Chapter 5

Hydrogen Storage for Mobile Application: Technologies and Their Assessment

Lars Baetcke and Martin Kaltschmitt
Hamburg University of Technology (TUHH), Institute of Environmental Technology and Energy Economics (IUE), Hamburg, Germany

5.1 INTRODUCTION

For the development of modern transport systems fulfilling the demanding greenhouse gas (GHG) reduction goals stated in the Paris Agreement of late 2015, it is necessary to think about new technologies and innovative concepts to power vehicles. Besides the contractually agreed and accelerating necessity to contribute to a significant reduction of greenhouse gases, such a development would also help to substitute for finite fossil fuel energy, in which most of the countries around the globe are very much dependent on imports. Thus, fossil fuels cannot be a substantial part of a sustainable transportation system.

One promising technological concept that fulfills the demands outlined above is the use of hydrogen in combination with fuel cells and electric engines. Compared to battery electric vehicles, such an approach has the advantage that hydrogen cars could be operated for much longer distances without a refueling stop. But such a hydrogen-based mobility concept will only be successfully implemented within the existing mass market if hydrogen can be stored safely, quickly, and in a technically mature, economically efficient, and environmentally friendly way. For this reason, mobility concepts based on hydrogen depend directly on the availability of storage options fulfilling these requirements.

Thus, all frame conditions set by national governments, as well as the international community of states, point to a mobility system based on electric vehicles in the years to come. Therefore, the combustion engines used today within cars and trucks will most likely be phased out in the years to come due to this transformation within the mobility sector. For the resulting future mobility concepts characterized by much lower GHG emissions, the still open question is in which form the necessary energy will be transported. Promising approaches are

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electrical energy stored in batteries or hydrogen as an energy carrier. The most important difference between these two technologies is the energy storage and, depending on the option chosen, the subsequent conversion into mechanical energy to realize motion.

In battery electric cars, the energy is stored in the form of electricity within an accumulator. Thus, the energy can be used directly by the electric power train of the car. In comparison, a fuel cell electric vehicle needs more energy conversion steps before the energy can be used for propulsion. First, hydrogen as a secondary energy carrier is produced within a stationary process from electrical energy. Hydrogen needs then to be stored, for example, at a hydrogen refueling station, until it is needed. From this stationary storage, hydrogen is transferred to storage located within the hydrogen vehicle. During vehicle motion, and thus depending on the given energy demand, this stored hydrogen is used within a fuel cell where it is again converted into electricity to provide the power demanded for the electric car.

Crucial for both options are the storage safety, storage density, storage capacity, storage losses, storage weight, storage costs, and other characteristic figures defining the storage of hydrogen or electricity. These aspects have to be solved in a competitive way on the market. In the longer term, systems are needed that are affordable by basically all customers and that can compete with the existing solutions based on fossil fuel energy. The system characterized by the lowest specific cost, the highest energy density, and other important technical, systemic, economic, environmental, and social points specific to the application, will be implemented within the mobility sector in the years to come to fulfill the GHG reduction goals. Thus, it may be possible that different solutions for different sub-segments could become market mature (e.g., battery electric vehicles for local personal mobility and fuel cell vehicles for supra-regional light duty traffic).

Against this background the overall goal of this chapter is it to present and to analyze the technical possibilities for hydrogen storage, especially for mobile applications (Fig. 5.1). Hydrogen storage is possible in pure form by applying physical effects (compression, liquefaction) or material-based effects (e.g., reversible chemical reaction with solid or liquid materials, physisorption with highly porous materials, for example, metal organic framework (MOF)). All the respective technologies are explained and categorized below. Finally, a short outlook on the possible use of each technology is given. By assessing and comparing the various solutions it will be seen that many of the described technologies are still within an early research and development (R&D) phase and, so far, they are not market ready. This fact makes a scientifically sound comparison very difficult.

5.2 HYDROGEN STORAGE IN PURE FORM

Storage of hydrogen in pure form includes all storage options in which hydrogen is stored directly without any interaction with other materials in any chemical

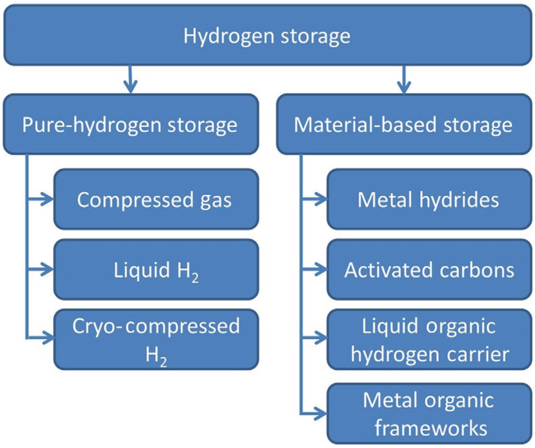


FIG. 5.1 Hydrogen storage options.

and/or physical way. Therefore, these options are typically relatively simple. The complexity, and thus the technical challenge, of these storage vessels lie in the tank design, and especially in the tank shell, as well as in the pretreatment of hydrogen. These kinds of storage options are mostly comparable with storage possibilities for many other liquids and/or gases.

So far three different hydrogen storage concepts exist for pure hydrogen: high-pressure storage, liquid storage, and cryo-compressed storage. Below these three options are explained in detail.

5.2.1 High-Pressure Storage

The storage of hydrogen in high-pressure vessels of varying size is currently the most widely used technological approach. In nearly all mobile applications that are commercially available, or that will be introduced into the market during the months and years to come, hydrogen is stored in high-pressure tank systems with a pressure level of up to 700 bar. Therefore, it is important to look more precisely at the design of such hydrogen high-pressure storage tanks.

Basically, high-pressure storage tanks for hydrogen are similar to other high-pressure gas storage tanks. Additionally, more or less all high-pressure hydrogen storage tanks available on the market or under development have basically the same main components. They have a valve, a tank shell made out of different materials to withstand the high pressure, and they have to be gas tight and have enough free space for containing hydrogen. High-pressure storage tanks are available in two different shapes (cylindrical and spherical); these shapes deal with the forces resulting from the high stresses inside the tank shell in a most efficient way.

One advantage of such high-pressure tanks is that no complex thermal management is necessary. Additionally, the weight of the storage tanks is not too high. Also, no other problems, such as chemical reactions inside the structure, typically occur. In addition, there are no losses during long parking times, because the storage tanks operate at ambient temperature (pressure does not change over time). The only significant disadvantage is the high operating pressure and the resulting demands on the strength of the tank materials. Nevertheless, experience shows the pressure is typically manageable from a technical point of view. However, such high pressure levels are also a severe safety problem. Therefore, a lot of effort is put into ways to protect the pressure vessel in case of an accident. All that effort has led to storage tanks in which an explosion is nearly impossible, even under very challenging conditions.

5.2.1.1 State of Technology

The state of the art for hydrogen storage tanks are CFRP-tanks (Carbon Fiber Reinforced Polymer) with a pressure level of 350 or 700 bar. The assembly of such a tank is explained in more detail below.

One very important design aspect for such high-pressure storage tanks is to ensure that hydrogen cannot diffuse out of the tank over time. For this reason, typically, a thin and absolutely gas-tight liner is placed inside of the CFRP shell. Thus, the CFRP shell only compensates the stresses resulting from the high pressure and does not guarantee a gas-tight system.

Such high-pressure tanks for hydrogen storage are typically divided into four different categories.

- The first category of tank (type I) is made out of steel only; that is, they can achieve a pressure level of around 200 to 300 bar.
- The second category of tank (type II) is made out of steel combined with carbon fiber reinforced plastic wrapped around the cylinder. This design approach makes the storage tank a bit lighter compared with type I. Additionally, the energy density, as well as the pressure of the storage tank, may be increased.
- The third category of tank (type III) is a cylinder made out of CFRP or GFRP (Glass Fiber Reinforced Polymer). This material is strong enough to withstand the stresses due to the high pressure. Inside the storage tank is a thin liner made from steel and/or aluminum to guarantee the gas-tightness. These storage tanks usually operate at a pressure of 350 bar.
- The fourth category of tank (type IV) is similar to the type III tanks. The difference is the liner inside the tank, which is made out of polymer, and the tank shell, which is always made out of CFRP. The consequence is that the storage tank is lighter again and can withstand a pressure of 700 bar. Thus, type IV tanks are usually used in modern vehicles (Mori and Hirose, 2009).

CFRP type IV high-pressure tanks are not a fully developed technology yet; a continuous improvement realized by different companies and research groups can be observed. Nevertheless, the solutions available already are quite advanced.

One example typical of several other approaches is presented in Fig. 5.2 (Nonobe, 2017), showing a pressure tank with a relatively high energy density for the overall tank system. The standard structure of such a CFRP type IV tank has three different layers. The inner layer is a plastic liner that seals the tank. After that the CFRP shell functions to withstand the stress that results from the pressure level inside the tank. This is also the layer in which weight reduction is realized by optimizing the structure of the single carbon fiber layer. The last layer of the storage tank consists of GFRP for safety reasons, as the function of this layer is to protect the storage tank from outside mechanical loads (e.g., events like a rock fall or other external impacts). Additional safety features for impacts or car accidents consist of two protectors that mainly protect the tank shell against dropping. In addition to the tank shell, there are also two aluminum fittings or bosses, which allow the implementation of valves required for the refilling and the safety blow-off.

There is also the possibility to implement sensors inside the tank to measure pressure and temperature (Nonobe, 2017). These sensors are necessary, because such high-pressure storage tanks show a clear temperature increase during loading with high pressure, especially at fast loading. According to international regulations and the material characteristics, the temperature limit for CFRP tanks is defined to be 85°C (Simonovski et al., 2015). To fulfill this requirement securely hydrogen is precooled at the fueling station to a temperature of –70°C. Under these conditions, the limits defined above can be met, thus allowing a comfortable refilling time.

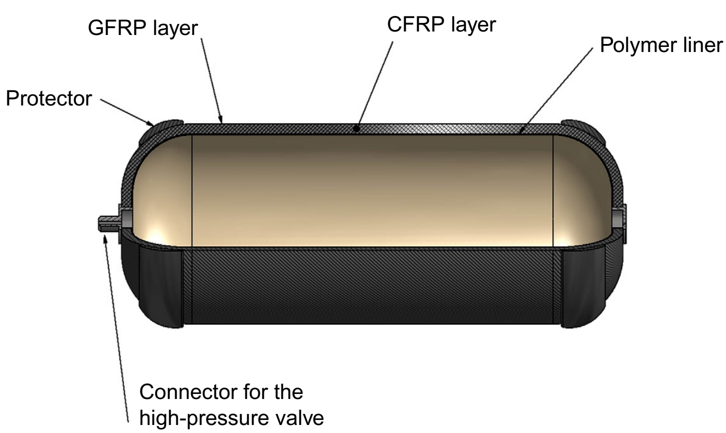


FIG. 5.2 CFRP-Tank Type IV for the use in cars. *(Based on Nonobe, Y., 2017. Development of the fuel cell vehicle mirai. IEEJ Trans. Electr. Electron. Eng. 12 (1), 5–9.)*

Besides lightweight design, the safety issues of hydrogen pressure storage tanks are an important issue. Therefore, different standards (e.g., ISO/TC 197) already exist that define and regulate selected parts of hydrogen supply, hydrogen storage, and other hydrogen-related components. All the tanks available so far do meet these challenging requirements.

If the pressure increases above the design pressure, safety valves (overpressure valves) react and blow off part of hydrogen in a controlled and predefined way. In comparison to "classical" fuel (e.g., gasoline) the fact that hydrogen is much lighter than air is a clear advantage. The consequence of this physical property is that hydrogen that gets outside the tank just disappears and does not lead to a dangerous atmosphere around and beneath the car. Also, in case of fire, hydrogen is much safer than liquid fossil fuels (e.g., gasoline, diesel fuel) because hydrogen released by the blow-off valve leads to one single flame of burning hydrogen. This is in contrast to "classical" liquid transportation fuels in which a big fire on the ground below the car occurs when gasoline or diesel tanks leak in an accident.

5.2.1.2 Characterization

The tank material used and the realized pressure level of the storage tank depend on the application it is designed for. For the mobile application assessed here, typically various types of compound materials (e.g., Glass Fiber Reinforced Polymer (GFRP) or Carbon Fiber Reinforced Polymer (CFRP)) are used for the tank shell. The two most common versions are CFRP storage tanks with 350 or 700 bar pressure, depending on the application.

