Review Article
Material Demands for Storage Technologies in a Hydrogen Economy

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A hydrogen economy is needed, in order to resolve current environmental and energy-related problems. For the introduction of hydrogen as an important energy vector, sophisticated materials are required. This paper provides a brief overview of the subject, with a focus on hydrogen storage technologies for mobile applications. The unique properties of hydrogen are addressed, from which its advantages and challenges can be derived. Different hydrogen storage technologies are described and evaluated, including compression, liquefaction, and metal hydrides, as well as porous materials. This latter class of materials is outlined in more detail, explaining the physisorption interaction which leads to the adsorption of hydrogen molecules and discussing the material characteristics which are required for hydrogen storage application. Finally, a short survey of different porous materials is given which are currently investigated for hydrogen storage, including zeolites, metal organic frameworks (MOFs), covalent organic frameworks (COFs), porous polymers, aerogels, boron nitride materials, and activated carbon materials.

1. Motivation

Today's energy sector is accompanied by a number of environmental inconveniences. In order to overcome those problems, future energy concepts have to be put into practice. In particular, renewable energies are needed, because (i) fossil energy promotes global warming and environmental contamination, (ii) the supply of nonrenewable energy sources is finite, and (iii) nuclear energy presents a serious danger due to its radioactive waste products. Among renewable energies, technologies for hydrogen storage will be an important piece of the jigsaw.

The world's current energy supplies are mainly based on fossil energy resources. These resources have their origin in organic (and therefore carbon-containing) compounds, which have been converted throughout millions of years. By burning them today, these resources are reintroduced into the natural carbon cycle and increase the CO_2 content of the atmosphere. CO_2 gas increases the world's greenhouse effect, leading to global warming [1]. In Figure 1 it can be seen that, since the industrialization in the 19th century, the atmospheric CO_2 content is continuously rising. Also the evolution of the global temperature is shown in Figure 1. For the same time period, an overall increasing tendency can be observed, which suggests a relationship between both trends that could be something more than casual.

Another problem with natural and fossil energy resources is their limited availability. In the case of oil, this fact can be exemplified by the so-called peak oil phenomenon. The term "peak oil" was introduced by Shell-company scientist Hubbert more than 50 years ago, who correctly predicted that the oil production of the USA would have a maximum in the 1970s [2, 3]. Nowadays, this theory is applied to predict the worldwide production of oil. According to the peak oil theory, oil production reaches a maximum at a specific date and then drops by the same rate as its increase, leading to a symmetrical curve. While the main concept of peak oil finds wide acceptance, opinions diverge when it comes to questions of details. Particularly the present and future impacts of peak oil on science, technology, society, politics, business, and so forth are being lively discussed throughout the fields [4–13]. While some claim that peak oil already occurred, others speculate that this date is still far-off [6]. Indeed, the phenomenon turned out to come true for a number of single countries, and,
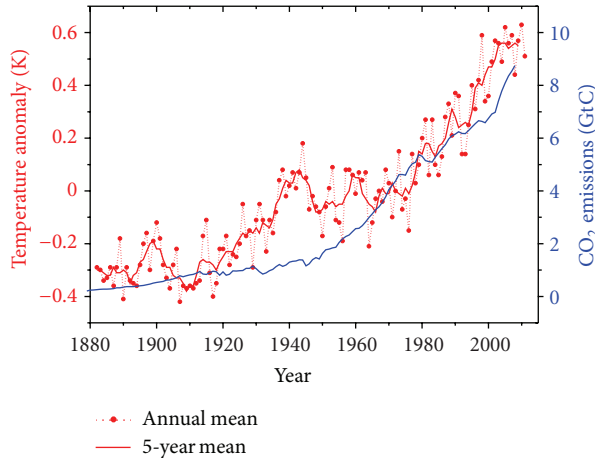
Figure 1: Global temperature (red) and CO_2 emissions (blue) over the past decades [14–16].

Figure 2: Discovery of conventional oil reserves (blue) and oil consumption (red) [5].

apparently, it is also correct if only "conventional" oil fields are taken into account. This refers to oil fields of a considerable size which are easily accessible. In Figure 2, the world oil consumption is shown over the years, together with the discovery of conventional oil fields. It can be seen that the consumption increases continuously. The discovery of large oil reservoirs, on the other hand, increased rapidly in the beginning, having its peak in the 1960s. From then on, the curve decreases as rapidly as it had increased, leading to a bell-shaped curve. In the 1990s, the consumption overreached the discovery. Thus, the oil that is consumed today has been found already decades ago or emanates from less accessible, and therefore more costly, oil sources. Summing up, natural resources are finite and will run out sooner or later.

