niche applications, such as remote power supplies, such hydrolytic storage systems may still be useful; however, for large-scale transportation applications, hydrolytic systems do not seem to be a promising line of development.

2.2.1.2. ***Reversible Hydride Systems***

2.2.1.2.1. *Metal Hydrides*

The amount of hydrogen in classical metal hydrides is limited to roughly 2 wt% H_2, which is due to the fact that most of the typical metal hydrides are intermetallic transition metal compounds with the associated high atomic weight, even if several hydrogen atoms can be stored per metal atom, such as in the rhenium compounds $K_2[ReH_9]$[28] with the $[ReH_9]^{2-}$ anionic unit.

Binary hydrides are conventionally categorized as being salt-like, covalent, and metallic hydrides. In the latter compounds, the hydrogen typically occupies interstitial sites, which may lead to wide ranges of non-stoichiometry. Although this categorization may be helpful for didactic purposes, there are a number of problems associated with it, as is discussed in more detail by Grochala and Edwards.[29] Herein, these categories will not be used, and the hydrides are only classified as metal hydrides, irrespective whether they are salt-like, covalent, or metallic, and also irrespective whether they are binary, multinary, or complex hydrides in which a hydridometallate (or in the case of boron, a hydridoboranate) anion is present as a defined structural unit.

As stated above, hydrogen atoms in many technically relevant alloys occupy interstitial sites in the host lattices. The number of interstices in a lattice is normally much greater than the amount of absorbed hydrogen, but the occupation of all interstices has never been observed, although this would be very interesting to increase the hydrogen storage capacity. Electronic[30] and geometric[31] parameters are proposed to explain this phenomenon.

Typical alloys for hydrogen storage are the AB_5 compounds, such as $LaNi_5$ with a hydrogen content of roughly 1.4 wt% and an equilibrium pressure around 0.2 MPa at room temperature.[32] The high price of lanthanum and the low storage capacity of the alloy make this material unattractive for on-board hydrogen storage. This is also true for the AB_2 compounds, in which hydrogen storage capacity can reach up to 2 wt% H_2. These materials are cheaper compared to the $LaNi_5$ alloy (A = Ti, Zr, Mg; B = V, Cr, Fe, Mn), but their hydrogen equilibrium pressures are not sufficiently high at room temperature for fuel cell applications.

The storage capacities of the intermetallic hydrides are not high enough to meet the requirements for an on-board storage system. Nevertheless, these materials are implemented in fuel cell systems with solid state hydrogen storage in niche applications. Typical examples are a German Navy submarine that runs on a fuel cell, in which a Fe/Ti/Mn/Zr alloy (Hydralloy) is used as hydrogen storage material, or fork lift trucks with fuel cells and metal hydride storage systems, where a heavy counterweight is essential. For dive cruises of a submarine, a high ballast weight is necessary and the low storage capacity of the alloy of roughly 1.5 wt% is thus of no disadvantage.

A new approach for enhancing the storage capacity of a mobile system is the combination of a metal hydride with a high-pressure tank.[33] This tank is designed based on a conventional high-pressure gas tank. Together with the Ti/Cr/V alloy used (with a storage capacity of roughly 2.2 wt% H_2), an overall storage capacity of 7.3 kg H_2 in a 180 L tank volume can be reached. The equilibrium pressure of the metal hydride is 0.5 MPa at a temperature of −30 °C, which is thus high enough to start the fuel cell without external heating of the tank even at low temperatures. The overall weight of more than 400 kg for the whole tank system is much too high for practical applications, and new metal hydride materials with higher storage capacities are being intensively sought to reduce the weight of the system. Nevertheless this approach is a new attempt for the development of mobile tank systems for vehicular transportation units. It seems that the combination of different storage methods, such as a metal hydride and high pressure tank, or, as discussed above, cryoadsorption, can solve the low storage capacities of currently known tank systems.

With a hydrogen storage capacity of 7.7 wt% H_2, low material cost, and good reversibility during the cycling process, MgH_2 could be an interesting candidate for on-board hydrogen storage. However, the thermodynamic properties of the material are a severe obstacle against on-board use. MgH_2 is a typical high-temperature metal hydride with an equilibrium pressure of 0.1 MPa at temperatures of as much as 300 °C.[2n] This temperature is much too high for PEM fuel cell applications in combination with on-board hydrogen storage, as a sufficiently high hydrogen pressure should ideally be available at the operation temperature of the PEM fuel cell of around 90 °C. Nevertheless, MgH_2 has been the subject of extensive investigations for more than 20 years to improve the kinetics of the desorption and absorption of hydrogen and cycle stability. Ball-milling is the method of choice for the preparation of Mg/MgH_2–catalyst composite materials. Extremely short hydrogen absorption and desorption times of less than two minutes are observed with ball-milled MgH_2 and different types of oxides, for example, V_2O_5 or Nb_2O_5, as catalyst.[34,35] Altering the thermodynamics of the Mg/MgH_2 system may be a possibility to allow the high storage capacity of the system to be used under more moderate conditions. Theoretical calculations have shown that the thermodynamics change strongly with the size of magnesium clusters. Particles with sizes of only of 0.9 nm and containing 20 magnesium atoms are less stable than the bulk material. This destabilization results in a desorption temperature of approximately 200 °C.[36] However, it should be noted that these calculations were performed in vacuum; the results may change if a more realistic hydrogen environment is used. Melt infiltration was recently used to prepare carbon-supported magnesium nanoparticles.[37] Depending on the pore size of the carbon material, magnesium nanoparticles less than 2 nm in size can be prepared. However, experimental evidence of a material that attains the required equilibrium pressure of 0.1 MPa at lower temperatures has not yet been demonstrated. On the other hand, MgH_2 has a very high energy density of 9 MJ per kg of magnesium. Whilst perhaps not a promising material for hydrogen storage, it shows promise for the reversible storage of high amounts of thermal energy over an technically relevant temperature range.[38]

2.2.1.2.2. Complex Hydrides

In contrast to the classical metal hydrides, in which interstitial sites are occupied with hydrogen atoms, in complex metal hydrides,[2b,g] hydrogen is covalently bound to a metal (or, as in the case of boron, a non-metal) atom to form a complex anion. The charge of the anion is balanced by a cation, which is usually an alkali or alkaline earth ion. The storage capacity thus depends on the weight of the metals and the number of possible bound hydrogen atoms in conjunction with the charge of the complex anion. Ideally, light metals with high valency are desired for high storage capacity; therefore, on the basis of storage capacity alone, beryllium and boron hydrides with lithium or magnesium as cations would be ideal. Although different lithium berylliumhydrides have been studied,[39] and a compound $Li_3Be_2H_7$ with a storage capacity of about 8 wt% and an equilibrium pressure of 0.1 MPa at about 250 °C has been identified, the high toxicity of beryllium compounds will certainly prevent large-scale applications. The best known boron hydrides, $LiBH_4$ and $NaBH_4$, are too stable; furthermore, boron hydrides suffer from the disadvantage that volatile boranes are possible decomposition products. Even if these boranes are only formed at trace levels, their formation could lead to substantial loss of storage capacity over many cycles and to damage to the fuel cell.