The compression of hydrogen up to a pressure of 700 bar consumes around 18 MJ/kg_{H2}. This equals approximately 15% of the lower heating value of hydrogen. Thus, the cost of such high-pressure storage is typically relatively high, on account of losses as well as the compression. This results in an overall Well-to-Fuel Cell efficiency for the 700-bar tank of 54% and for the 350-bar tank of 56%. Therefore, this storage approach is already close to the ultimate DOE goal of 60%.

Storage costs also depend on the pressure level of the tank. On average a storage system with 700 bar costs roughly 20 US$/kWh. In comparison, a storage system with 350 bar is slightly cheaper, costing approximately 13.4 US$/kWh. The refueling rate sums up to 1.5–2 kg_{H2}/min for both pressure levels (Ahluwalia et al., 2010).

5.2.1.3 Markets and Perspectives

During implementation within the automotive market, a clear path for each of the two pressure levels outlined above can be seen. Currently cars are commonly equipped with storage tanks of approximately 700 bar because they show a higher energy density compared with storage tanks with a lower pressure. Such a high energy density is typically a clear advantage, especially in cars where space is very limited in most cases. In contrast, busses have mostly more available room. Therefore, it is easier to implement 350-bar storage tanks within such vehicles (e.g., on the roof). The resulting advantage is that such a “low-pressure” storage tank can be loaded more quickly and easily than the 700-bar tank. Additionally, a 350-bar storage tank shows overall better efficiency due to the lower pressure level. And, last but not least, the 350-bar storage tanks are typically slightly cheaper.

Thus, it is most likely that pressure tanks with the two pressure levels of 350 and 700 bar will remain on the market in the years to come. This is mainly due to the experience that has already been gained and the fact that the management of compressed gases is common within industry.

5.2.2 Liquid Hydrogen Storage

Another option to store hydrogen with high energy density is to store it in the liquid phase. For purely technical reasons there are a lot of benefits in dealing with liquids instead of compressed gases. However, the challenge with hydrogen is that it condenses at a very low temperature. Thus, such a storage concept can only be realized by guaranteeing sufficient cooling and re-gasification capacity at the entry into, and the exit from, the actual hydrogen storage tank. Even with these infrastructural challenges, some mobility concepts are based on liquid hydrogen. Therefore, this option is discussed in detail below.

5.2.2.1 State of Technology

Due to the physical characteristics outlined above, liquid hydrogen needs to be stored constantly below 20 to 30 K. Thus, one of the most important parts of such a liquid hydrogen tank is the insulation, which is needed due to the high temperature difference between inside and ambient conditions. Thus, for efficiency reasons, a tank design is chosen with a low surface-to-volume ratio because the thermodynamic losses depend directly on the surface area to the ambient environment. Therefore, nearly all liquid hydrogen storage tanks have a spherical shape. Additionally, some, especially smaller liquid storage tanks for mobile applications, have a shape that is a mix between a sphere and cylinder because this shape may be much better integrated within the design of a vehicle. Around the storage volume super insulation is assembled out of a combination of evacuated space and aluminum foil. The overall goal of such a design is to keep the convection losses, as well as the radiation losses, as low as possible. The possibilities are basically defined by the available technologies, as well as techno-economic constraints. Additionally, components, such as valves, heat exchangers, safety features, and measuring instruments, are needed. A system is also needed to take care of the boil-off losses. If such a tank is used within a vehicle that requires gaseous hydrogen as a fuel, there are some options to use the gas instead. But most times it is released to the atmosphere.

Thus, technological solutions are under development to make use of these boil-off losses. One option is to burn the gaseous hydrogen in a continuous process. Another possibility is to store this hydrogen gas within pressure storage that is able to deal with higher temperatures. There are also some concepts that use a part of the energy of the blow-off hydrogen to liquefy hydrogen again to minimize the losses (Schlapbach and Zuttel, 2001; Hirscher, 2010). So far, all these concepts are still very expensive and increase the overall cost of the storage.

Liquid storage is characterized by a considerably higher storage density than compressed hydrogen. Additionally, the volumetric storage density is in the same range, or even a higher range, compared to hydrogen storage in metal hydrides. This high energy density of liquid hydrogen is also the reason that it is still discussed as a storage option for some airplanes. But this clear advantage is realized at the expense of the need for around one-third of the stored hydrogen energy to be devoted to the operation of the cooling device to provide a liquid state. Another disadvantage is that, so far, there are no technically feasible possibilities to build a storage tank that can store the liquid hydrogen for more than a couple of days without considerable loss. This is due to the high temperature difference between the liquid hydrogen and the ambient temperature; this temperature difference might come to 275 K, or even more in the summer. Thus, some of hydrogen necessarily vaporizes, resulting in a rising pressure level within the tank. After reaching the maximum pressure, it is necessary to blow off the gaseous hydrogen to allow for ongoing safe storage. Currently this blow-off gas is released into the ambient atmosphere. Therefore, a vehicle equipped with such a liquid hydrogen storage tank is not allowed to be parked within a parking garage. The reason is that the blow-off gas can form an ignitable mixture with the surrounding air and there might be the danger of explosion. Another consequence of the permanent boil-off losses is that the storage tank will become empty after a time (depending on the storage concept and storage design). Thus, it is necessary to refill vehicles equipped with such a tank regularly, even if they are not being used. For this reason, this storage concept is most efficiently used for commercial applications with a constant demand and a clearly predictable use (e.g., commercially operated vehicles like planes, trains, ships, trucks) because these applications typically have a constant hydrogen need that can be planned ahead. Thus, this storage option is most suitable for applications characterized by a high energy demand and a need for high energy densities.

5.2.2.2 Characterization

The main consequence of the liquefaction of hydrogen is the significantly higher density of 70.8 kg/m^3 compared with hydrogen at standard conditions with 0.09 kg/m^3. Based on this significant difference, the resulting benefit for the required storage volume becomes obvious. But on the other hand, very challenging conditions are needed to provide hydrogen in a liquid phase. The temperature has to be between 20 and 30 K, because the triple point of hydrogen is 32 K (above this temperature hydrogen is always gaseous). The pressure typically realized for such a storage facility is in a range between ambient pressure and 6 bar (Schlapbach and Zuttel, 2001; Hirscher, 2010).

Liquefaction needs about 35% of the energy stored inside hydrogen; that is, the storage efficiency is around 22.3%. The system storage capacity has a gravimetric value of around 7 wt% and a volumetric value of 0.04 kg_{H2}/l. Liquid hydrogen can be transferred to a suitable tank with a speed of 1.5 to 2 kg_{H2}/min. But so far, no commercial application of this is available on the market. Thus, there are no reliable cost estimates, but it is expected that the cost for such storage (liquefaction, storage, re-gasification) exceeds the cost of a high-pressure storage, even at a pressure level of 700 bar and above (Hirscher, 2010; Paggiaro et al., 2010a; Emonts and Stolten, 2016a; Ahluwalia et al., 2010; Stolten et al., 2016).

5.2.2.3 Markets and Perspectives

The technology for the liquefaction of hydrogen has been proven in space applications (e.g., the Space Shuttle and Ariane rocket are fueled with liquid hydrogen). Therefore, it is possible to use this technology for some very specific applications (where costs do not play a major role). But for the time being, liquid hydrogen storage is not seen in the mass market for cars or other privately used technologies. Even if some automobile companies have developed such storage systems for passenger cars and performed many expensive tests, it is not expected that this storage option will be seen within the broader mobility market in the years to come. Additionally, the spread of this type of storage tank is also not supported by the fact that the refueling stations under operation and/or under construction are designed basically only for the provision of high-pressure hydrogen. So far, the most promising application for liquefied hydrogen is its use as a fuel for airplanes equipped with hydrogen turbines.

Overall there is limited scope for the storage of hydrogen in a liquid form. But when liquid hydrogen is used, most likely it will only be economically feasible for large amounts of hydrogen to minimize the boil-off losses (that is, to minimize the surface-volume ratio) (Klebanoff, 2013; Schlapbach and Zuttel, 2001).

5.2.3 Cryo-Compressed Hydrogen

Cryogenic hydrogen can also be stored under pressure; this option is called cryo-compressed storage. Besides the storage of liquid hydrogen, this is a storage option characterized by a relatively high volumetric energy density that does not change the chemical appearance of hydrogen.

5.2.3.1 State of Technology

In this storage concept, hydrogen is cooled down to the temperature of liquid hydrogen (20*K*) and additionally hydrogen is compressed to a pressure of up to 350 bar or even 700 bar. Under these challenging conditions, an energy density of maximum 7 wt% and maximum 0.07 kg_{H2}/l may be achieved. This is only possible at the expense of an enormous amount of energy and technological effort to cool and compress hydrogen. Additionally, the demands in the design of a storage vessel containing a fluid at such a low temperature level for a long time and at such a high pressure, are extremely high. To describe it in a simple way, usually a type IV pressure tank (Section 5.2.1) covered with the vacuum insulation typically used for liquefied hydrogen tanks (Section 5.2.2) is needed (Aceves et al., 2010; Brunner et al., 2016).

Due to these challenges, a technically less demanding compromise aims at realizing cyro-compressed hydrogen storage tanks characterized by around 4 bar and 50 K. This leads to a storage density of 5 wt% hydrogen inside the fully-loaded tank (Blagojević et al., 2012). Other concepts currently under development that are in various development stages use different storage parameters to try to optimize the amount of stored hydrogen in relation to the necessary technical effort.

5.2.3.2 Characterization

The cost of a cryo-compressed storage tank is in a range of 12–30 US$/kWh. Due to significant technical uncertainties, these values are more along the lines of the expected cost than the real cost for the few prototypes that exist. The storage efficiency is characterized by values somewhere in between the storage efficiency of liquid and compressed hydrogen; 41% is a realistic order of magnitude for the time being (Stolten et al., 2016; Ahluwalia et al., 2010).

5.2.3.3 Markets and Perspectives

Several attempts have been made to implement and test cryo-compressed storage for mobile applications. This is especially true for application in passenger cars because the high energy density is very attractive for this application. For example, a Toyota Prius has been equipped with a cryo-compressed storage tank and has achieved the longest driving distance so far (1050 km) with a single tank filling for a hydrogen-powered car (Aceves et al., 2010). This storage tank was a specially designed cyro-compressed storage tank filled either with liquid or compressed hydrogen; in the case it is filled with liquid or cryo-compressed hydrogen the storage tank contains 2–3 times more hydrogen than a storage tank of compressed hydrogen.

Cryo-compressed hydrogen storage has some advantages in comparison to other options (e.g., high storage capacity) and opens the technical possibility to fill the storage tank either with compressed, cryo-compressed, or liquid hydrogen. But so far cryo-compressed tanks are not available on the market and the longest possible time without losses if unused is seven days so far; compared to liquid hydrogen storage, this is around seven times longer (Brunner et al., 2016).

Because of these challenges it is unlikely that cryo-compressed storage will become a considerable part of the consumer market in the years to come. Additionally, all currently built refueling stations are designed for the distribution of compressed hydrogen. This might not be true for highly specialist fleets of company vehicles (e.g., trains, planes, ships), which might be refueled in only one place or a very limited number of places.

5.3 MATERIAL-BASED STORAGE

Besides the three options already discussed for the storage of pure hydrogen, there are also many other possibilities. These other options have one thing in common: without exception the hydrogen reacts with or accumulates on other materials based on reversible physical effects or chemical reactions. Such options are discussed below, limited to storage concepts that are the most promising based on the current state of knowledge. In interpreting the statements made below, it is important to keep in mind that all of the material-based hydrogen storage options are not market ready at this moment. So far, they are still in an advanced, or even an early, research and development (R&D) phase; some of them exist already in the demonstration phase, or even in small pilot applications, while others are still in at the early lab scale.

The border between the group of material-based storage options and the various options for storing hydrogen in a pure form is not always clearly defined, because there are numerous combinations of these different possibilities. Such combinations can be very promising because they might allow some system specific drawbacks of a single-storage option to be overcome. For example, in the most current applications of Metal Organic Frameworks (MOFs; Section 5.3.3) and in activated carbon (Section 5.3.4), hydrogen is stored also under cryogenic conditions.