Based on the aforementioned facts, it can be concluded that alternatives need to be found for the future energy market and that, in the long run, only renewable energy sources can provide sustainability. However, the usage of renewable energy sources leads to a number of new problems. On one hand, there is the temporal misfit between energy generation and consumption. For example, electricity can be produced by solar energy at daytime, but not during the night when it is needed for illumination. On the other hand, primary renewable energy sources are not efficient enough to be used in mobile applications, where space is limited and weight has to be low. Both of these problems can be solved by means of the so-called "hydrogen economy".

2. Introduction

2.1. The Hydrogen Economy. Fundamental research on hydrogen was firstly made in the middle of the 18th century by Henry Cavendish, who discovered the element in 1766, and by Antoine Lavoisier, who gave it its name in 1783 [17]. Despite the attention which is paid to it today, the idea of using hydrogen as an energy carrier is not new at all. In fact, syngas and coal gas found widespread use for heating, illumination, and engines since around 1800, and for more than 150 years, until being replaced by natural gas [17, 18]. These gases are
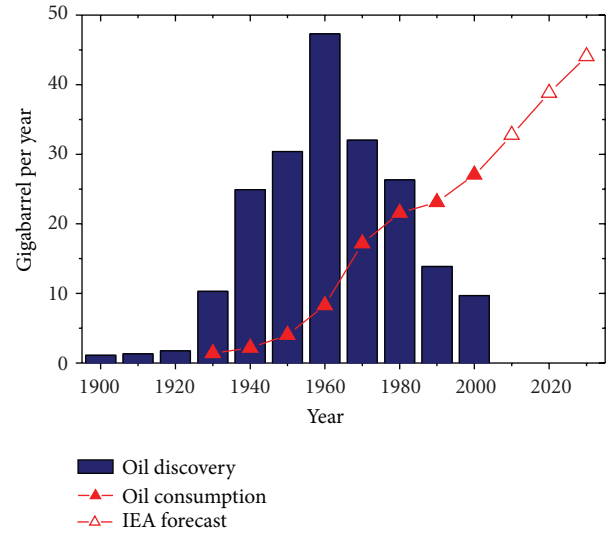
synthesized by steam gasification of different carbon sources and contain about 50% hydrogen mixed with other gases [17]. In fact, syngas is still being utilized today, in locations where natural gas is unavailable or costly [18]. Already in 1874, the novelist and science-fiction pioneer Jules Verne imagined a self-sustaining energy system based on electrolyzed hydrogen in his novel "The Mysterious Island".

However, the term "hydrogen economy" was not introduced until 1972 by Bockris [19]. The concept of the hydrogen economy gained great public attention as a consequence of the oil crises in the 1970s and moreover after the nuclear disasters of Chernobyl in 1986 and Fukushima in 2011. The basic idea behind the hydrogen economy is that hydrogen is produced by renewable energy sources, transported over large distances, stored in large amounts, and finally used to generate electricity, heat, and propulsion for the consumer [19]. Hydrogen could be produced centrally as well as locally and from numerous sources like wind, water, wave, solar, or biomass. Furthermore, its distribution could coexist with a conventional electricity network in order to provide households, industry, and vehicles with energy. For the distribution of hydrogen, a pipeline network, similar to today's natural gas system, could be used, if materials are found to be compatible [18].

2.2. Hydrogen Properties. Hydrogen is the lightest of all elements and the most abundant one in the universe [18, 20]. On earth, however, it only ranks the 15th element, and its concentration in the atmosphere is very low (0.5 ppm) [20, 21]. Yet it forms the largest number of chemical compounds, water being the most abundant of them [20, p. 351 f.].

In its gaseous state, hydrogen forms the diatomic molecule H_2 (dihydrogen). Some basic properties of hydrogen are listed in Table 1. It can be seen that it is a solid below 13.85 K, and its liquid form exists only in a small range of temperatures up to 20.25 K. Above its critical point ($T_C = 32.97$ K; $p_C =$

TABLE 1: Hydrogen properties.