For these reasons, researchers have concentrated on lightweight complex aluminum hydrides. The most intensively studied reversible complex aluminum hydride is the sodium compound $NaAlH_4$, with a reversible hydrogen content of 5.6 wt% H_2. It decomposes in three steps according to Equations (4)–(6).

$$3\,NaAlH_4 \rightarrow Na_3AlH_6 + 2\,Al + 3\,H_2 \tag{4}$$

$$Na_3AlH_6 \rightarrow 3\,NaH + Al + 1.5\,H_2 \tag{5}$$

$$3\,NaH \rightarrow 3\,Na + 1.5\,H_2 \tag{6}$$

The first decomposition step has an equilibrium pressure of 0.1 MPa at around 30 °C, which means that this material is comparable to a typical low-temperature metal hydride. The hydrogen content for this first decomposition step (3.7 wt% H_2) is higher than a classical low-temperature metal hydride by a factor of two. The second decomposition step releases 1.9 wt% of hydrogen. The equilibrium pressure of this step is 0.1 MPa at about 130 °C, which is typical for a medium-temperature metal hydride. The decomposition temperature for the third step is too high for technical applications and can therefore not be used as a hydrogen source. $NaAlH_4$ shows the typical structural changes of most of the complex aluminum hydrides. The aluminum atom in sodium alanate is tetrahedrally coordinated, and the aluminum atom in the intermediate Na_3AlH_6 octahedrally coordinated.[40] Pure aluminum metal is produced as a separated phase during the decomposition. The mechanism of this segregation process is still a point of discussion; some arguments for a transport process via volatile Al_xH_y compounds are presented at the end of this section.

$NaAlH_4$ was first synthesized about 50 years ago as a substitute of the more expensive $LiAlH_4$ for reduction reactions in organic synthesis.[41] Unfortunately, in contrast to $LiAlH_4$, $NaAlH_4$ has a very low solubility in diethyl ether. The best solvent for $NaAlH_4$ is tetrahydrofuran, which was not available for organic synthesis procedures at that time. This and other complex hydrides had not been seriously considered as hydrogen storage material, because it could effectively not be rehydrogenated unless very harsh conditions were used.[42,43] Recently, however, it was observed that nanosizing of $NaAlH_4$ by deposition on a support could lead to improved kinetics and milder rehydrogenation conditions.[44]

However, in 1997 Bogdanović and Schwickardi[45] showed that $NaAlH_4$ can be used as a solid reversible hydrogen storage material by doping it with titanium compounds, such as $Ti(Obutyl)_4$. Since these fundamental studies were carried out, research efforts on complex metal hydrides as reversible hydrogen storage materials have increased dramatically. The particular thermodynamic properties combined with the high hydrogen content are the reasons for the outstanding interest in complex metal aluminum hydrides. One of the most frequently used doping precursors is $TiCl_3$. The active catalytic species is produced during the treatment of the material in a ball-milling procedure.[46–48] During the ball-milling, the dopant is highly dispersed within the hydride material, which is necessary for good kinetics in solid-state reactions. More important however is the reduction of $TiCl_3$ to metallic titanium according to Equation (7).

$$\mathrm{TiCl_3 + 3\,NaAlH_4 \rightarrow Ti + 3\,Al + 3\,NaCl + 6\,H_2} \quad (7)$$

The high activity of the metallic state for the de- and rehydrogenation process was also shown with Ti_{13} nanoparticles[49,50] which have rehydrogenation times of only minutes at 10 MPa and 100 °C. As the synthesis of these colloids is expensive and time-consuming, and the reaction rates decrease over the time, titanium colloids are no longer preferred as doping materials. Similarly short hydrogenation times can now be attained with other transition metal chlorides, for example $CeCl_3$ and $ScCl_3$.[51,52] Once again, the reduction to the metallic state can be expected for these chlorides during the ball-milling method, but this has not been satisfactorily shown to date.

For several years, the status of the catalyst during the hydrogenation/dehydrogenation reaction remained unclear and highly disputed, owing to the difficult analytical problems. A simple measurement of the hydrogen evolution during the doping process using the ball-milling method gave a first insight in the status of the dopant. When titanium compounds in different oxidation states ($TiCl_4$, $TiCl_3$, $TiCl_2$) were used, the amounts of hydrogen gas produced [8, 6, and 4 moles of hydrogen, see Eq. (7)] correspond to a reduction of all titanium compounds to the metallic state.[53] From extensive X-ray absorption studies of titanium-doped $NaAlH_4$, it was concluded that the formal titanium valence is zero and does not change during the cycling process.[54–56] The titanium atoms are largely dispersed in the metallic aluminum phase in a state which resembles the $TiAl_3$ alloy. An increase in the surface area of the titanium species may enhance the catalytic effect.[57] It was recently shown that the dopant also alters the thermodynamics of the system.[58] This was determined by the change of the equilibrium pressure of titanium-doped $NaAlH_4$ depending on the doping concentration (Figure 8). During the dehydrogenation reaction, the highly concentrated $TiAl_3$ alloy produced in the doping reaction, is diluted with the generated aluminum. It is this dilution process that gives an additional contribution to the free energy of the system and destabilizes it at higher dopant concentrations.

In the preceding paragraph, the nature of the titanium catalyst was described, and it seems to be clear that titanium in doped alanate is in the zerovalent state both in the hydrogenated and the dehydrogenated state. The mode of action of the catalyst is however still unclear. Hydrogen/deuterium scrambling experiments of titanium-doped $NaAlH_4$ have shown that the catalyst dissociates hydrogen on the surface of the material and facilitates diffusion in the bulk of the material.[59] However, the rate limiting step during rehydrogenation seems to be the mass transfer from the separated NaH and aluminum phases to each other. Similar conclusions were reached from the determination of the activation energies for absorption and desorption with hydrogen and deuterium.[60] Both reactions are slower if deuterium is used. This effect could be explained if a heavier species than hydrogen, for example, Al_xH_y (or NaH), is important for the diffusion process. Inelastic neutron scattering (INS) experiments have shown the presence of a volatile species during the hydrogenation of titanium-doped $NaAlH_4$. It was concluded that such species can act as a hydrogen and aluminum shuttle for the recombination of the separated NaH/Na_3AlH_6 and aluminum phases.[61]

A new approach for the preparation of doped complex hydrides is the reactive ball-milling synthesis starting from cheap industrial chemicals. Figure 9 shows a ball-milling experiment under a hydrogen pressure of 8 MPa starting from aluminum metal, NaH, and $TiCl_3$ as doping agent for the preparation of $NaAlH_4$ [Eq. (8)].[62]

$$\mathrm{NaH + Al \xrightarrow[\text{ball milling}]{\mathrm{TiCl_3/8\,MPa\,H_2}} Ti\text{-doped }NaAlH_4} \quad (8)$$

The evolution of the experimental data is recorded with a telemetric data transfer system for the observation of the reaction progress. Compared to the direct synthesis of $NaAlH_4$ without ball-milling, the reaction time is much shorter, the reaction temperature is lower, and the prepared material is more reactive during the hydrogenation and dehydrogenation reactions. Optimization of these processes

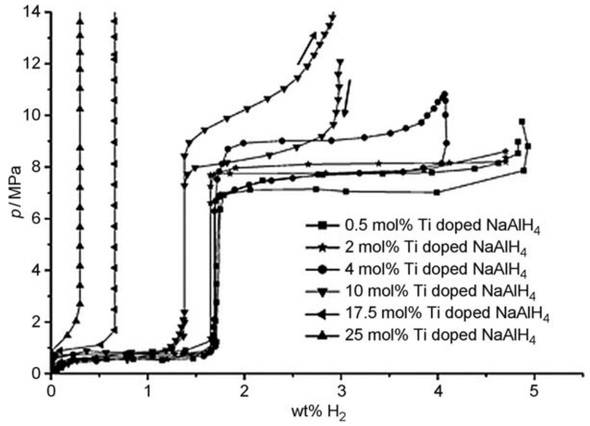

Figure 8. PCI (pressure–composition isotherm) measurements of $NaAlH_4$ doped with different amount of $TiCl_3$; all measurements were made at $T = 160$ °C.[60] (Reproduced by permission of the PCCP Owner Societies).