The four storage options discussed below should not be considered a complete list of all approaches. There are many more options under investigation by public research organizations, such as universities and state-owned research organizations, as well as by small startup and large-scale companies globally; some examples are nonmetal hydrides, ammonia, and carbohydrates. Basically, however, the functionalities of these various possibilities are mostly very similar to the ones described below and the main difference is the material or material combination used. Nevertheless, research is ongoing in this area and it is expected that new ideas, other materials, innovative combinations, and alternative concepts, including the combination of different options, will come up.

5.3.1 Metal Hydride Storage

The storage of hydrogen in metal hydrides is a long-known technology. In the 1980s, there were some field tests with metal hydride hydrogen storage tanks for a car fleet. The storage tanks tested in those days had a weight of 140 kg and had a storage capacity of 1.4 kg of hydrogen (1 wt% of the overall tank mass). TiFe was used as an active material in these demonstration activities. This metal hydride allows a theoretical hydrogen load of 1.8 wt%. Since then a lot of progress has been made. Today a modern complex light-weight metal hydride (e.g., $LiBH_4$) is characterized by a theoretical hydrogen capacity of up to 18 wt %, but this storage capacity has not been verified experimentally so far (Wenger, 2009; Thiangviriya and Utke, 2016).

5.3.1.1 Principle

Metal hydride storage is based on chemical adsorption, that is, hydrogen atoms diffuse inside the metal lattice and react there with the metal to form metal hydride. This is the reason why metal hydride storage is often compared to a sponge. To understand the principle of metal hydride storage, it is essential to look into the reaction mechanism of the material. Due to the fact that the reaction takes place inside the metal hydride, it is very important to optimize the structure in a way that supports the diffusion of hydrogen inside the metal lattice.

The general reaction of metal hydrides is shown in Eq. (5.1).

$$H_2 + \text{Metal} \rightleftharpoons \text{Metal Hydride} + \Delta H_R; \quad \Delta H_R > 0 \tag{5.1}$$

The chemical reaction of metal with hydrogen to metal hydride is exothermic. Thus, the backward reaction (the release of hydrogen from the metal) is endothermic. Therefore, in the storage of hydrogen in metal hydrides, there is always a heat flux that has to be taken into consideration during use.

This reaction, according to Eq. (5.1), proceeds in four steps (Fig. 5.3). At first the molecular hydrogen reaches the metal surface (Fig. 5.3A). There hydrogen dissociates into atomic hydrogen (Fig. 5.3B). Then the atomic hydrogen dissolves into the crystal lattice of the metal (Fig. 5.3C). Afterward, the atomic hydrogen reacts with the metal to form metal hydride with the release of heat, because the hydrogenation of metal is exothermic (Fig. 5.3D).

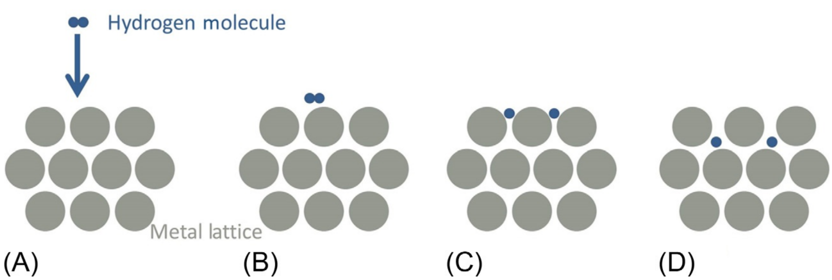


FIG. 5.3 Adsorption of hydrogen into a metal. (A) A hydrogen molecule reaches the metal surface; (B) hydrogen dissociates at the surface; (C) the atomic hydrogen dissolves into the metal lattice; (D) hydrogen reacts with the metal to metal hydride.

For dehydrogenation the same procedure takes place backward. But this time it is necessary to provide enough thermal energy to allow the reaction to take place, because dehydrogenation is an endothermic reaction.

While hydrogen reacts with the metal lattice, the lattice changes its volume. This means that it expands during absorption and contracts again during desorption. This results in a volume change of up to 30 to 40% that depends on the material and the amount of absorbed hydrogen (Klebanoff, 2013).

5.3.1.2 Characterization and Status

Nearly all elements can form hydrides. They are sorted into three different groups outlined below in order to give an overview of the differences between them. The main indicator of each group is the chemical bond of the element with hydrogen.

1. *Ionic or saline hydrides*. Here, all alkali metals and alkaline earth metals are included. These hydrides often have relatively similar physical properties to the original metal; that is, the crystal structures, the hardness, the brittleness, and the other properties do not change much due to the reaction with hydrogen. Hydrogen acts only as a negative loaded ion within these hydrides. Typical hydrides of this group are lithium hydride (LiH), sodium hydride (NaH), and calcium hydride (CaH_2) (Hirscher, 2010; Klebanoff, 2013).
2. *Covalent hydrides*. These hydrides are a combination of a nonmetal and hydrogen. Here the linking forces between the molecules are van der Waals forces (relatively weak forces). Therefore, most covalent hydrides are liquid or gaseous at room temperature. Some examples are water (H_2O), methane (CH_4), and aluminum borohydride ($Al(BH_4)_3$). This group does not form hydrides easily. Thus, most covalent hydrides cannot be built via a simple reaction of hydrogen and the element; a considerable effort is required for the synthesis of such complex chemical reactions, or as in the case of water, it is the reaction product of the combustion. This is the reason that there are no promising candidates for use in hydrogen storage or, in case of water, that it is thermodynamically impossible to store hydrogen in this form (Hirscher, 2010; Klebanoff, 2013).
3. *Metal hydrides*. In this kind of hydride, hydrogen acts as a metal so that there is a metal-hydrogen bond in the conduction band of the metal atom. These hydrides are formed by transition metals. In contrast to the ionic and saline hydrides, some physical properties of the metal hydride change significantly (e.g., they become brittle). But they still have a high thermal and electrical conductivity (Hirscher, 2010; Klebanoff, 2013). These metal hydrides can be sorted into two groups according to their stability. Group A contains metals that form easily stable hydrides (e.g., Li, Na, V). Group B metals, on the other hand, do not form stable hydrides. By combining these two different metal groups it is possible to create complex metal hydrides. Such a combination of both groups has the advantage that some of the material

properties can be modified to the range required by the application. Mostly the reaction temperature and pressure are adjusted by such modifications (Hirscher, 2010). Some of the currently most promising materials for this application are sodium alanate ($NaAlH_4$) and lithium boron hydride–magnesium hydride ($LiBH_4$-MgH_2). For example, $LiBH_4$ has a theoretical hydrogen capacity of 19wt%, which is the highest possible for metal hydride storage, but unfortunately the highest hydrogen loading realized in a lab has been 10wt%. Another challenge is that many metal hydrides only allow around 20cycles or less before the hydrogen concentration decreases rapidly.

The thermal management is very important in the technical realization of hydrogen storage based on metal hydride. The storage tank needs to be cooled during charging and heated up during discharging. Thus, it is helpful if the hydrogen consumer produces some waste heat that can be used for heating the storage tank. In this case, the temperature level is important because in most mobile applications a PEM-Fuel Cell is used. This fuel cell operates at temperatures around 100°C or less. Thus, in combination with a metal hydride storage tank, which needs much higher temperatures, an additional heating device is needed (e.g., part of the electricity produced by the fuel cell or a share of hydrogen is used to provide high temperature heat); this lowers the overall storage efficiency.

Metal hydride storage tanks have some advantages compared to other storage options. They are characterized by a relatively high volumetric energy density. Depending on the material used, such storage devices could operate at ambient pressure, and they are able to store hydrogen at ambient temperature when there is no hydrogen demand. Additionally, a very compact construction is possible. Also, hydrogen coming out of the metal hydride is ultrapure. But there are also some disadvantages. The gravimetric energy density is low, which leads to a very heavy storage tank. Some metal hydrides require very high temperatures for the reaction; the thermal management of metal hydride storage tanks is one of the major challenge to be solved successfully during the development of such storage devices (Capurso et al., 2016). Additionally, the filling of this type of storage tank is quite slow and the thermal management is complex and demanding.

5.3.1.3 Markets and Perspectives

There are already some applications for which metal hydrides are used as hydrogen storage.

One popular example of the use of metal hydrides in hydrogen storage is in submarines, in which a fuel cell is integrated into the propulsion system. To release hydrogen from storage, it is heated with the cooling fluid of the fuel cell. Under these very special frame conditions metal hydrides have some advantages, which are not applicable for other mobile applications. Additionally, due to the high weight, the use of extra weight in the form of lead can be reduced within the submarines; lead is typically used to stabilize a submarine. Also the high volumetric energy density is advantageous, because space is scarce in submarines (Emonts and Stolten, 2016a).

Another example is a small delivery scooter, which has been designed for the French post. This car was tested in the "MobyPost project" and it used a fuel cell and metal hydride storage for the propulsion system. The metal hydride storage tank inside the car could store about 0.9 wt% of hydrogen (MAHYTEC, 2015).

Furthermore, there are commercially available scooters equipped with a hydrogen tank called "H2Tank2Go" that are based on metal hydrides. A stored hydrogen amount of 1.8 wt% in the material is claimed for this tank (Zoz GmbH, 2011). Another related storage tank contains a reactive hydride composite (RHC) made of $LiBH_4$ and MgH_2; this allows a storage capacity of around 8 wt% (Zoz GmbH, 2016).

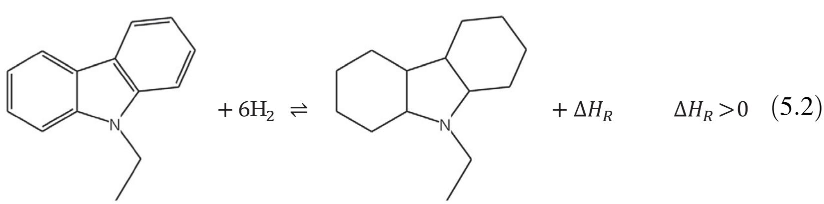
These examples show that metal hydrides for hydrogen storage are very promising and have a realistic chance to be implemented in the market at some point. Another advantage is that metal hydride storage vehicles may be refueled at gas stations for compressed hydrogen; that is, they are compatible with the infrastructure for hydrogen cars currently under development. Nevertheless, considerable research and development effort is still needed to provide a cheap, efficient, and reliable storage system with a long technical lifetime.

5.3.2 Liquid Organic Hydrogen Carrier (LOHC)

A liquid organic hydrogen carrier (LOHC) is a fluid that can be loaded and unloaded more or less easily with hydrogen. In such LOHCs, hydrogen can be stored essentially without any loss for a long time at ambient conditions. Additionally, the liquid phase of the storage medium allows some considerable advantages during the storage operation. Thus, this options has been discussed more frequently recently (Müller et al., 2013).

5.3.2.1 Principle

LOHCs are organic fluids (e.g., N-ethyl-carbazole (NEC), dibenzyltoluene (MSH), benzyltoluene (MLH)) that are able to absorb and desorb hydrogen in a fluid state. Therefore, the storage principle is comparable with that of metal hydride storage, with the main difference being that metal hydrides are solid and LOHCs are liquid. This fact has a great influence on the storage as well as on the vehicle design. Exemplarily for the various LOHCs currently under investigation, the chemical reaction of NEC is shown in Eq. (5.2).



$$\text{NEC} + 6H_2 \rightleftharpoons \text{H}_{12}\text{-NEC} + \Delta H_R \qquad \Delta H_R > 0 \qquad (5.2)$$

During a storage interval, first these fluids are hydrogenated. This is typically realized within a reactor. Here a chemical hydrogenation reaction takes place at pressures between 20 and 50 bar and at temperatures ranging from 150°C to 200°C, depending on the fluid. Typically, this chemical reaction is controlled by a catalyst (e.g., ruthenium or nickel-based).

During the withdrawal cycle, hydrogen is dehydrogenated from the fluid again within a reactor. Here the catalyst-controlled back-reaction typically takes place at a relatively low pressure level and at temperatures of 270–310°C depending on the storage fluid (LOHC). This reaction is controlled by a catalyst consisting, for example, of platinum on an aluminum oxide structure or of noble metals on carbon (Müller et al., 2016; Teichmann et al., 2011).