Atomic weight	1.0079	$g\,mol^{-1}$
Van der Waals radius	120	pm
Covalent radius	31	pm
$\Delta H\ (H_2 \rightarrow 2\,H)$	436	$kJ\,mol^{-1}$
Density at 273 K and 0.1 MPa	0.0899	$g\,l^{-1}$
Liquid density (20.25 K)	70.8	$g\,l^{-1}$
Boiling point	20.25	K
Critical temperature	32.97	K
Critical pressure	1.276	MPa
Self-ignition temperature	747	K
Flammability limit in air	4.1–74.2	Vol.%
Explosive limits in air	18.3–59	Vol.%
Diffusion coefficient in air	0.634	$cm^2\,s^{-1}$

1.276 MPa) hydrogen is a supercritical fluid. Hydrogen gas is transparent, odorless, and nontoxic.

Hydrogen burns with invisible flame and over a wide range of concentrations in air. These points call critics into action and provoke concerns about hydrogen safety. The Hindenburg Zeppelin disaster from 1937 is a popular example which is often cited by critics against hydrogen technology. However, the subject is controversially discussed, and some studies of the accident have revealed that, instead of its hydrogen charge, a highly flammable skin material of the airship may have caused the fire [22, 23]. Hydrogen is around 14 times lighter than air and has a high diffusion coefficient. In the case of an accidental release, this causes a strong buoyancy and a fast volatilization into the atmosphere. Gasoline, in contrast, does not disperse rapidly and builds nonbuoyant, toxic fumes. In Table 2, properties of different fuels are compared. It can be seen that the ignition energies at the lower flammability limit are in general very low. Thus, already electrostatic sparks may have sufficient energy for igniting fuel/air mixtures under these conditions [18]. Regarding the flammable and explosive ranges, the lower limits are generally considered more important in the case of an accident [18]. Despite the fact that hydrogen has a broad range of flammability, its lower flammable limit is significantly higher than for a number of other fuels. This includes widely used combustibles, like, for example, gasoline, butane, propane, and ethanol. Its autoignition temperature lies in a range similar to other fuels. According to a report on behalf of Ford Motor Company, the safety of a hydrogen FC vehicle would be potentially better than that of a gasoline or propane vehicle [18, 24]. For a large number of solid materials, hydrogen embrittlement is a problematic issue. Hydrogen can easily penetrate these materials via several mechanisms. Inside the host material, the hydrogen impedes the plastic flow of the material and decreases its ductility [25]. For high pressure applications and storage tank designs it is particularly important to take into account hydrogen embrittlement, in order to avoid the failure of system and tank components.

Due to its high conversion efficiency and its zero emission (referring to emissions of toxic pollution or greenhouse gases like, e.g., CO_2), hydrogen is regarded as an ideal secondary energy carrier. It can be produced using renewable energy and water, and, by means of storing it, the hydrogen can be retransformed to energy and water in another time and space. During those conversions no contamination is produced. For energy conversion, well-established technologies like internal combustion engines (ICEs) may be operated with hydrogen fuel if they are slightly modified [20]. By combustion in air, the emission is primarily water vapor. Only traces of nitrogen oxides are formed, which can be controlled to very low levels [18]. In ICEs, the conversion efficiency is thermodynamically limited by the Carnot efficiency to a relatively low value (below 30%) [25]. In terms of both, emission and efficiency, fuel cells (FCs) outperform classical combustion engines. Thus, they are able to convert the chemical energy of hydrogen to electricity with an efficiency of up to 60% [18, 22]. Thereby, water vapor is the sole emission [18]. Today, one of the main drawbacks of FCs is that they are expensive, amongst others because of their dependency on precious catalyst materials.

Aside from high costs of FCs, there are two other main obstacles which impede the introduction of hydrogen as an important energy vector today: hydrogen production and its storage. Thus, inexpensive methods for hydrogen mass production need to be found, and efficient, economic, and safe hydrogen storage technologies need to be developed in order to compete with less expensive fossil fuels and for introducing a hydrogen economy [18].

3. Hydrogen Storage

As an energy carrier, hydrogen has to compete against other fuels. For the use in electric vehicles, hydrogen could outperform electric batteries which are relatively bulky and heavy [18]. According to General Motors, running an electric vehicle with hydrogen and fuel cells instead of batteries has a number of advantages [26]. For example, costs can be reduced, and considerably higher energy densities can be reached [26].