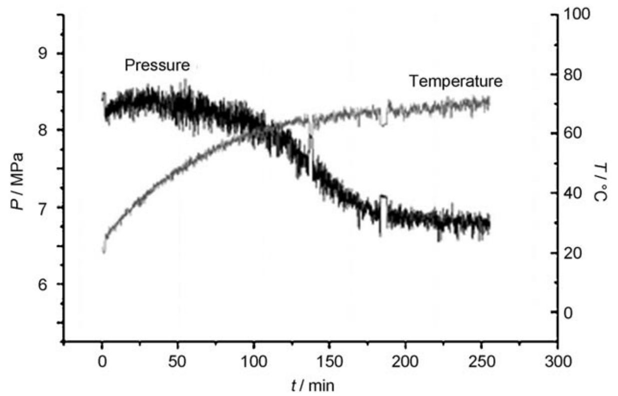

Figure 9. Hydrogen pressure and temperature evolution during the ball-milling hydrogenation of a 1:1 mixture of NaH/Al (2 mol% $TiCl_3$ as catalyst). (Reproduced by permission of the Royal Society of Chemistry).

for industrial production is under development.[63] Reactive ball-milling under high hydrogen pressures can also used for the preparation of other hydrides, such as CaH_2, in pure form and nearly quantitative yield at room temperature.[64]

Other complex hydrides that have a high hydrogen content are the alkaline earth compounds $Mg(AlH_4)_2$[65,66] and $Ca(AlH_4)_2$. With a total hydrogen content of 9.3 wt% H_2 for the magnesium compound and 7.9 wt% H_2 for the calcium compound, both materials are in principle potential hydrogen storage materials. According to Equation (9), the synthesis of these materials is a simple metathesis process, and can be carried out in solution or in the solid state with the ball-milling method.

$$MgCl_2 + 2\,NaAlH_4 \xrightarrow{\text{ball milling}} Mg(AlH_4)_2 + 2\,NaCl \tag{9}$$

Unfortunately, from measurements of the decomposition enthalpies it must be concluded that both alanates do not react reversibly under technologically relevant conditions.[67,68] $Mg(AlH_4)_2$ decomposes at temperatures of about 130 °C in one step without observation of an octahedral intermediate state, and it releases 7 wt% hydrogen [Eq. (10)].

$$Mg(AlH_4)_2 \xrightarrow{130\,^\circ C} MgH_2 + 2\,Al + 3\,H_2 \tag{10}$$

$Mg(AlH_4)_2$ is an unstable hydride, with a decomposition enthalpy of circa 0 kJ per mol of H_2 and therefore not useful as a reversible metal hydride. The end-products of the decomposition reaction are MgH_2 and aluminum metal. In contrast to this pathway, calcium alanate decomposes in a two-step mechanism with $CaAlH_5$ as an octahedral intermediate [Eq. (11), (12)].

$$Ca(AlH_4)_2 \xrightarrow{180\,^\circ C} CaAlH_5 + Al + 1.5\,H_2 \tag{11}$$

$$CaAlH_5 \xrightarrow{230\,^\circ C} CaH_2 + Al + 1.5\,H_2 \tag{12}$$

2.9 wt% H_2 is released in the first step, and additional 3.0 wt.% H_2 in the second step, thereby producing CaH_2 and aluminum metal. The first decomposition step is exothermic, but the second step is endothermic with a decomposition enthalpy of 31.6 kJ mol^{-1}. This value lies in the right region for reversible metal hydrides, but it is not yet clear whether the material is a reversible hydride compound or not, as no full rehydrogenation to a fully characterized $CaAlH_5$ has been achieved to date. In contrast to the isolated AlH_6^{3-} units in the alkali metal alanates, the octahedral units in the calcium alanate intermediate are bridged over two corners, producing polyanionic chains with the empirical formula $CaAlH_5$.[69] Figure 10 shows the helical structure of these chains. A similar structural pattern with polyanionic chains is observed in the homologous compound $BaAlH_5$.[70]

The complex boron compounds are not only hydrogen storage materials in aqueous solutions; they can be used under more rigorous conditions as a reversible storage material. In spite of the disadvantages described at the beginning of the section, boron hydrides are widely discussed as possible hydrogen storage materials because of their high hydrogen content. The overall hydrogen amount of $LiBH_4$ is 18.5 wt%, which is much higher than in the alanate systems.

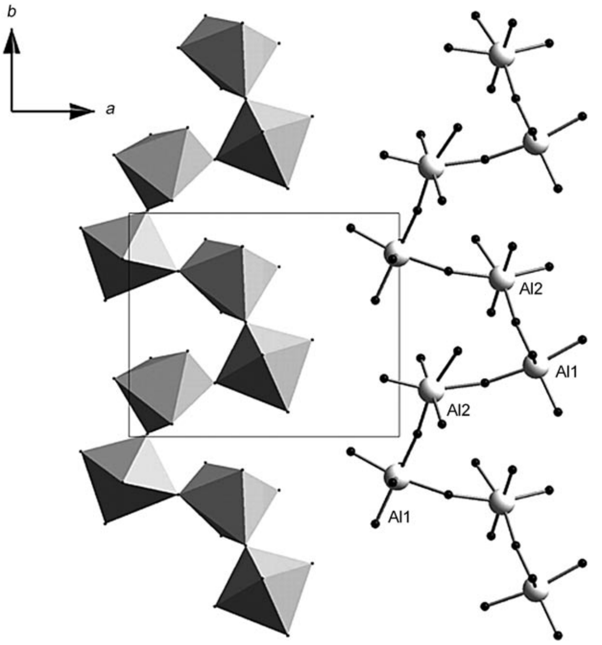

Figure 10. Structure of the corner-shared AlH_6 octahedra in $CaAlH_5$. (Reproduced with kind permission from the American Chemical Society).

Starting from a pure metal and boron, the preparation, of boron hydrides, such as $LiBH_4$, by direct synthesis is possible at temperatures between 500–700 °C and hydrogen pressures of up to 15 MPa according to Equation (13).[71,72]

$$LiH + B + 1.5\,H_2 \xrightarrow[15\,\text{MPa}\,H_2]{500\text{–}700\,^\circ C} LiBH_4 \tag{13}$$

As for the alanate systems, the ball-milling method can be used to prepare complex boron hydrides via a metathesis reaction, using $LiBH_4$ or $NaBH_4$ and the corresponding metal chlorides [Eq. (14)].[73]

$$MeCl_2 + 2\,Li(Na)BH_4 \rightarrow Me(BH_4)_2 + 2\,Li(Na)Cl \tag{14}$$

The overall decomposition reactions of boron hydrides can be described by Equation (15) and (16) for alkali metal boron hydrides, and by Equations (17)–(19) for the alkaline earth boron hydrides. Possible products of the decomposition reaction are a metal hydride and elemental boron; alternatively, the formation of an alloy may occur.

$$MeBH_4 \rightarrow MeH + B + 1.5\,H_2 \tag{15}$$

$$MeBH_4 \rightarrow MeB + 2\,H_2 \tag{16}$$

$$Me(BH_4)_2 \rightarrow MeH_2 + 2\,B + 3\,H_2 \tag{17}$$

$$Me(BH_4)_2 \rightarrow MeB_2 + 4\,H_2 \tag{18}$$

$$Me(BH_4)_2 \rightarrow 2/3\,MeH_2 + 1/3\,MeB_6 + 10/3\,H_2 \tag{19}$$

Octahedral intermediates as found in alanate decomposition are not observed in thermolysis reactions of boron hydrides. Nevertheless, in dehydrogenation reactions of $LiBH_4$ with very low heating rates, several desorption peaks were detected at different temperatures with the liberation of roughly 50 % of the hydrogen at about 490 °C.[74] From Raman spectroscopy and X-ray diffraction measurements, the existence of the boron hydride cluster $B_{12}H_{12}^{2-}$ as an intermediate of the thermolysis was concluded.[75,76] Other boron hydride clusters also probably form as intermediates of the thermolysis of boron hydride systems can be expected, but they have not yet been detected. Rehydrogenations of decomposed boron hydrides such as $LiBH_4$ can be carried out at temperatures of 400 °C and pressures of 35 MPa. The quantity of rehydrogenation products was not determined, but it was shown by spectroscopic methods that $LiBH_4$ was produced at least partially during the hydrogenation process.[77]

The thermodynamic properties of boron compounds may be altered by the addition of a second (or a third) compound. These influences are described in the Section 2.2.4.