The liquid storage fluid contains between 5.8 and 7.2 wt% hydrogen. Thus, the efficiency of such LOHC storage is around 44%. The filling rate of LOHCs is comparable to the filling rate of fueling stations for liquid fuels based on fossil energy. Thus, a fill rate of 4 kg_{H2}/min might be possible.

5.3.2.2 Characterization and Status

Such storage systems can be used for mobile applications (e.g., within a car or a truck) following several different concepts (Teichmann et al., 2011). The loaded or unloaded LOHC can be transported and stored within an ordinary tank used typically for fossil fuels. But in contrast to standard tanks, the loaded as well as the unloaded fluid needs to be transported and stored separately. This might be possible by placing a membrane inside the tank, thus subdividing the tank into two different segments with varying volume. This would allow using only one tank instead of two.

The storage of the loaded and unloaded LOHCs might be realized based on the already available technology from tanks for diesel and gasoline. Additionally, a lot of experience is available from the storage of liquid fluids within the chemical industry. Thus, easy solutions can most likely be identified. In addition, a catalytic-controlled hydrogen discharge unit is needed to realize the release of hydrogen from the loaded organic fluid. This process needs heat, clearly above 100°C. But the fuel cell (PEM) used inside cars provides waste heat typically only at a temperature of 100°C. Thus, additional heat is needed, for example, by burning hydrogen; this will lower the overall storage efficiency (Teichmann et al., 2011; Müller et al., 2016). Additionally, a fuel cell needs highly purified hydrogen to avoid destruction of the electrodes. But most likely hydrogen coming from the discharge unit will not be completely pure because the gas might still contain some traces of LOHC or decomposition components of the LOHC. Thus, an additional cleaning step might be necessary.

LOHCs are liquid in a loaded and unloaded state. Thus, such liquids as are under discussion can be easily transported with the known and existing distribution technology used for fossil fuels or chemicals. Thus, it is not necessary to build completely new fueling stations, nor to develop new technologies for the refueling. When a car with a LOHC tank comes to a fueling station, two steps have to be performed. First, the old (dehydrogenated) LOHC has to be removed from the tank, and second, fresh (hydrogenated) LOHC has to be filled into the tank in succession or in parallel. While it is only required to change the fluid, the refueling process is very fast and might be comparable to the fueling times currently needed for gasoline or diesel.

5.3.2.3 Markets and Perspectives

One major advantage of LOHCs is the possibility to use the existing infrastructure with this kind of energy storage to a certain extent. This is especially true, because the LOHCs currently under discussion show more or less the same properties as gasoline at ambient conditions (Teichmann et al., 2011). Thus, it is easy to transport LOHCs in large quantities to the various fueling stations with typical trucks, as is done with other conventional fuels.

There are already some examples of LOHCs in stationary applications. These show that the technology could be used to store large amounts of hydrogen (Hydrogenious Technologies GmbH, 2016). Furthermore, there has been some effort to implement LOHCs as hydrogen storage for large-scale fuel cell ships or for powering large-scale combustion engines on ships. For this application, a high refueling rate is most important, because a very large amount of energy has to be refueled in a short time.

Concepts for this technology, especially for mobile applications, are under development. Most of them are dedicated to ships, because the machinery to load and unload the LOHC requires a large volume. That is also one of the reasons that this technology is only commercially available to bring hydrogen to industrial facilities which do not have hydrogen production on their own grounds.

For other applications, it is not expected that this storage technology will become market mature in the years to come. One reason is that the side aggregates are very expensive. Additionally, hydrogen is not yet fully clean and it might be necessary to add another cleaning step before hydrogen can be used, for example, within a fuel cell. Besides this, the loading and unloading is relatively energy intensive.

5.3.3 Metal Organic Framework (MOF)

A Metal Organic Framework (MOF) consists of coordinated polymers combined from metal ions, metal oxide cluster, or inorganic parts of larger dimensionality. The structure is composed of organic ligands, which coordinate the inorganic 1D chains or 2D layers that form in combination a regular structure able to absorb hydrogen. The hydrogen accumulates at the corner with the inorganic part of the materials (Hirscher, 2010).

5.3.3.1 Principle

Here hydrogen is stored with physisorption inside the porous media. Hydrogen is adsorbed and fixed with van der Waals forces at the surface of the inorganic part of the pores of the MOF. This is possible because the metal organic framework (MOF) is usually characterized by a highly porous structure resulting in a very big surface area per gram (approximately $1000\,m^2/g$). But this type of storage works only at relatively low temperature (below 100 K), allowing it to store 5–7.5 wt% hydrogen.

One of the first-used MOFs (MOF-5; Fig. 5.4) has an inorganic part (Zn_4O unit), that is connected with 1,4 benzene-dicarboxylate within a regular cubic structure. Thus, in comparison to activated carbon (Section 5.3.4), different possibilities exist to optimize the adsorption behavior for hydrogen. On one hand, the surface area could be increased by using shorter organic link molecules. On the other hand, the adsorption enthalpies could be optimized by using organic link molecules that have hydrogen or oxygen terminations and are not dominated by graphitic hexagonal groups (Klebanoff, 2013).

5.3.3.2 Characterization and Status

Another example of a MOF is the material MIL-101. Bimbo et al. (2016) have tested whether it is possible to increase the volumetric storage density, or to reduce the pressure with equal storage density, in comparison with 700-bar

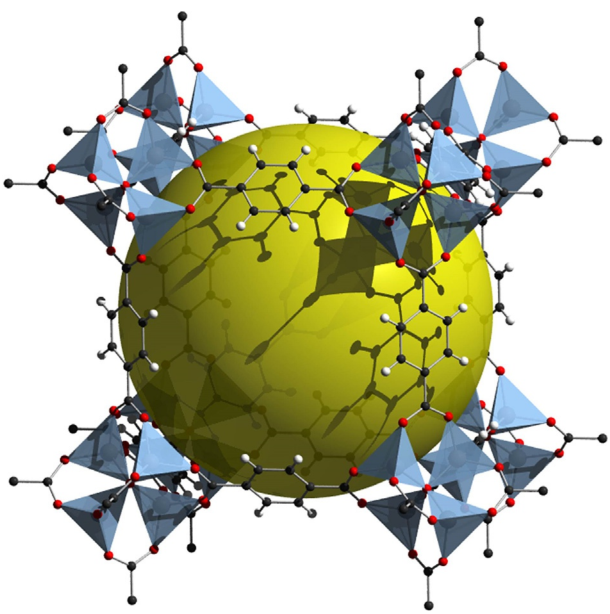


FIG. 5.4 MOF-5 Structure (the triangular parts are the inorganic component, the thin lines and small balls are the organic components, and the big ball represents the free pore).

pressure tanks based on several simulations and experiments. The main aim was to reduce the refilling pressure while filling the storage tank with hydrogen at a temperature of 70 K, and then to store it at ambient temperature. The idea was that no expensive insulation is required. The result was that the refilling pressure could be reduced significantly for an empty pressure tank, as well as for a tank filled with MOF MIL-101, if hydrogen was cooled down to 70 K. This temperature was chosen because it is the temperature of liquid nitrogen, which is technically easy to realize. The crucial factor here is the pressure that should be reached after the refilling process. The best results are achieved when the pressure in the tank should reach 350 bar at 298 K. At these conditions, in all analyzed options, the loading pressure is much lower than the final pressure. Therefore, the loading pressure for the tank without MOF is 72 bar, for the half-filled tank 22 bar, and for the tank fully loaded with MIL-101 3 bar. So, the compression work is reduced by about 69 bar in that case. The final storage pressure at 298 K is in all three cases nearly equal, ranging from 340 to 350 bar. With such a system, it is possible to reduce the effort of filling the storage tank even if the forces that keep hydrogen closer together only work during the filling process. Unfortunately, this concept only works up to a final pressure of 350 bar, because with higher final pressure the storage pressure of the half-filled and fully filled tank rise substantially above the aim of 700 bar; this concept creates then a new safety problem because of the high pressure (Bimbo et al., 2016).

5.3.3.3 Markets and Perspectives

So far only small test storage tanks, or experiments with a small amount of material, exist. Thus, it is not expected that this technology will become market ready in the years to come. One advantage of this concept is the possibility to combine this storage with other options to lower, for example, the refueling pressure of high-pressure storage tanks or to maximize the energy density in cryo-compressed storage tanks. In addition to the efforts to use different MOFs as hydrogen storage, MOFs can also be used for methane storage. Perhaps MOFs will be used in combination with cryo-compressed tanks. This option needs much more R&D before reliable statements can be made about possible market introduction.

5.3.4 Activated Carbon

Activated carbon is a highly porous material, widely used for many different industrial, chemical, medical, and other applications. This material is very interesting for hydrogen storage because hydrogen can be adsorbed on the large free surface of the pores. Thus, quite similar to the MOF storage, activated carbon accumulates hydrogen on the free surface.

5.3.4.1 Principle

In activated carbon, hydrogen is stored by adsorption at the surface of the carbon based on van der Waals forces. These forces are typically not stable enough to hold hydrogen at ambient temperature. Thus, hydrogen needs to be cooled to cryogenic temperature (approximately 70 K before storage). Therefore, oftentimes, activated carbon is combined with cryo-compressed storage to optimize the volumetric energy density of the vessel (Bimbo et al., 2016). Additionally, carbon is easy to handle, has a low cost of synthesis, and is light weight. Therefore, this material has been investigated by many different research groups (Burchell et al., 2017; Javaid, 2017; Klebanoff, 2013).

Although storage in activated carbon usually employs the powder form, there are also other possibilities to store hydrogen in carbon, such as graphite, carbon nanotubes, and activated carbon fibers; all these options are characterized by a high specific inner surface on which the hydrogen can accumulate. The main difference between the various modifications of porous carbon is the appearance.

- Graphite is usually formed in trigonal planer sheets leading to a relatively small surface of 20 m^2/g. This results in a very limited capacity for hydrogen storage. Therefore, graphite needs to be modified by implementing spaces between the different planes to allow for the accommodation of hydrogen molecules. These pores are called slit-pores, and they have an optimal size of twice the diameter of a hydrogen molecule; that is, both layers could hold one molecule. But under these conditions, hydrogen only absorbs at supercritical temperatures. Thus, further modifications are necessary, and this is a subject of intensive research. Because of these challenges, it cannot be foreseen whether or not this option can be more promising than storing pure hydrogen at the same conditions (Klebanoff, 2013).
- The hydrogen-adsorbing properties of carbon nanotubes are very similar to activated carbon (see below).
- Activated carbon fibers have a high micropore volume that is easily accessible from the surface. The good accessibility of the pore volume may be traced back directly to the fiber form, because there are many more open pores directly at the surface. But the carbon fibers used for hydrogen storage so far are in the same range of hydrogen storage conditions and storage parameters as the best activated carbon (like AX-21, Maxsorb). Therefore, activated carbon powders are mostly used in most of the ongoing research activities because the packaging of these materials is typically easier.

The best performance of granular activated carbon that has been reached at room temperature so far is close to 1 wt% at 100 bar and around 2 wt% at pressures up to 400 bar. If the material is loaded at low temperatures (77 K), it is possible to reach 5.5–6 wt% at 20 bar. Thus, this is the configuration that has been most used so far (Klebanoff, 2013). An amount of up to 8 wt% of hydrogen has been stored at cryogenic temperature (77 K) and high pressure (400 bar) (Burchell et al., 2017).

5.3.4.2 Characterization and Status

Most prototype tanks that store hydrogen in highly activated carbon (e.g., AX-21) work usually at a temperature of around 70 K; that is, mostly cryogenic storage is realized with physisorption, similar to MOF storage (Paggiaro et al., 2010a; Paggiaro et al., 2010b; Ahluwalia and Peng, 2009).

Recently a research project has been carried out on a cryo-compressed storage tank filled with activated carbon (Bimbo et al., 2016). Here the influence of the refueling conditions on the possible increase of the volumetric energy density has been tested. Therefore, the loading pressure as well as the temperature has been reduced. After loading, the temperature increases slowly to room temperature and in parallel the pressure rises. The goal is to reach the standard pressure of compressed hydrogen at room temperature and to reduce the energy for the hydrogen compression. The results are similar to the results described above for MOF storage (Section 5.3.3), so the reduction of the loading pressure is possible. However, at most of the values investigated, AX-21 has a tiny drawback in comparison to the MOF. As described above this is only possible up to a pressure of 350 bar, because when attempting to reach 700 bar, the pressure always increases up to 816 bar, leading to severe safety risks. However, there is still an advantage related to the necessary energy for the loading of the high-pressure storage. Also, it is possible to increase the volumetric hydrogen density of the storage with activated carbon to 13.1 kg_{H2}/m^3 instead of 0.3 kg_{H2}/m^3, without any active material inside the tank at the right temperature (Bimbo et al., 2016).

Sometimes activated carbon is tested at room temperature (298 K) (Schaefer et al., 2016). But under these conditions, the hydrogen stored inside amounts to only 0.59 wt%. Even though this is an easy and safe storage option, the question arises whether such an approach can be economically viable within a competitive market.

5.3.4.3 Markets and Perspectives

At the moment there is no market-ready hydrogen storage with activated carbon. However, compared to MOF, a lot of experience with this material is already available and it can be produced easily and cheaply. Thus, if hydrogen storage based on activated carbon is to be introduced, it is foreseeable that this storage will most likely be a combination of activated carbon and a cryo-compressed storage vessel. The reason concerns the weak forces that lead to the physisorption of hydrogen inside the pores of the activated carbon. This works best at cryogenic conditions. But it is not foreseeable that in the years to come such concepts will become market ready, because all projects are currently at the lab scale.

5.4 COMPARISON

Hydrogen storage concepts for mobile application have to fulfill numerous demands, and thus need to be compared using various factors, as it is not enough to meet the expectations and overarching goals in only one aspect. The figures used for characterization that are assessed here are defined in detail below. A distinction is made among them between technical values, economic figures, market aspects, and the research and development (R&D) status.

When possible, the values summarized below will be compared with the DOE targets. These targets, published by the US DOE, represent the internationally accepted technical and economic development targets for hydrogen storage systems for the time horizon 2020 as well as the overall long-term goals (so-called DOE ultimate targets). They are shown in Table 5.1 and will be compared with the single values in all figures, where such targets exist.

- Technical values. Under this category, the technical aspects of the different technologies are summarized.
  - Gravimetric energy density. This value describes the amount of hydrogen or energy that can be stored in 1 kg of storage material; it is expressed in wt% of hydrogen inside the storage material.
  - Volumetric energy density. This figure depicts the amount of hydrogen or energy that can be stored in 1 L of hydrogen storage material; it is expressed mostly in kg_{H2}/L or kWh/L of hydrogen inside the storage material.
  - Overall energy density. This figure combines the gravimetric and the volumetric energy density. Thus, the ideal mobile hydrogen storage material or system is characterized by a high volumetric and a high gravimetric energy density.
  - Well-to-Fuel Cell (WtFC) efficiency. This characteristic value describes the efficiency of the overall hydrogen storage system. It includes all treatment processes of hydrogen after production necessary to reach the right status for the storage within the respective storage system (e.g., liquefaction, compression, cooling) as well as redelivery to the fuel cell at the required conditions (e.g., regasification, pressure reduction, purification).
  - System fill rate. This figure describes the amount of hydrogen or storage material that can be refueled in 1 min; it is expressed mostly in kg_{H2}/min.
  - Storage conditions at idle state. This value depicts the pressure and temperature conditions needed for storage when there is no hydrogen demand; these conditions are expressed in bar and °C.
- Economic figures. In addition to the technical values, the performance of a hydrogen storage system or concept is also characterized by economic figures. Here the following characteristic values are investigated.
  - Storage system costs. This figure describes the specific investment for one kWh stored hydrogen within an overall hydrogen storage system; it is expressed in US$/kWh.
  - Infrastructure costs. This parameter describes the expenditures needed for the infrastructure required by the overall hydrogen storage system.

TABLE 5.1 Comparison of the Values of Different Hydrogen Storage Technologies (Lozano Martinez, 2010; Zoz GmbH, 2016; Nonobe, 2017; Brunner et al., 2016; Toyota, 2016; Long and Head-Gordon, 2015; Durr et al., 2017; Franzen, 2009; Kunowsky et al., 2014; Emonts and Stolten, 2016b; DOE, 2015; US Department of Energy, 2015)

Storage Technology	Gravimetric Energy Density in kg_{H2}/kg	Volumetric Energy Density in kg_{H2}/L	System Fill Rate in kg_{H2}/min	WtFC Efficiency in %	Storage Conditions at Idle State		Storage System Cost in $/kWh	Investment Cost	Market Proximity Today	Market Proximity 2025–30	Compatibility With the Existing Infrastructure	Research and Development Status
					p in bar	*T in °C*						
Pressure (350 bar)	0.055	0.017	1.5–2	56	350	Ambient	13	Low	Market ready	Established	Yes	Optimization of existing technology
Pressure (700 bar)	0.057	0.04 [a]	1.5–2	54	700	Ambient	20	Low	Market ready	Established	Yes	Optimization of existing technology
Liquid	0.075	0.062[a]	1.5–2	22	1–70	−253 to −244	x	Very high	Demonstrators available	Market ready, for commercial vehicle	No	Basic and applied research
Cryo-Compressed	0.055	0.072[a]	1.5–2	41	50–350	−223 to −203	12–30	High	Demonstrators available	Market ready, for commercial vehicle	With some modifications	Basic and applied research
Metal hydride (LiB + MgH_2)	0.08[a]	0.08[a]	slow	x	Ambient	Ambient	x	Medium	Demonstrators available	Market ready for special applications	With some modifications	Basic and applied research
Metal hydride ($NaAlH_4$)	0.035[a]	0.07[a]	0.5	x	Ambient	Ambient	x	Medium	Demonstrators available	Market ready for special applications	With some modifications	Basic and applied research

Continued

TABLE 5.1 Comparison of the Values of Different Hydrogen Storage Technologies (Lozano Martinez, 2010; Zoz GmbH, 2016; Nonobe, 2017; Brunner et al., 2016; Toyota, 2016; Long and Head-Gordon, 2015; Durr et al., 2017; Franzen, 2009; Kunowsky et al., 2014; Emonts and Stolten, 2016b; DOE, 2015; US Department of Energy, 2015)—cont'd

Storage Technology	Gravimetric Energy Density in kg_{H2}/kg	Volumetric Energy Density in kg_{H2}/L	System Fill Rate in kg_{H2}/min	WtFC Efficiency in %	Storage Conditions at Idle State		Storage System Cost in $/kWh	Investment Cost	Market Proximity Today	Market Proximity 2025–30	Compatibility With the Existing Infrastructure	Research and Development Status
					p in bar	*T in °C*						
Liquid organic hydrogen carrier (LOHC)	0.065[a]	0.056[a]	4	44	Ambient	Ambient	2–20[a]	Medium (conversion of fossil filling station)	Far, for the usage in vehicle	Market ready for hydrogen delivery	No	Basic and applied research
Metal organic framework (MOF-05)	0.05[a]	0.013[a]	1.5 - 2	41	3–350	−203 to Ambient	18–25	High	Far away	Demonstrators inside cryo-compressed storages	With some modifications	Basic research
Activated Carbon	0.054[a]	0.016[a]	1.5–2	39	3–350	−203 to Ambient	x	High	Far away	Demonstrators inside cryo-compressed storages	With some modifications	Basic research
DOE 2020 Targets	0.055	0.04	1.5	60	x	x	10	x	x	x	x	x
DOE Ultimate Targets	0.075	0.07	2	60	x	x	8	x	x	x	x	x

[a]*Data for the storage material without the system.*

This includes the process steps needed to be performed before hydrogen is in the right state for the refueling (e.g., compression, cooling, liquefaction); this includes the cost for the overall required infrastructure. Because of the strongly scattered values, the respective overall investments are here compared to a hydrogen refueling system based on 700-bar tanks, as these are currently the most widely used technology. Thus, this economic parameter is rated as (0) if the investment costs are comparable to this storage system. If they are most likely lower, the system is rated with a (+). If they are higher, it is assessed with a (-) and with a (- -) for significantly higher investments compared to the 700-bar option.

- Market aspects. Under this category, the market-related aspects are considered. This category covers how far the technologies are distributed already and which developments are expected.
  - Market proximity today. This aspect depicts the current development status of a hydrogen storage system. It is rated with a (+) for a market-ready technology, (0) for technology that has been already successfully demonstrated in a vehicle, and (-) for technologies that have been demonstrated on an industrial scale, but not yet in vehicles, and (- -) for technologies that are only available at the lab scale so far.
  - Market proximity 2025/30. This figure describes the expected development status of the hydrogen storage systems for the time horizon 2025/30. Here, the results will be represented with (+ +) for a technology most likely established by 2025/30, (+) for technologies that are market ready for commercially used vehicles, (0) for technologies that can be used for some special applications, and (-) for technologies that are expected to still be in a demonstration or lab status. Always the reference point is the time horizon 2025/30.
  - Compatibility with the existing infrastructure. This figure describes the ability of a storage technology to provide refueling with the already existing infrastructure. The assessment is shown with the following symbols: (+) hydrogen storage system is more or less fully compatible with the existing infrastructure, (0) compatibility with some modifications, and (-) for an incompatible technology.
- R&D status. This figure describes the research and development (R&D) status of a hydrogen storage system. If the technology has already been implemented in cars available on the market (in theory), a (+) is given. If there exits already a demonstrator, it is rated with (0). If the storage technology is only available at lab scale, it is rated with (-).

Based on these characterizing figures, the various hydrogen storage options outlined in Sections 5.2 and 5.3 are discussed in detail below. In addition, Table 5.1 provides an overview of the comparison of the different figures.

5.4.1 Technical Values

Below the technical data on the storage options that have been described are compared to each other. The data are presented according the various characterizing figures defined above. In addition to Table 5.1, Figs. 5.5–5.7 also provide a sound overview of the technical data of hydrogen storages options.

5.4.1.1 *Gravimetric Energy Density*

The highest value occurs in complex metal hydride storage materials (e.g., LiB + MgH_2 show a value of 0.08 kg_{H2}/kg). Liquid hydrogen storage is characterized by an energy density of 0.075 kg_{H2}/kg; this is the second highest value of all storage options discussed here. Therefore, liquid hydrogen is being widely discussed for vehicles that need high gravimetric energy density. Most hydrogen storage options (pressure, cryo-compressed, LOHC, MOF, activated carbons) are characterized by a gravimetric energy density of roughly 0.055 kg_{H2}/kg. The lowest values are found in most metal hydrides (e.g., $NaAlH_4$ with a value of 0.035 kg_{H2}/kg). But these values are only comparable to a limited extent because the values for the material-based storage systems do not include the required tank shell. So, it is possible that liquid hydrogen has a higher value in reality, taking the overall storage system into consideration.

In conclusion, to compare these values with the DOE targets, the values for pure storage material (metal hydride (LiB + MgH_2)) even exceed the DOE ultimate target of 0.075 kg_{H2}/kg. But there is one important difference between these values; the goal refers to the whole storage system while the figure for

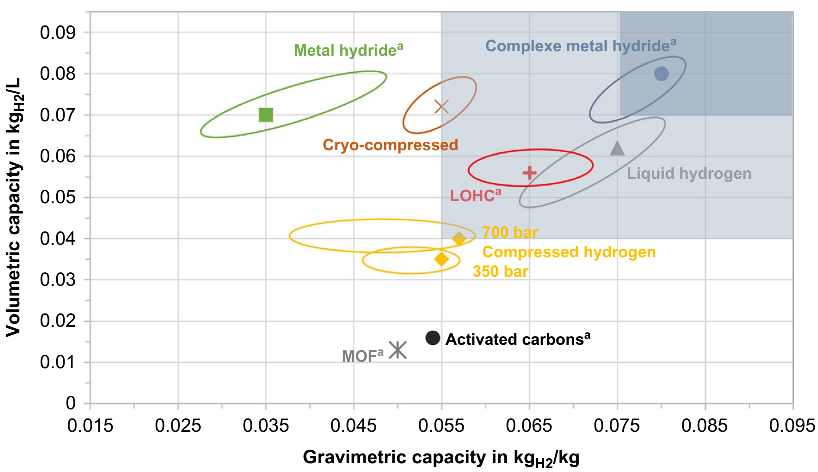


FIG. 5.5 Overview of the capacities of the explained hydrogen storage technologies (*bright gray*: DOE 2020 targets; *dark gray*: DOE ultimate targets) ([a] data for the storage material without the overall storage system).