2.2.2. Amine–Borane Adducts

Amine–borane adducts[78,79] are unique materials with a very high hydrogen content. The simple compound ammonia–borane BH_3NH_3 contains 19.6 wt % hydrogen, which can be partially delivered at temperatures of about 130 °C in a multistep decomposition process.[80–82] Because the decomposition steps are exothermic, these materials are not useable for reversible on-board hydrogen storage. An overall yield of 14 wt % hydrogen is released in two decomposition steps up to 130 °C, with borazine as end product of the thermolysis. Traces of diborane were found in the hydrogen gas, which means that the thermolysis of amine boranes is less promising for fuel cell applications.

Like $NaBH_4$, the amine–borane compounds can release hydrogen in a hydrolytic process. An interesting material for this hydrogen delivery process is ammonia–triborane $NH_3B_3H_7$, which has a hydrogen content of 17.8 wt % H_2.[83] According to Equation (20), eight moles of hydrogen can be released during the hydrolysis. The solubility in water is 33 wt %, which is slightly higher than NH_3BH_3 (26 wt %). Rapid hydrogen release can be achieved using noble metals as catalysts; rhodium compounds supported on alumina appear to be best-suited. It was reported that 6.1 wt % H_2 was released at room temperature based on materials ($NH_3B_3H_7 + H_2O +$ Rh/alumina).

$$NH_3B_3H_7 + 6\,H_2O \rightarrow NH_4^+ + 2\,H^+ + 3\,BO_2^- + 8\,H_2 \qquad (20)$$

Nevertheless, the same reservations hold for amine–boranes as for the hydrolytic routes for hydrogen storage discussed above for metals or metal hydrides. The system is comparable to the $NaBH_4$ system introduced by Millennium Cell, with the advantage of higher storage capacities, but the disadvantage of the possible breakthrough of ammonia to the fuel cell, which requires additional safety precautions and gas clean-up. For practical applications, new methods for the regeneration of the borates from aqueous solutions are also required. This process is highly energy-intensive, because the reduction of borate compounds into the amine–boranes in an aqueous solution appears to be impossible, which then requires further isolation of the boron oxide.

Upon infusion of ammonia–borane in a mesoporous silica material SBA-15, the kinetics (not the thermodynamics) of the hydrogen release can significantly be enhanced at low temperatures.[84] The incorporation of hydrogen storage materials in porous systems may alter the kinetic of desorption and absorption of H_2 of the solid-state material, but it reduces the storage capacity of such composites drastically.

2.2.3. Amides/Imides

Hydrogen uptake by Li_3N was first observed in 1910.[85] Since the rediscovery of the hydrogen storage properties of lithium imide/lithium amide systems in 2002 by Chen and co-workers,[86] amides are one of the most promising materials for hydrogen storage. Lithium nitride can absorb two moles of hydrogen according to Equation (21), producing a mixture of one mol of lithium amide and two mol of lithium hydride (described as Li_3NH_4 in reference [85]). An overall theoretical amount of 10.4 wt % H_2 is desorbed or absorbed in a two-step reaction.

$$LiNH_2 + 2\,LiH \rightleftharpoons Li_2NH + LiH + H_2 \rightleftharpoons Li_3N + 2\,H_2 \qquad (21)$$

At temperatures of up to 200 °C, 6 wt % H_2 can be desorbed. For a complete desorption of hydrogen, temperatures of up to 420 °C are necessary. Calometric measurements have shown that both desorption processes are endothermic, with a value of approximately 60 kJ per mol of H_2 for the second step. This means that the equilibrium pressure of 0.1 MPa is reached at temperatures around 250 °C, thus excluding the $LiNH_2$/LiH system for practical applications in combination with PEM fuel cells. The decomposition enthalpy of the first step is much higher, and it is therefore not useable for the rehydrogenation reaction in connection with PEM fuel cell systems. One other disadvantage of amide systems is the thermodynamically favored evolution of ammonia from the pure amide compounds at higher temperatures.[87] Since the first description of the hydrogen storage properties of amide systems in 2002, numerous research groups have dealt with these compounds. A material with a high capacity is the $Mg(NH_2)_2/MgH_2$ system, with a total of 7.4 wt % H_2 evolution during a milling process. It appears that hydrogen is released in a two-step decomposition process, with magnesium imide (MgNH) as the intermediate. Nevertheless, the low endothermic decomposition enthalpy of only 3.5 kJ per mol of H_2 excludes these systems for practical hydrogen storage systems.[88]

The reduction of the desorption temperature is one important challenge of the amide systems. For the lithium system, it was proposed from theoretical calculations that the substitution with more electronegative elements, such as magnesium cations, can reduce the temperature for hydrogen release depending on the amount of Mg^{2+} cations.[89] Indeed, it was shown that hydrogen can be released at 100 °C at a substitution level of up to 30 atom % Mg^{2+}.[90] This temperature is much lower than in the pure $LiNH_2$ system, which has decomposition temperatures of around 200 °C.

2.2.4. *Thermodynamically Tailored Systems*

One great challenge in the field of hydrogen storage materials is discovering of new reversible systems that function under technically viable conditions. In some cases, high hydrogen-containing systems are too unstable, such as $Mg(AlH_4)_2$ with 7 wt% H_2 theoretical storage capacity, or they are much too stable, as in the complex boron hydride compounds. In these cases, thermodynamic tailoring may be a possibility to stabilize or destabilize a decomposition reaction. For thermodynamic tailoring, a second or sometimes a third component is added to a hydrogen storage material, which can open up new reaction pathways with a different thermodynamics [Eq. (22)]. With the addition of MgH_2 to lithium borohydride, formation of the MgB_2 as a product provides an additional enthalpic driving force; in other words, $LiBH_4$ is destabilized. The result is a reduction of the decomposition enthalpy for the system of about 25 kJ per mol of H_2 relative to pure $LiBH_4$.[91,92]

$$2\,LiBH_2 + MgH_2 \rightleftharpoons 2\,LiH + MgB_2 + 4\,H_2 \qquad (22)$$

Extensive ab initio calculations for the prediction of the decomposition thermodynamics of metal hydride mixtures have been published in recent years.[93] After examining these hydride mixtures with high hydrogen storage capacities, other considerations, such as kinetics or cycle stability, will become crucial and must be tested in experimental work.[94] On the other hand, these calculations are a helpful support for the development of new metal hydride systems for hydrogen storage.

2.2.5. *Hydrogenation/Dehydrogenation of Liquid Hydrogen Carriers*

Some systems have been suggested that are based on the hydrogenation and dehydrogenation of cyclic hydrocarbons, such as benzene/cyclohexane, toluene/methylcyclohexane, or naphthalene/decalin. These systems are organic liquids, have a storage capacity of 7.1 wt% (cyclohexane), 6.1 wt% (methylcyclohexane), and 7.2 wt% (decalin), and all have reasonable volumetric storage capacity of between 47 and 65 $kg\,m^{-3}$. However, use of these storage media has a number of related problems. First, the temperature for a sufficiently high equilibrium conversion of the hydrogenated compound to release hydrogen is rather high (Figure 11).[95] For essentially full conversion, over 300 °C are required, and for rehydrogenation, the aromatic hydrocarbon would need to be transported back to a central facility. Moreover, a separation unit may need to be installed to avoid slip contamination of the hydrocarbon if dehydrogenation is incomplete.