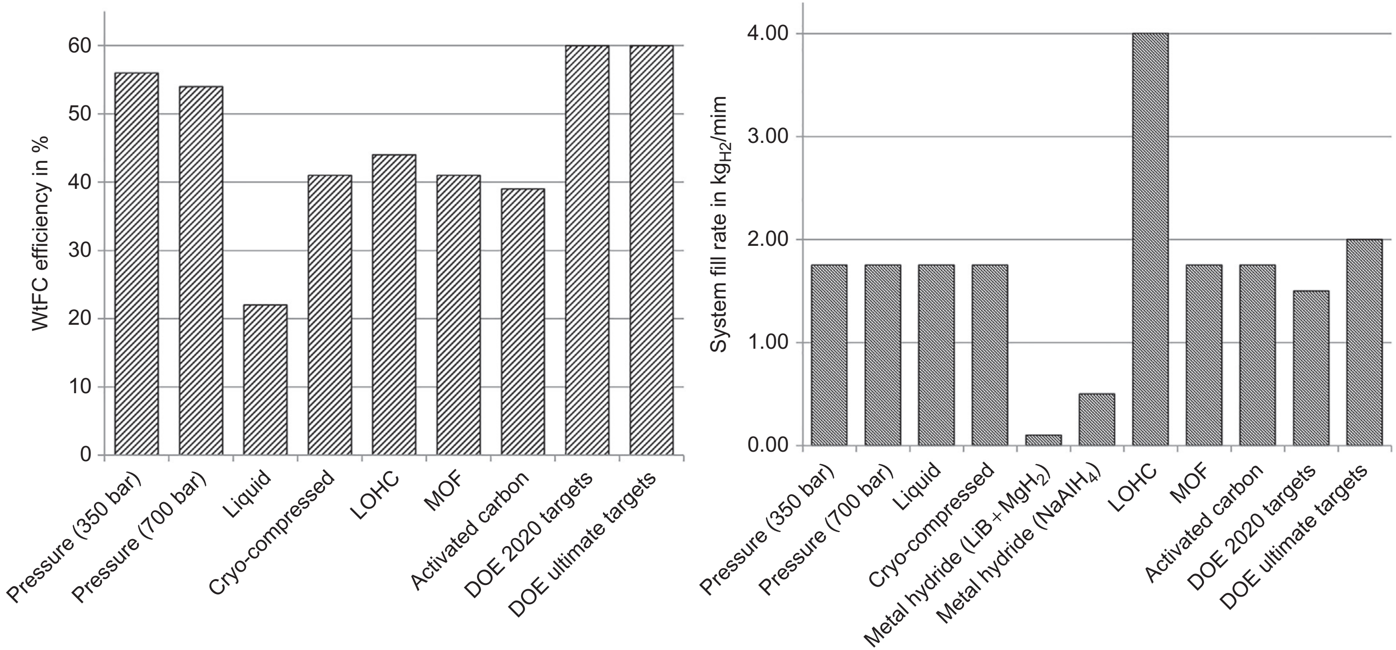


FIG. 5.6 Comparison of the system fill rate and the efficiency of the single storage systems.

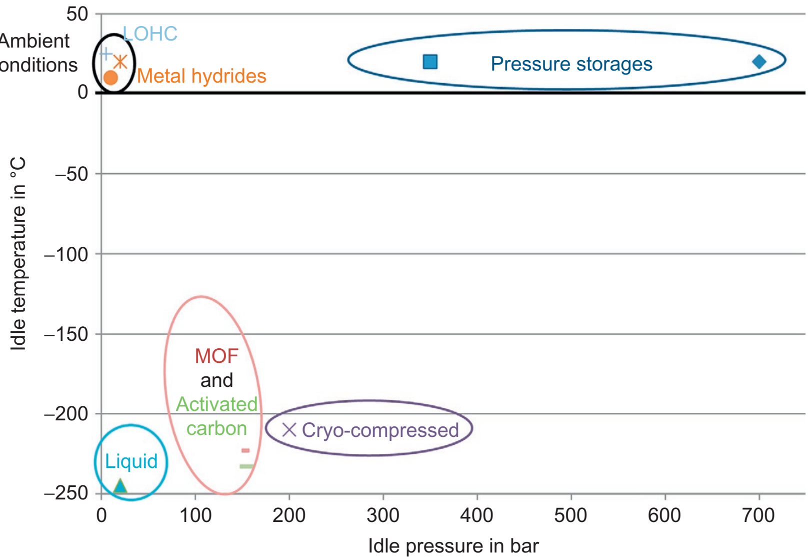


FIG. 5.7 Idle storage conditions of different technologies.

metal hydride takes only the material into consideration. This leads to lower values for the overall system. Therefore, the only system that comes near the DOE ultimate target is liquid hydrogen storage. The DOE 2020 target of 0.055 kg_{H2}/kg_{System} is met by the most advanced high-pressure storage systems and it is possible that some of the material-based storage systems will also meet the target.

5.4.1.2 Volumetric Energy Density

The distribution of the characteristic values for the volumetric energy density within the various analyzed storage options is slightly different compared to the gravimetric energy density (Fig. 5.5). Metal hydride ($LiB+MgH_2$) again shows high characteristic values, but here all metal hydrides are characterized by high energy densities. Other storage technologies that allow a high volumetric energy density are cryo-compressed hydrogen (0.072 kg_{H2}/L), liquid hydrogen (0.062 kg_{H2}/L), and LOHC (0.056 kg_{H2}/L). Compared to these possibilities, pressure tanks are characterized by a volumetric energy density of 0.04 kg_{H2}/L. The lowest values are found for MOF and activated carbon.

A comparison of these material values with the DOE ultimate targets leads to a similar result as for the gravimetric energy density; the DOE goals are mainly met by the storage materials assessed here, but not by the overall storage system. The only storage system that attains the DOE 2020 targets is liquid hydrogen.

5.4.1.3 Overall Energy Density

The overall energy density (gravimetric and volumetric) describes the characteristics of hydrogen storage systems that focus on compact design and light weight (Fig. 5.5). Metal hydride ($LiB+MgH_2$) shows the best performance on the development goal (a high volumetric as well as a high gravimetric energy density), in general. But liquid hydrogen is also a more promising solution in this respect, because lightweight metal hydride only has high values without the surrounding system. The other options mostly have either high volumetric energy densities or high gravimetric energy densities. Therefore, cryo-compressed hydrogen as well as metal hydrides (e.g., $NaAlH_4$) only have high volumetric values. In comparison, compressed hydrogen, activated carbon, and MOFs are characterized by higher gravimetric values.

5.4.1.4 Well-to-Fuel Cell (WtFC) Efficiency

An overview and comparison of the well-to-fuel cell efficiency of all technologies assessed here is shown in Fig. 5.6. Therefore, both high-pressure storage systems show the highest efficiency values (approx. 55%). The efficiency of most other storage options is roughly 15%-points lower (approx. 40%). Liquid hydrogen storage has the lowest value; this is due to the fact that a significant amount of energy is needed for the liquefaction and re-gasification. Thus, options characterized by less cooling, less compressing, and/or fewer transformation steps show higher values on average (they are more efficient on average). Moreover, the efficiency of the pressure storage systems nearly meets the DOE ultimate target of 60% already today.

5.4.1.5 System Fill Rate

The fastest filling rates can be realized with LOHC. Nearly all other storage technologies discussed here have system fill rates on the same order of magnitude, namely 1.5 up to $2\,kg_{H2}/min$. These values already meet the DOE 2020 targets. This is the reason that the filling rate is not the main focus of the globally ongoing R&D activities at this time. Only hydrogen storage systems based on metal hydrides are slower so far (Fig. 5.6).

5.4.1.6 Storage Conditions at Idle State

This parameter is the more advantageous the closer the pressure and/or temperature conditions are to ambient values (Fig. 5.7). This is true because especially high or very low storage temperatures require an expensive technological effort to keep these challenging temperature and/or pressure conditions throughout the overall storage time; it is challenging from a technological point of view to achieve storage of hydrogen under these conditions for a long time. Metal hydride and LOHC storage have values that are the closest to ambient conditions. The pressure storage options follow, because they are operated at ambient temperature and the high pressure does not generate any leakage over time as would be the case, for example, for liquid or cryo-compressed hydrogen storage systems.

5.4.2 Economic Figures

Economic figures are important to assess market readiness. Thus, the storage system costs, as well as the infrastructure costs, are assessed below. The latter includes the costs of the pretreatment of hydrogen before the refueling takes place and the necessary infrastructure. An overview of the values for each technology assessed here is given in Fig. 5.8.

5.4.2.1 Storage System Costs

A scientifically sound comparison of the storage costs is challenging because most of the options for hydrogen storage systems assessed here are not produced at a technical scale that allows a prediction of the cost after the technology has entered the market and the option is market mature. Thus, the figures discussed below represent only rough first estimations and there are only data available for a few storage options.

High-pressure storage with a pressure level of 350 bar has storage system costs of 13 US$/kWh. This cost is the lowest one at the moment for mobile hydrogen storage systems. All other systems assessed here have estimated costs roughly on the same order of magnitude. This includes high-pressure storage systems with 700 bar, characterized by approximately 20 US$/kWh; this is a commercial value found on the current (limited) market.

The values for the other options are only rough estimates.

- The technology with the widest range is LOHC. Here, the investment costs for the material are expected to be between 2 and 20 US$/kWh. In addition, the storage shell, as well as the hydrogenation and the dehydrogenation reactor, have to be paid for and operated. Thus, currently, in total the costs are expected to be equal or higher than these of the other options.
- The other two technologies for which the possible costs are available are cryo-compressed hydrogen storage systems, with a cost of 12–30 US$/kWh, and MOFs, with an expected cost of 18–25 US$/kWh.

In comparison with the DOE goals for 2020, all of these storage options are still too expensive, and none of them reach the goal of 10 US$/kWh for the time being.

5.4.2.2 Infrastructure Costs

For this assessment criterion, all technologies are compared to the infrastructure investments, including a refueling station, for high-pressure storage systems (350 and 700 bar) as these systems are market mature. Thus, the high-pressure

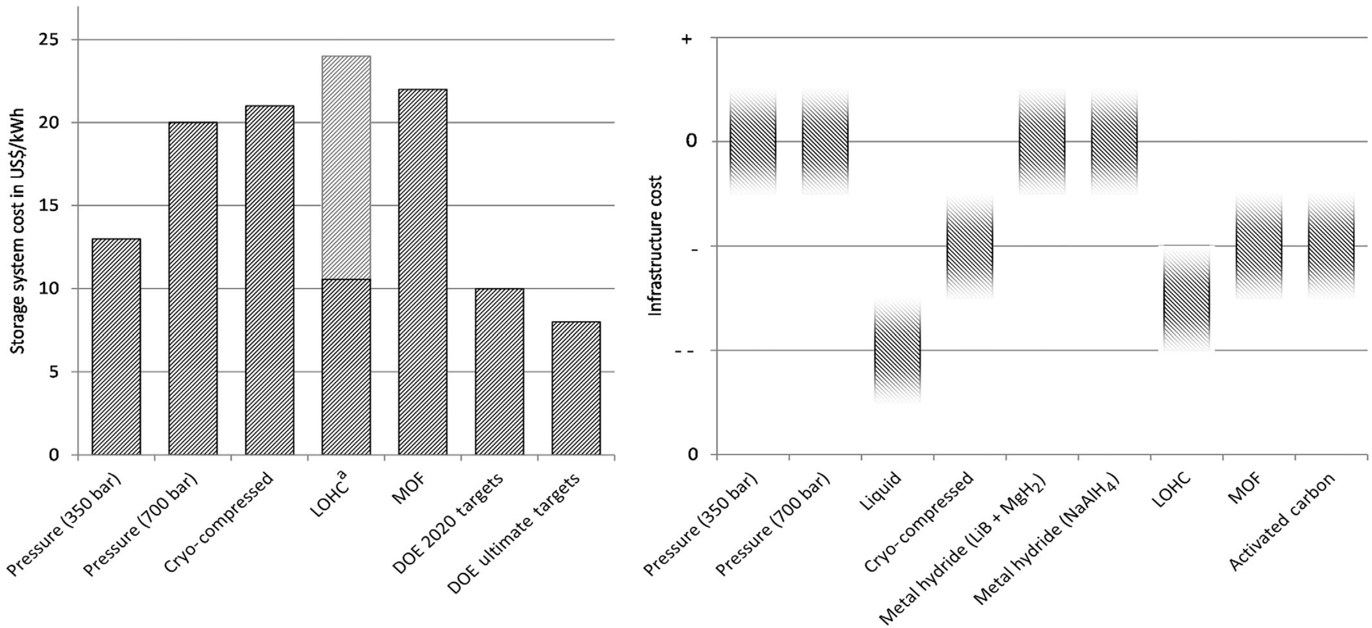


FIG. 5.8 Comparison of the economic figures (Infrastructure cost: 0 comparable costs; - higher costs; - - significantly higher costs); ([a] Data for the storage material without the system, light gray part: expected storage system cost).

storage tank is rated by definition as (0). Additionally, during the assessment, it is taken into consideration whether the infrastructure currently under development can be used or adapted to the other storage systems.