Nevertheless, hydrogen supply proposals based on the dehydrogenation of cyclic hydrocarbons have been intensively discussed. However, the target application is not on-board hydrogen storage in automobiles, in which the technical problems in operating the dehydrogenation reactor would be too demanding. Rather, these systems are intended as a storage medium to buffer seasonal changes in demand and supply of renewable energy[96] or as a transport medium for a hydrogen infrastructure that would be dehydrogenated at the hydrogen filling station for fuel-cell-powered cars.[95] On board a vehicle, another technology for hydrogen storage would be required.

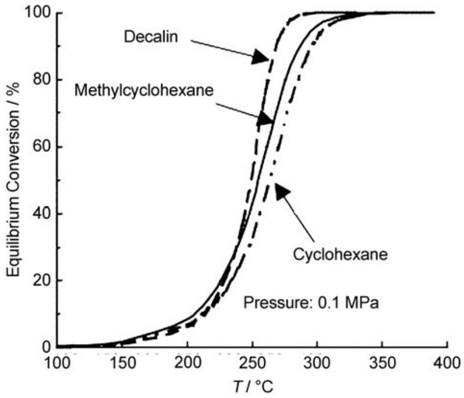

Figure 11. The temperature dependence of the equilibrium conversion for the dehydrogenation of typical organic chemical hydrides. (Reproduced from Ref. [95]).

The technology is essentially available for such applications of hydrogenation/dehydrogenation, and costs seem to be competitive compared to other hydrogen supply solutions.[95] The catalyst for dehydrogenation used to be a problem, as coke formation is always a danger in such systems. However, this problem seems to have been solved, and with a potassium-promoted Pt/γ-Al_2O_3 catalyst, stable operation at high activity and selectivity over 3000 h on-stream has been reported.[95] At a temperature of 300 °C and a storage capacity of around 7 wt%, the system competes with many other alternative storage technologies that have similar or better performance data, such as MgH_2 or the reforming reactions of other liquid hydrogen carriers, as will be discussed below.

Carbazoles and substituted carbazoles are further organic materials with potential hydrogen storage properties. *N*-Methylcarbazole stores 6.2 wt% of hydrogen, and can be used as a reversible storage material. Under the influence of a 5% Pt/Al_2O_3 catalyst, hydrogen is delivered at temperatures of about 200 °C. The dehydrogenated perhydro-*N*-methylcarbazole can take up 8 moles of hydrogen under a pressure of 5 MPa H_2. Other carbazoles and similar compounds can store hydrogen amounts in the range of 4–6 wt% H_2. One disadvantage of all the carbazole materials is their high decomposition temperature and high melting point. *N*-Methylcarbazole has a melting point of 88 °C, but decomposition and rehydrogenation is obtained only in the liquid phase. Attached substituents can reduce the melting of the compounds; for example, 9-ethylcarbazole has a melting point of 68 °C, but the storage capacity is reduced to 5.7 wt% and the material is still a solid under ambient conditions.

2.2.6. *Reforming of Liquid Hydrogen Carriers*

Hydrocarbons are currently used directly as a fuel for internal combustion engines. However, hydrocarbons could also be considered as a means of hydrogen storage with a relatively high volumetric and gravimetric storage density, the exact values of which depending on the composition of the hydrocarbon. In addition to the hydrogenation/dehydrogenation reactions discussed above, a practically more useful route are catalytic reforming reactions, which can either proceed with water [so called steam-reforming, Eq. (23)], or via a partial oxidation reaction [Eq. (24)], or as a combination of both, the so-called autothermal reforming.[97,98]

$$C_nH_{2n+2} + n\,H_2O \rightarrow n\,CO + (n+1)\,H_2 \tag{23}$$

$$C_nH_{2n+2} + n\,O_2 \rightarrow n\,CO_2 + (n+1)\,H_2 \tag{24}$$

Similar reactions can be used for the hydrogen release from alcohols, such as methanol and ethanol, but these reactions proceed at substantially lower temperatures than for hydrocarbons. Peters gives a comprehensive overview of both types of reforming reactions, and discusses the problems especially with regard to the technical implementation for mobile reformers,[99] and issues of Catalysis Today were devoted to the reforming of liquid hydrocarbons for fuel-cell applications.[100,101]

For both the reforming and the partial oxidation pathways, two other reactions are highly relevant: the water gas shift reaction [Eq. (25)], and the methanation reaction, [Eq. (26)].

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{25}$$

$$CO + 3\,H_2 \rightarrow CH_4 + H_2O \tag{26}$$

Carbon formation may be a problem, especially if it occurs on the catalyst. The carbon is formed primarily by two reactions: the Boudouard reaction, and methane decomposition [Eqs (27), (28)]. The most problematic reactions are those in which CO is formed, as CO would poison the PEM fuel cell at concentrations exceeding about 10 ppm. Complex reformate purification processes may therefore be required for practical applications. The problem could be minimized in the future, because the higher the operation temperature of the fuel cell, the higher the allowed CO concentration can be. However, for thermodynamic reasons, CO formation increases strongly with increasing temperature. As steam reforming or partial oxidation of hydrocarbons proceeds at substantially higher temperatures than that of methanol, the challenges in hydrocarbon as hydrogen carrier for PEM fuel cells are substantially higher.

$$CO_2 + C \rightleftharpoons 2\,CO \tag{27}$$

$$CH_4 \rightarrow C + 2\,H_2 \tag{28}$$

2.2.6.1. *Reforming of Hydrocarbons*

There is long tradition of industrial hydrogen production by reforming hydrocarbons. However, industrial plants are very large, size is not a critical issue, and heat management on an industrial site is therefore usually relatively straightforward. This situation is completely different for hydrogen generation from hydrocarbons in cars, in which the fuel processor system has to fit into the limited space and heat integration and avoiding heat losses in relatively small reactors is a complex issue.

In principle, any hydrocarbon could be used for reforming. However, in practice, systems have been developed for gasoline, diesel fuel, liquefied petroleum gas (LPG, mainly propane and butane), or methane (natural gas). Whereas gasoline and diesel fuel are preferred for on-board power generation in cars and trucks, LPG has advantages in leisure applications, as it is easily available as camping gas. Methane reforming seems to be most promising for stationary applications, for which the available natural gas infrastructure could be used. The specific types of reforming used for the production of hydrogen all have their specific advantages and disadvantages. Steam reforming results in higher hydrogen concentrations in the reformate (70–80 %) than autothermal reforming or partial oxidation (40–50 %). However, steam reforming is highly endothermic, and therefore requires heating. As the heat has to be supplied externally, the dynamic response of steam reforming systems is slower than for the other options, which is a substantial disadvantage. Start-up times are also typically longer than for autothermal reforming or partial oxidation. However, based on systems simulations, fuel processing efficiencies appear to be higher with steam reforming, followed by autothermal reforming, and finally partial oxidation.[102,103] The overall efficiency of any of these technologies depends crucially on optimized heat integration processes to minimize energy losses and avoid the requirement of excessive auxiliary cooling. Experimentally achieved efficiencies (lower heating value of reformate/lower heating value of the fuel entering the reformer) for the fuel processing units were reported to be around 80 %;[104–106] exact values depend on the details of the system design and on system size.

A fuel processing unit for operation in combination with a PEM fuel cell normally consists of several components, with a number of central catalytic reactors augmented by other components, such as heat exchangers, blowers, and controllers (Figure 12).[107] The fuel, mixed with oxygen and/or water depending on the reformer configuration, first enters the reforming reactor, followed by a high-temperature water gas shift reactor, a low-temperature shift reactor (in some systems more than two shift units are implemented), and finally a reactor for fine cleaning of the reformate to reduce the CO concentration to acceptable levels. The fine-cleaning unit is either a preferential oxidation reactor (PROX) or a methanation reactor. Alternatively, hydrogen separation membranes could be used at this stage, but this format does not seem to be implemented frequently. The complexity of the system and the requirement of high temperatures for some of the reactors create a severe problem, as the start-up time to reach stable operation of the system is at least several minutes. To our knowledge, the best reported value for a system that is sufficiently large to power a car is slightly less than four minutes.[107] The CO concentration in the reformate is then sufficiently low, although full efficiency of the system is only reached after about 15 minutes. This is not sufficient for practical operation, and substantial development work is required.

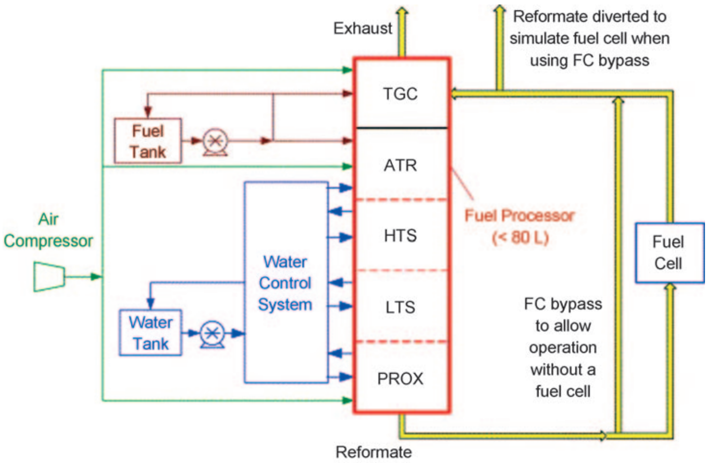

Figure 12. Representation of a fuel processor system. ATR = autothermal reactor, FC = fuel cell, HTS = high-temperature shift reactor, LTS = low-temperature shift reactor, PROX = preferential oxidation, TGC = tail gas combustion. (Reproduced from Ref. [107]).

For other types of fuel cells that are mainly used in stationary applications, which operate at higher temperatures of up to 1000 °C and are not operated under such quickly changing loads as systems for cars, less sophisticated fuel processing units are necessary: The reformer is typically sufficient, and part of the reforming reaction can actually take place in the anode chamber of solid electrolyte fuel cells itself (internal reforming).[108] The essential steps of a fuel processor system shall be discussed briefly below. Many of the issues concerning the catalytic problems in fuel processors are discussed in excellent reviews.[109–111]

The reforming reaction for hydrocarbons requires temperatures above 600 °C to reach sufficiently high equilibrium concentrations of hydrogen (Figure 13). Apart from this reason, carbon formation, which would block parts of the system and poison the catalyst, is also suppressed at high temperatures (Figure 14).

The reformer itself is thus the hottest part of the overall fuel processor unit. Many catalysts are available for the reforming reactions, but as in reforming units in industry, for the production of hydrogen for fuel cells, nickel-based catalysts are also most frequently used and perform well,[112] although monolithic supported noble metal catalysts may be an alternative.[109] Other metals, including noble metals and especially ruthenium, have been used as reforming catalysts in a number of studies and have often been reported to be superior to nickel-based systems.[113,114] However, the higher price and lower availability would probably prohibit the large scale use of such catalysts. Furthermore, activity does not appear to be the most critical issue: development should rather be targeted at higher sulfur tolerance, as the reforming catalysts are easily poisoned by sulfur (concentrations exceeding several 10 ppb are harmful for non-precious-metal catalysts[99]) and thus require a desulfurization unit. An alternative is to use a fuel that is extremely low in sulfur. As sulfur specifications of fuels are tightened, however, this problem will greatly diminish in the years to come.

The gas leaving the reformer typically has CO concentrations exceeding 10 %. Depending on the anode catalyst of the fuel cell, this concentration has to be reduced to 10–100 ppm. Therefore, strategies have to be developed to minimize the CO concentration to acceptable levels (see the review by Trimm[115]). The major part of this reduction is achieved by the water gas shift reaction, which has the added benefit that additional hydrogen is produced. The reaction is exothermic; that is, the equilibrium is more favorable at lower temperatures. Therefore, two stages are usually used, with the first operating at high temperatures of up to 400 °C, and the second at lower temperatures of around 200 °C. The water gas shift reaction has been carried out for decades on an industrial scale as part of ammonia production, which needs pure hydrogen. Thus, there is a lot of basic knowledge on the catalyst systems suitable for this reaction. However, the requirements of the shift catalyst for automotive applications are substantially different to those of an industrial catalyst. Industrial catalysts are highly pyrophoric and require careful activation,[116] both of which are not acceptable for consumer applications. Furthermore, shift catalysts for automotive applications have to tolerate strongly changing load conditions and must be stable against condensation of water in the system; both points are not valid for the conventional Cu/Zn-based catalysts. Noble-metal-based systems can partly minimize this problem, but the high costs are a clear disadvantage. Nevertheless, noble-metal-based catalysts have also been commercialized, both for the high-temperature shift and the low-temperature shift stage.[117] Other base metal catalysts for the

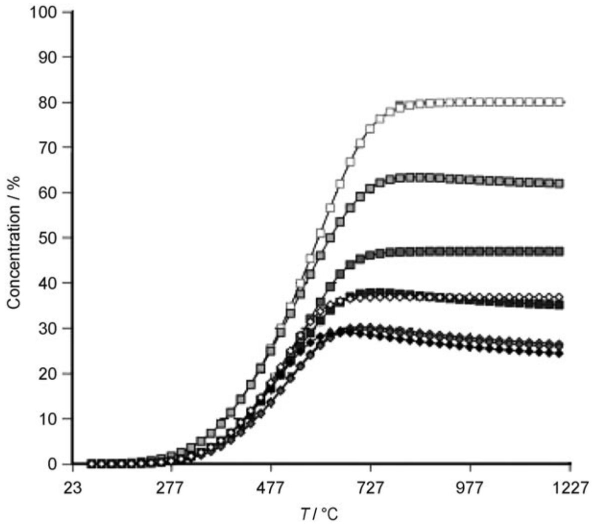

Figure 13. Temperature dependence of H_2 and the sum of the H_2 and CO concentration for different reforming processes of hydrocarbons at chemical equilibrium and at 0.2 MPa. Steam reforming (SR) $H_2O/C = 2:1$, autothermal reforming (ATR) $H_2O/C = 2:1$, $O_2/C = 0.45:1$. □: SR of CH_4 (H_2 and CO); ■: SR of CH_4; ◇: ATR of CH_4 (H_2 and CO); ■: ATR of CH_4; ■: ATR of C_8H_{18}; ◆: ATR of $C_{14}H_{30}$; ◆: ATR of diesel fuel (H_2 and CO); ◆: ATR of diesel fuel. The sum of the H2 and CO concentration is given because a subsequent CO conversion reactor can produce additional hydrogen according to Equation (25). (Reproduced from Ref. [99]).