Metal hydride storage systems need, in comparison to high-pressure storage systems, a lower pressure and sometimes higher temperatures. Additionally, some metal hydride storage systems also require cooling during recharging, but the necessary system elements can be installed within the vehicle. Thus, metal hydrides are rated (0) because they can use the high-pressure infrastructure.

In comparison, LOHC needs a completely different infrastructure than that used for pressure storage. However, for LOHC a filling station similar to the gas stations in operation today can, in general, be used. The only difference is that it is necessary to implement a system to pump the discharged LOHC out of the vehicle and store it for recharging. This leads to some technical effort in converting an existing gas station before it can be used for LOHC refueling. Thus, LOHC is rated (0 to -) because there are some changes necessary, but part of the existing infrastructure and know-how can be used.

Activated carbon and MOF require a lower temperature, and depending on the respective storage concept, a lower pressure. The lower temperature especially will increase the effort needed for the necessary infrastructure. Here, they are both rated (-).

The cryo-compressed hydrogen systems have the advantage that it is possible to refuel them with compressed, liquid, or cryo-compressed hydrogen. But if they are to have an advantage in comparison to high-pressure storage, a refueling infrastructure with a very low temperature and a high pressure is needed (comparable to the required infrastructure for activated carbon and MOF). Therefore, this technology is also rated (-).

The last option to consider is liquid hydrogen storage. This technology requires a completely different infrastructure compared to the other options, one that allows for refueling the vehicle with liquid hydrogen. This makes the technological needs high and the investment for the refueling station quite expensive; special material and safety requirements have to be considered because of the extremely low temperatures. Thus, the infrastructure throughout the overall provision chain for the hydrogen pretreatment is very costly. For these reasons, liquid hydrogen storage systems are rated (- -).

There are no currently available technologies that are expected to have lower infrastructure costs than high-pressure refueling. For this reason, no technology is rated with (+).

5.4.3 Market Aspects

Market aspects include all figures that are important for market integration of the hydrogen storage systems for today and in the years to come. These are discussed below (Fig. 5.9).

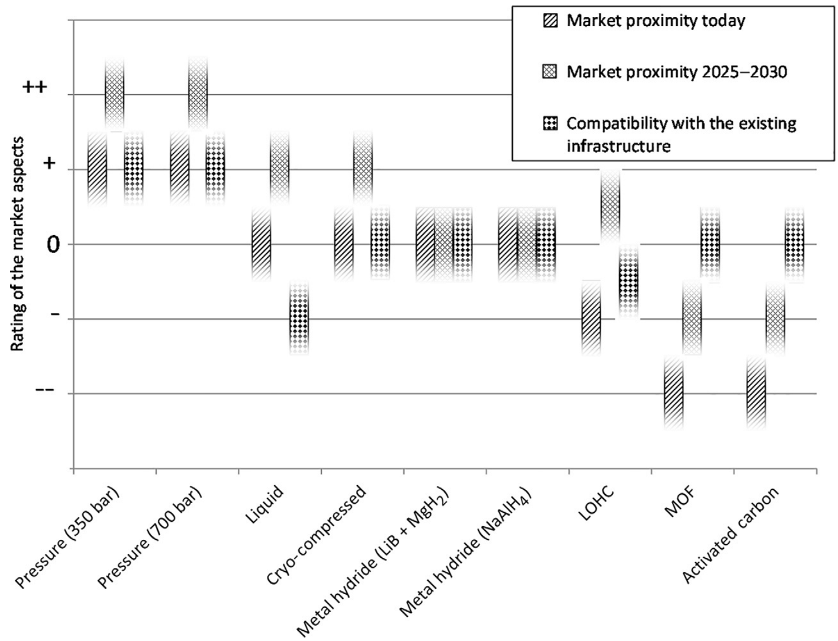


FIG. 5.9 Comparison of the market aspects (+ + very high value; + high value; 0 medium value; - low value; - - very low value).

5.4.3.1 Market Proximity Today

An important point for the use of a hydrogen storage technology is the possibility for an upscale to mass production of the storage as well as of the needed material and other auxiliary devices.

At the moment, only high-pressure storage tanks are made in small-series production, due to the fact that hydrogen can be stored in such devices at ambient temperature. Additionally, there are no storage losses during long parking times as would be the case with, for example, liquid or cryo-compressed storage systems. In addition, high-pressure storage tanks show the best efficiency and can be produced based on technologies that have already been developed for other technical applications; this advantage can contribute to cost reduction in the manufacture of such storage tanks. Thus, it is likely that in the coming years, the state of the art storage technology for hydrogen in vehicles will be 700-bar high-pressure storage for private cars and 350-bar storage for urban busses. These systems have the advantage that all available infrastructure for hydrogen mobility that has been built so far delivers high-pressure hydrogen at these pressure levels. Therefore, for other hydrogen storage technologies, it will be very difficult to achieve the same status in the market and/or to compete with high-pressure storage. This observation is supported by all commercially available hydrogen cars that are currently available (e.g., Toyota Mirai, Hyundai IX35, Honda Clarity, Mercedes GLC F-Cell), as all of them have 700-bar pressure tank systems. All these points lead to a (+) rating.

For some other hydrogen storage technologies, a few demonstrators are available for different vehicles. These include liquid, cryo-compressed, and metal hydride demonstrators. Thus, these technologies are rated (0).

For LOHC, the first commercial systems are available. But these systems are all intended for industrial processes; no vehicular demonstrator exists for the time being. Therefore, LOHC is rated here with (-).

The two technologies that are far away from market readiness are active carbon and MOF. Because these options are still in an early research stage, with only some existing lab-scale applications, the rating for these is very low (- -).

5.4.3.2 Market Proximity 2025/30

In 2025/30 the overall market for mobile hydrogen storage systems will also still be dominated by high-pressure storage systems. They are characterized by an advanced tank shell structure and maybe even a pressure exceeding the 700-bar level. Thus, this storage system is rated here with (+ +).

In the years to come, the use of liquid or cryo-compressed hydrogen storage systems is not expected for cars or other private vehicles. The high temperature difference to ambient temperatures and the resulting boil-off gas are only one important reason. The expensive infrastructure that would have to be developed is another one. Therefore, this kind of storage is perhaps expected for public transportation or heavy-duty vehicles in the next 10 years. Thus, there are limited market opportunities for the time horizon 2025/30; therefore, the rating for these technologies is (+).

LOHCs are characterized by a very fast refueling rate, making this option very attractive for vehicles to be recharged quickly. The same is true in a figurative sense for big consumers (e.g., large ships), which need a large amount of fuel within a relatively short time frame. Additionally, the energy density is comparable to pressure storage, which is the state of the art technology at the moment. The most important drawback of the LOHC storage concept is the hydrogenation and de-hydrogenation device needed to get hydrogen in and out of the LOHC. Therefore, on a medium time horizon, it is expected that this technology will be used to deliver hydrogen to the refueling station only and not for direct use within a fuel cell car. Therefore, the rating is (+ to 0).

Metal hydride storage might become market mature in 2025/30 on a very small scale. Thus, it is rated (0). This technological option can be used for special applications, depending on the respective storage material as well as the given storage demands. An example of a possible application is a high-end sports cars, for which light weight is a very important criterion and the price is not as important as for other commodity markets. Other niche markets might arise for applications in which space is very limited, but weight is not so important (e.g., use in submarines).

By 2025/30, pressure storage systems combined with some of the materials used for material-based storage (e.g., MOF or activated carbon) might gain more maturity in the marketplace. Such combinations allow an optimization of the storage energy density and would most likely avoid the disadvantage of boil-off gas. Thus, there is a chance that such systems might become a realistic option with a time horizon of 10–15 years. Nevertheless, due to numerous uncertainties and the very early R&D-status of such systems, they are rated (-).

5.4.3.3 Compatibility With the Existing Infrastructure

One important point is to use the existing refueling infrastructure for fossil energy or biomass-based transportation fuels. This is true because it is not expected that a completely new hydrogen refueling infrastructure, except for the already partially built high-pressure hydrogen infrastructure, will be built in the next 10 or 20 years in the public domain on account of the economic constraints. Therefore, high-pressure storage is rated with (+).

Most of the other technologies can, in theory, use the high-pressure refueling stations because the 700-bar hydrogen is usually delivered at −70°C. Thus, it is possible to use this already existing hydrogen refueling infrastructure, at least partly, for cryo-compressed storage systems, for MOF, and/or for activated carbon. But to get a very high energy density, hydrogen has to be delivered at even lower temperatures. Thus, these options are rated with (0).

A similar problem is expected for the use of high-pressure refueling stations with metal hydrides, because concepts based on such materials need much lower pressures and also mostly warmer hydrogen. Thus, this option is rated with (0).

Compared to other hydrogen storages options, LOHC can be integrated into conventional fueling stations due to similar characteristics; there might be a chance for integration of this technology within the existing infrastructure. However, some modification of the infrastructure would be required. Thus, this technology is rated (0 to -).

Under the preconditions described, it is not expected that liquid hydrogen can be used for private cars. Thus, this option is rated with a (-). For this technology to be used, a completely new refueling station would be necessary at each location where such vehicles should be refueled.

Concerning infrastructure, there is no big chance for technologies that need their own infrastructure (e.g., liquid hydrogen) in the coming years. This is true because, at the moment, the high-pressure infrastructure has just started to be built and therefore it will take some time before the infrastructure currently under development will be further developed and adjusted to the ongoing developments and latest findings. At the least, the money to be spent has to bring the desired return on investment.

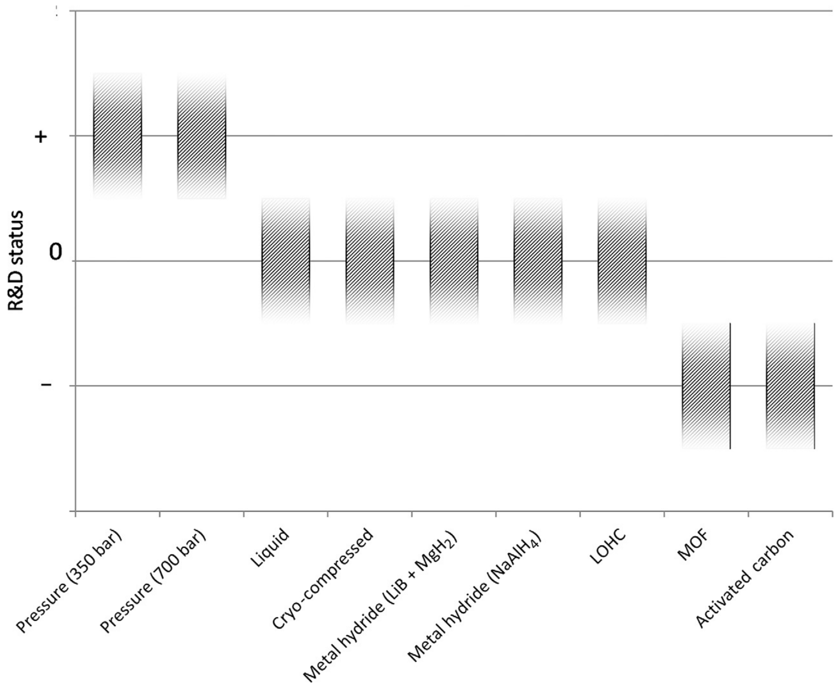


FIG. 5.10 R&Dstatus of the different storage technologies (+: advanced R&D status; 0: applied R&D status; -: basic R&D status).

5.4.4 R&D Status

In addition to the technical, economic, and market related aspects, the actual and foreseen R&D status is another important assessment metric for hydrogen storage systems (Fig. 5.10).

For all pure storage systems (storage of pure hydrogen), at least a prototype that could be used inside a vehicle exists. Compared to this, most options based on material-based storage are still in a basic research status. Even if some prototypes already exist for special materials (e.g., different metal hydrides), so far, the overall concepts have not been much developed. Additionally, it is not clear for the time being which material or material combination has a chance to be developed to a market-ready storage system or that would have the possibility of being scaled up for use in commercial products at a later stage.

Within the single storage options, high-pressure storage is already quite advanced, and therefore the focus is on the further optimization of the shell structure (+).

By comparison, the development of cryo-compressed and liquid storage systems is less advanced. But many companies and research institutions conduct R&D work on these two storage systems because of the high energy densities. Therefore, these options are rated with (0). More or less the same status is found for metal hydride systems; promising results have been published in recent years showing great potential to be exploited in the years to come. Thus, this option is also rated with (0).

LOHCs are different. They are also rated with (0), but here the focus of the research is not on the development of a storage system to be used for mobility of cars. The main focus of the R&D-activities ongoing within the field of LOHCs is currently on the implementation of the technology for transportation of hydrogen from the place of production to industrial facilities lacking their own hydrogen production; the same is true in a figurative sense for the transport of LOHCs from outside Europe to a destination inside the EU. Thus, all four technologies marked with (0) are still in an applied research phase.

The remaining two storage options, MOF and activated carbon, are still in a very basic research stage. Additionally, there is less ongoing R&D activity compared with the other technologies. Therefore, these are rated with (-).

In conclusion, still more R&D effort is needed for all storage options to meet the DOE targets in all categories. But it is expected that the DOE targets for 2020 will be reached by 2025 in nearly all values. The most challenging point is the cost reduction, because there is a large gap between the goal and the actual manufacturing costs.

5.5 FINAL CONSIDERATIONS

After describing and assessing the possible methods of mobile hydrogen storage, it is obvious that the overarching goal of storing hydrogen for mobile applications in a cheap, energy-efficient, and compact way has not been fully reached yet. For the time being, the best and most market mature compromise is storage at a high-pressure level of around 700 bar. This technology represents a good mix between a high energy density, good reliability, easy integration into existing refueling infrastructure, and the necessary cost efficiency. Thus, this option is the only storage technology that is available for mobile application on a commercial scale so far.

However, there are also other technologies that have a chance to become market mature in the years to come, for example, metal hydrides or LOHC. But these options have the highest potential in some special applications or niche markets, such as heavy-duty applications in which weight or temperature are not so crucial.

The decision on which storage solution to use does not only depend on the storage technology inside the car. It is also necessary to provide a compatible provision system (the refueling stations). Also in this respect the compressed-hydrogen storage has a clear advantage for the time being, because all stations, both existing and those under construction, are designed for the refueling of high-pressure storage tanks with either 350 or 700 bar. Thus, for every new hydrogen storage technology implemented on the market in the years to come, it is a precondition that they are based on the infrastructure currently under development (or on the already existing refueling stations as might be the case for LOHC).

Nevertheless, even with the quite promising R&D results in recent years, and with significant progress also in the years to come, it is most likely that high-pressure tanks will stay on the market. It is even more likely that they will gain greater market importance. This will be true even if the ongoing R&D activities are extraordinarily successful.

REFERENCES

Aceves, S.M., Espinosa-Loza, F., Ledesma-Orozco, E., Ross, T.O., Weisberg, A.H., Brunner, T.C., Kircher, O., 2010. High-density automotive hydrogen storage with cryogenic capable pressure vessels. Int. J. Hydrog. Energy 35 (3), 1219–1226.

Ahluwalia, R.K., Hua, T.Q., Peng, J.K., Kumar, R., 2010. System Level Analysis of Hydrogen Storage Options. DOE Hydrogen Program Review.

Ahluwalia, R.K., Peng, J.K., 2009. Automotive hydrogen storage system using cryo-adsorption on activated carbon. Int. J. Hydrog. Energy 34 (13), 5476–5487.

Bimbo, N., Xu, W., Sharpe, J.E., Ting, V.P., Mays, T.J., 2016. High-pressure adsorptive storage of hydrogen in mil-101 (Cr) and Ax-21 for mobile applications. Cryocharging and cryokinetics. Mater Des 89, 1086–1094.

Blagojević, V.A., Minić, D.M., Minić, D.G., Novaković, J.G., 2012. Hydrogen economy: modern concepts, challenges and perspectives. In: Minic, D. (Ed.), Hydrogen Energy—Challenges and Perspectives. Intech Open Access Publisher, London.

Brunner, T., Kampitsch, M., Kircher, O., 2016. Cryo-compressed hydrogen storage. In: Stolten, P.D., Samsun, D.R.C., Garland, D.N., Stolten, D., Garland, N., Samsun, R.C. (Eds.), Fuel Cells: Data, Facts, and Figures. Wiley-VCH, Weinheim, pp. 162–174.

Burchell, T.D., Contescu, C.I., Gallego, N.C., 2017. Activated carbon fibers for gas storage. Elsevier, Activated Carbon Fiber and Textiles, Washington, DC, pp. 305–335.

Capurso, G., Schiavo, B., Jepsen, J., Lozano, G., Metz, O., Saccone, A., De Negri, S., Bellosta Von Colbe, J.M., Klassen, T., Dornheim, M., 2016. Development of a modular room-temperature hydride storage system for vehicular applications. Appl. Phys. A. 122(3).

DOE (Ed.), 2015. Annual Progress Report IV. Hydrogen Storage.

Durr, S., Muller, M., Jorschick, H., Helmin, M., Bosmann, A., Palkovits, R., Wasserscheid, P., 2017. Carbon dioxide-free hydrogen production with integrated hydrogen separation and storage. ChemSusChem 10 (1), 42–47.

Emonts, B., Stolten, D. (Eds.), 2016a. Hydrogen Science and Engineering: Materials, Processes, Systems and Technology. Wiley-VCH, Weinheim.

Emonts, B., Stolten, D. (Eds.), 2016b. Hydrogen Science and Engineering: Materials, Processes, Systems and Technology. Wiley-VCH, Weinheim.

Franzen, J., 2009. Modellierung Und Simulation Eines Wasserstoffspeichers Auf Der Basis Von Natriumalanat. Fortschritt-Berichte Vdi Reihe 6, Energietechnik, Vol. 583. Als Ms. Gedr, VDI-Verl, Düsseldorf. Zugl.: Hamburg-Harburg, Techn. Univ., Institut Für Apparatebau, Diss.

Hirscher, M. (Ed.), 2010. Handbook of Hydrogen Storage: New Materials for Future Energy Storage. Wiley-VCH, Weinheim.

Hydrogenious Technologies Gmbh, 2016. Hydrogenious Produktlinien. Available at: http://www.hydrogenious.net/de/produkte/ (Accessed 21 December 2016).

Javaid, A., 2017. Activated carbon fiber for energy storage. In: Activated Carbon Fiber and Textiles. Elsevier, Oxford, pp. 281–303.

Klebanoff, L. (Ed.), 2013. Hydrogen Storage Technology: Materials and Applications. CRC Press, Boca Raton, FL.

Kunowsky, M., Marco-Lozar, J.P., Linares-Solano, Á., 2014. Activated carbon fibre monoliths for hydrogen storage. Adv. Sci. Technol. 93, 102–111.

Long, J.R., and Head-Gordon, M. Hydrogen storage in metal-organic frameworks, In: Doe, Doe Annual Progress Report, Hydrogen Storage, 2015, pp. Iv-63–Iv-69.

Lozano Martinez, G.A., 2010. Development of Hydrogen Storage Systems Using Sodium Alanate. Tuhh Universitätsbibliothek, Germany.

MAHYTEC, 2015. Solid and Compressed Hydrogen Storage Solutions.

Mori, D., Hirose, K., 2009. Recent challenges of hydrogen storage technologies for fuel cell vehicles. Int. J. Hydrog. Energy 34 (10), 4569–4574.

Müller, K., Aslam, R., Fischer, A., Stark, K., Wasserscheid, P., Arlt, W., 2016. Experimental assessment of the degree of hydrogen loading for the dibenzyl toluene based Lohc system. Int. J. Hydrog. Energy 41 (47), 22097–22103.

Müller, K., Völkl, J., Arlt, W., 2013. Thermodynamic evaluation of potential organic hydrogen carriers. Energy Technol. 1 (1), 20–24.

Nonobe, Y., 2017. Development of the fuel cell vehicle mirai. IEEJ Trans. Electr. Electron. Eng. 12 (1), 5–9.

Paggiaro, R., Bénard, P., Polifke, W., 2010a. Cryo-adsorptive hydrogen storage on activated carbon. I. Thermodynamic analysis of adsorption vessels and comparison with liquid and compressed gas hydrogen storage. Int. J. Hydrog. Energy 35 (2), 638–647.

Paggiaro, R., Michl, F., Bénard, P., Polifke, W., 2010b. Cryo-adsorptive hydrogen storage on activated carbon. II. Investigation of the thermal effects during filling at cryogenic temperatures. Int. J. Hydrog. Energy 35 (2), 648–659.

Schaefer, S., Fierro, V., Izquierdo, M.T., Celzard, A., 2016. Assessment of hydrogen storage in activated carbons produced from hydrothermally treated organic materials. Int. J. Hydrog. Energy 41 (28), 12146–12156.

Schlapbach, L., Zuttel, A., 2001. Hydrogen-storage materials for mobile applications. Nature 414 (6861), 353–358.

Simonovski, I., Baraldi, D., Melideo, D., Acosta-Iborra, B., 2015. Thermal simulations of a hydrogen storage tank during fast filling. Int. J. Hydrog. Energy 40 (36), 12560–12571.

Stolten, P.D., Samsun, D.R.C., Garland, D.N., Stolten, D., Garland, N., Samsun, R.C. (Eds.), 2016. Fuel Cells: Data, Facts, and Figures. Wiley-VCH, Weinheim.

Teichmann, D., Arlt, W., Wasserscheid, P., Freymann, R., 2011. A future energy supply based on liquid organic hydrogen carriers (Lohc). Energy Environ. Sci. 4 (8), 2767.

Thiangviriya, S., Utke, R., 2016. Improvement of dehydrogenation kinetics of 2libh4–Mgh2 composite by doping with activated carbon nanofibers. Int. J. Hydrog. Energy 41 (4), 2797–2806.

Toyota, 2016. Mirai Product Information.

US Department of Energy, 2015. Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan. Hydrogen Storage. Available at: https://energy.gov/sites/prod/files/2015/05/f22/fcto_myrdd_storage.pdf (Accessed 27 January 2017).

Wenger, D., 2009. Metallhydridspeicher Zur Wasserstoffversorgung Und Kühlung Von Brennstoffzellenfahrzeugen. Zugl.: München, Techn. Univ., Diss., 2009, Fortschritt-Berichte Vdi Reihe 12, Verkehrstechnik/Fahrzeugtechnik, Vol. 699 Als Ms. Gedr, VDI-Verl, Düsseldorf.

Zoz Gmbh, 2011. H2tank2go® – Hydrogen storage cartridge. Fast, reliable and cost effective based on room temperature metal hydride hydrolium®. Available at: http://gmbh.zoz.de/wp-content/uploads/h2tank2go-e.pdf (Accessed 19 December 2016).

Zoz Gmbh, 2016. Komplexe Metallhydride - Wasserstoffspeicher Der Zukunft: Bor4store B4s-Sm/Mm Feststofftank. In: Erster Semi-Kommerzieller Borhydrid Feststoff-Wasserstoffspeicher Fertiggestellt. Wenden, Olpe.

FURTHER READING

DOE, n.d. Doe Annual Progress Report.