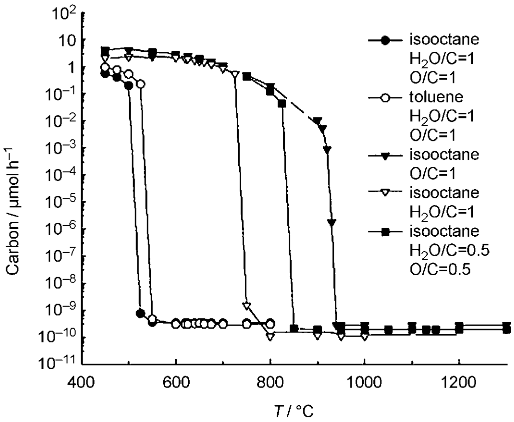

Figure 14. Reaction temperatures required to prevent the formation of carbon for several hydrocarbons and reaction gas compositions. (Reproduced with kind permission from Ref. [112]).

low-temperature shift stage have also been developed that avoid the problems of the Cu/Zn system in particular that is used for the low-temperature shift reaction.[116,117] Nanocrystalline ceria seems to be an interesting support for noble metals (Au, Pt) and copper in shift catalysts that are useful for fuel processors, as they are not associated with some of the problems of the Cu/ZnO catalysts.[118–120] However, under practical conditions, cerium carbonate formation was found to be a severe problem.[109]

After the reformate leaves the shift reactors, it has a typical CO concentration below 0.5%, which is still far too high for the PEM fuel cell. Therefore a fine cleaning is necessary, for which there are several options.[121] This cleaning is usually carried out by PROX. This reaction poses a substantial challenge however, because very small amounts of CO have to be oxidized in the presence of more than 65% of H_2, which is also easily oxidized. Moreover, the reverse water gas shift reaction and methanation have to be prevented as well. Fortunately, CO is much more strongly adsorbed on many transition metals than H_2, and thus selectivities for CO conversion exceeding 50% are routinely reached, and sometimes even values substantially above 90% were reported.[99] Numerous catalysts are known for the PROX reaction, but those most frequently used are platinum-based[122] with certain promotors, or ruthenium-based[123–125] catalysts. Although the latter has a clear cost advantage over the platinum systems, a problem is activity of ruthenium for methanation and its instability against start-up/shut-down cycles. Moreover, an ideal PROX catalyst to be operated in connection with a PEM fuel cell should have its operating window close to the temperature level of the fuel cell of around 80 °C, whereas ruthenium typically needs substantially higher temperatures of about 150 °C, thus requiring additional cooling. Gold-based catalysts have also been investigated,[126] but they do not seem to be the material of choice in industry. There are also a number of base metal oxides with appreciable activity in PROX;[127,128] some of which, such as Cu/CeO_2, appear to be quite promising.[129]

Considering the different units necessary in a fuel processor for reforming of hydrocarbons, it is no surprise that to date no unit capable for storing and delivering hydrogen for a car has been developed. In fact, in the USA and in most other countries, all efforts for the development of such systems have been terminated,[130] although some groups are still active in this field, with substantial progress being made.[105]

Currently, it appears that fuel processor systems would be insufficiently rugged and error-tolerant enough to be used to supply the hydrogen cars running on fuel cells on a large scale: the main concerns for practical implementation are the high volume and weight requirements of such systems, the required energy for start-up, and the start-up times. There is certainly still room for improvement; as at least four catalytic reactors are required, which have high space requirements, a substantial increase in catalyst activity would allow the system size to be reduced. Furthermore, if more CO-tolerant fuel cells become available, it may be possible to omit one shift stage or the PROX-unit, which would again lead to lower system size and weight. However, the catalysts are already developed to a very high standard and further progress without compromising other considerations, such as durability or cost, will be very difficult.

The engineering aspects of the system may also help to reduce size and weight. The reforming catalyst in particular is usually not kinetically limited but rather heat-transfer limited owing to the highly endothermic nature of the process.[109] Better heat exchangers could thus help to reduce the size of the reactor. Suitable monolithic and microstructured reactors are known for their excellent mass and heat transfer behavior, and thus they have been increasingly explored as a reactor configuration in the reforming stage. Ideally they would be built as cross- or counter-flow heat exchanger in which the endothermic reforming reaction would proceed in one channel system and an exothermic reaction in the other,[131–133] for instance the catalytic combustion of the anode off-gas, which needs to be carried out anyway. As attractive as such options appear, they have not yet made it beyond the laboratory scale, possibly owing to the limitations posed upon the system by the need to match both reactions ideally to each other at different temperature and load conditions. Moreover, most teams who have worked on fuel processor systems for cars prefer the autothermal reforming, because it has a better start-up characteristic and superior dynamic behavior.

Although reforming of hydrocarbons does not seem to be a highly promising way to supply the fuel cell for the power train of cars, there is a substantial work done on smaller units, such as auxiliary power units (APUs) for cars,[134] or as remote power source, for example in camping or boat applications. Such systems deliver from several hundred to 5 kW, and close-to-commercial units for use with LPG are available.[135] In such applications, noiseless operation is a clear advantage over other power supplies, such as diesel generators, and the higher power density of the system is an advantage over batteries. It can therefore be expected that hydrogen supply for powering PEM fuel cells from smaller scale fuel processing units based on hydrocarbons will eventually find their way into the marketplace.

2.2.6.2. Reforming of Methanol

Reforming of hydrocarbons is technically extremely challenging. It has been vigorously pursued, however, because it can be based entirely upon existing infrastructure and could thus allow a smooth transition to a hydrogen-based energy infrastructure. Methanol reforming is certainly not technically simple, but it is not as difficult as the reforming of hydrocarbons. On the other hand, the infrastructure is completely lacking, which is as big a hurdle as the technical problems in hydrocarbon reforming, and maybe even bigger.

One clear advantage of methanol over hydrocarbons for use as the hydrogen carrier in a reforming unit is the substantially lower temperature needed for methanol reforming (circa 250–300 °C).[136] Furthermore, in this temperature range, the steady-state CO concentration is about 1% or lower (equilibrium concentrations are somewhat higher, depending on temperature).[136] This means that it could be possible to operate the fuel processor without a shift stage, that is, include only the reformer and the PROX stage, which allows a much more compact design of the whole unit. Catalysts for this reaction are well developed; they resemble the $Cu/ZnO/Al_2O_3$ systems also used for methanol synthesis. This is understandable, as methanol steam reforming can be considered as the reverse reaction of methanol synthesis, which on the molecular level proceeds from CO_2, and not from CO. However, CO is continuously converted into CO_2 in the synthesis reactor via the water gas shift reaction.[137] There is still some controversy about the actual mechanism and the decisive steps involved, but the majority of research groups seem to favor the direct reforming pathway instead of coupled decomposition of the methanol/water gas shift reaction.[136] The mechanism is of interest, though, as the reaction pathway would determine the mode of the formation of the undesired CO, which is always present in the reformate below the equilibrium concentration at the corresponding temperatures.

Although $Cu/ZnO/Al_2O_3$ are presently the catalyst materials of choice, other oxides have been explored as additives as well, predominantly ceria and zirconia; both have been observed to reduce CO formation[138,139] and to stabilize the catalyst.[138,140,141] Other metals have also been studied as catalysts, and Pd/Zn alloy systems were found to be promising. These systems produce less CO than expected from equilibrium considerations, and they are more stable at higher temperatures and not pyrophoric, in contrast to the $Cu/ZnO/Al_2O_3$ system.[136]

The CO fine-cleaning of the reformate leaving a methanol steam reformer does not need the water gas shift stage, because the CO concentrations are at a level that is acceptable for direct feed into a PROX reactor. The same considerations hold as for the PROX stage as the last step of the hydrocarbon fuel processor (see Section 2.2.6.1).

From a systems point of view, methanol steam reforming appears to be superior as a hydrogen supply option over hydrocarbon steam reforming or autothermal reforming owing to the much lower temperatures required and the higher hydrogen yield. This is probably also the reason why one of the earlier cars that ran on a fuel cell, the NECAR III by Mercedes, was equipped with a methanol fuel processor hydrogen supply.[142] However, the development of fuel processors based on methanol for application in cars has been discontinued for the general problems described in Section 2.2.6.1 and because installation of an additional methanol infrastructure for such systems does not seem to be feasible.

In other smaller power applications, there appears to be a market for methanol as a hydrogen storage medium from which the hydrogen is released by reforming, and especially in low-power applications, such as portable devices and APUs. This requires a high degree of integration, and thus this is the field in which a number of microstructured reformers have been designed and built. Discussing these approaches in detail would exceed the scope of this Review, but there are several recent reviews available that cover such aspects thoroughly.[136,143,144] It should be kept in mind, though, that use of the methanol in a direct methanol fuel cell (DMFC) is an alternative to reforming and conversion in a PEM fuel cell; despite the lower power density of the DMFC, such systems may be preferable and are thus already on the market.[145]

2.2.7. Miscellaneous

2.2.7.1. Glass Microspheres

Glass microspheres, or glass microballoons, appear as a highly interesting hydrogen storage material on first sight. Many glasses have higher tensile strength than steel and a lower density, and thus glass should in principle be an interesting container material for hydrogen. Especially if small hollow spheres with sub-millimeter diameter are used, the walls can be made very thin and still withstand high pressures,[146,147] thus allowing theoretical gravimetric storage capacities to be reached that exceed 20% or even 30%, depending on the diameter and ratio between wall thickness and sphere diameter and the loading pressure.[146]

Closer investigations reveal that the volumetric storage capacities are unsatisfactory at below $40\,kg\,m^{-3}$ per sphere. Even this value is optimistic, as random sphere packings have packing densities of slightly above 60%,[148] which reduces the volumetric density further. Moreover, the materials have to be filled at high temperatures to allow sufficiently fast diffusion through the glass walls. As the maximum allowable pressure is governed by the loading temperature, the theoretical storage density at room temperature cannot be achieved, as the pressure decreases upon cooling. Furthermore, hydrogen release at sufficient rates, high temperatures are required that exceed about 250 °C (depending on the exact material parameters and sizes), which creates additional problems during use. Although doping of glasses has been proposed to allow infrared-radiation-enhanced diffusion,[149] the overall disadvantages, such as low volumetric capacity and kinetics and the necessity to handle solids, will probably prevent technical applications of such systems.

2.2.7.2. Ice Hydrates

Many gases can form crystalline hydrates in which large amounts of gas can be occluded in water clathrate cages. The most well-known system is the methane hydrates present on the floor of the oceans and in permafrost soil.[150,151] Many different gases, including hydrogen, can be occluded in the different cages present in the ice hydrates.[152] Somewhat more serious consideration of gas hydrates as media for hydrogen storage started with a discovery by Mao et al.,[153] who found that hydrogen and water crystallized to the sII hydrate at pressures of around 200 MPa and temperatures below −20 °C. As the cages of the clathrate are multiply occupied in this compound, the storage capacity was 5.3 wt %. The required pressure of 200 MPa is obviously too high for practical consideration, but it was found that THF as a second guest compound lowers the pressure necessary to stabilize the hydrate to 5 MPa around the freezing point of pure water.[154] However, as the THF fill the large cages of the sII hydrate, the gravimetric storage capacity is strongly decreased for the co-crystal. The capacity can be increased to some extent by tuning the THF content (about 4 % at 120 MPa and slightly above the freezing point of pure water).[155] Because storage in the form of hydrates provides a storage technology based on non-toxic, non-flammable and non-corrosive materials, this may appear as a highly promising route forward. However, the obstacles are also severe: the capacity remains too low, and with the known clathrate structures, one can not expect to increase it substantially, that is, new clathrates would need to be discovered. Furthermore, the material has to be constantly cooled, because otherwise the clathrates could decompose and rapidly release high amounts of hydrogen. Moreover, the kinetics of clathrate formation remains a challenge. Thus it appears that for the time being, such systems are fundamentally interesting and fascinating, but practically of little relevance.[156,157]

Table 2: Comparison of hydrogen storage systems for mobile applications.[a]

	System volumetric density	System gravimetric density	Refilling	Costs	Temperature range
Physical storage systems					
cryogenic H_2	0	0	+	0	−−
35–70 MPa pressure	0	0	++	0	++
cryo-adsorption	0	0	+	0	−
ambient adsorption	−−	−−	+	0	++
Reversible hydrides					
MeH_x	0	−−	0	−	+
MgH_2	0	−	+	−−	−−
complex hydrides	0	0	0	−	0
Miscellaneous systems					
NH_3BH_3	+	+	−−	0	0
hydrolytic hydrides	−	0	−−	−	++
Reforming[b]					
hydrocarbons	0	0	++	++	−−
MeOH	0	0	++	++	−

[a] Qualitative evaluation of the relative performance properties of the systems, with ++, +, 0, −, − (++ best, −− worst). [b] Only considered for portable or stationary applications.

3. Outlook: Which Routes are the Most Promising?

If the options for hydrogen storage discussed above are considered, it is obvious that no technology has yet reached a satisfactory level of performance. Prototype fuel-cell-powered cars today are based on high-pressure storage, but the space and weight requirements do not seem to make this option highly attractive.

A rough comparison of the different hydrogen storage methods for mobile applications with a PEM fuel cell is given in Table 2. Such a system would use the waste heat of the fuel cell for the decomposition or heating up of the storage systems together with the storage material. For all systems in which hydrogen storage and release is not nearly thermoneutral, heat management is a crucial issue. If short refueling times are desired, the heat exchanger must have a capacity of some hundred kW if the enthalpy of hydrogenation is in the order of 40 kJ per mol of H_2. This poses severe engineering problems and limits the use of some of the technology options.

For large volume storage, liquid hydrogen is probably the most promising option, as evaporation losses are not a severe problem under such conditions. For smaller-scale storage applications, such as in cars, pressure storage as used today appears to be the best solution, but this may change with possible advances in the other technologies. Reforming solutions do not seem to be able to reach the performance targets set for transportation applications, although they may play a role in hydrogen supply for APUs and the leisure sector. Adsorptive storage on high-surface-area materials has already reached a state which comes close to the limits expected from physical considerations, and thus it is improbable that much more progress can be achieved in this field. Advances of solid hydrogen storage materials based on hydrides are difficult to predict. Chemically, it appears that higher storage capacities can be achieved. The thermodynamics of these systems are not known at present, and the same holds for the kinetics. This is certainly a field where the exploration of possible storage materials still is worthwhile and promising materials may be discovered. Solid-state materials do have the potential to outperform physical methods of storage, such as cryostorage or high-pressure technologies. However, on a shorter time scale, these latter technologies seem to be the ones closest to practical large-scale applicability. Although this review focuses mostly on experimental studies into hydrogen storage, theoretical investigations have made great progress over the last years and may develop into a highly valuable tool to guide the search for new hydrogen storage options and new materials.[158–160]

As in all energy technologies, the whole system has to be considered, and not one particular element of the technology chain exclusively. This approach means that some of the disadvantages of the physical storage technologies for automotive applications no longer seem to be so severe. For example, for liquid hydrogen, the energy consumption for liquefaction was quoted as one of the most important problems. It has to be kept in mind, however, that the hydrogen has to be supplied in an infrastructure chain. If this infrastructure is based on liquid hydrogen, then there would not be an additional liquefaction step for fuelling a car, and there would not be an additional energetic penalty. However, if liquid hydrogen would be the infrastructure of choice, then great research efforts should be invested in technologies to recover the energy used in the liquefaction step. This would most probably be not viable in a car, but considering the filling station this could make sense; the overall system balance would then change for the better again.

This simple consideration shows that a sound prediction of the best future system is very difficult, as “best” may depend on progress in different technology sectors that only bring their full force to bear in combination. Thus the best course of action for scientists and engineers seems to be to simultaneously follow those leads that are not completely ruled out by fundamental physical reasons or technological problems which currently appear insurmountable.

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