In Figures 3 and 4, the heat of combustion of hydrogen is compared with other gaseous, liquid, and solid fuels. On a gravimetric basis (Figure 3), the value of hydrogen clearly exceeds those of other alternatives, reaching more than twice of their energy content. This characteristic predestines hydrogen, for example, as a rocket fuel [18, 21]. For application in a FC car a mass of only around 4 kg of hydrogen is sufficient in order to reach a range of 400 km [22]. A contrary tendency can be observed for the heat of combustion on a volumetric basis (see Figure 4). This is why, under standard conditions, gaseous fuels are in a clear disadvantage. In particular hydrogen reaches a significantly lower volumetric value, due to its low density. Thus, if the 4 kg of hydrogen, which is needed for a FC car, would be carried under normal conditions (at room temperature and under atmospheric pressure), then the tank would occupy a volume of approximately 45 m^3; by way of illustration this would correspond to a balloon of around 4.4 m diameter.

The aforementioned reveals that, for hydrogen storage application, the storage volume needs to be reduced. Putting it in another way, this means that, for a given storage

TABLE 2: Comparison of fuel safety properties in air [18, 24, 25, 27].

Fuel	Autoignition temperature K	Flammable limits Vol.%	Explosive limits Vol.%	Buoyant velocity m s^{-1}	Ignition energy[a] mJ
Hydrogen	673–858	4.1–74.2	18.3–59.0	1.2–9.0	10
Methane	923	5.3–15.0	6.3–13.5	0.8–6.0	20
Ethane	788	3.0–12.5	—	—[b]	—
Propane	723	2.3–9.5	3.1–7.0	—[b]	—
Butane	678	1.9–8.5	—	—[b]	—
Gasoline	553–729	1.4–7.6	1.1–3.3	—[b]	—
Ethanol	696	3.3–19.0	—	—[b]	—
Methanol	743	6.0–36.5	—	—[b]	—

[a]Ignition energy at the lower flammability limit. For stoichiometric mixtures, the value is significantly lower (e.g., 0.02 mJ for hydrogen) [18].
[b]Nonbuoyant, due to higher density than air (1.2 kg m^{-3}) under standard conditions.

FIGURE 3: Heat of combustion on a gravimetric basis, shown for various gaseous, liquid, and solid fuels under standard conditions. The ranges of values were obtained by utilizing a multitude of sources [18, 28–38].
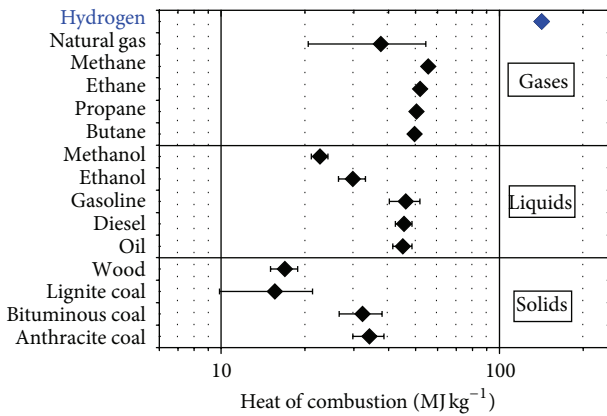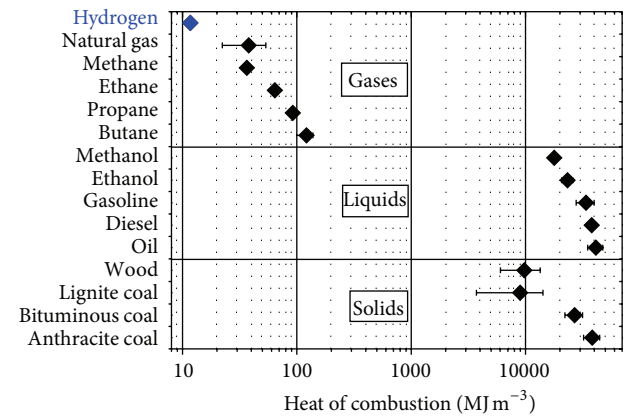

FIGURE 4: Heat of combustion on a volumetric basis, shown for various gaseous, liquid, and solid fuels under standard conditions. The ranges of values were obtained by utilizing a multitude of sources [18, 28–38].

volume, the distances between hydrogen molecules need to be decreased. However, such an increase of the volumetric storage density has to come along with maintaining the gravimetric storage density on a high level. An important aspect is that, even though systems for hydrogen onboard storage in vehicles may be bulkier and heavier than for other fuels, these constraints can be acceptable, taking into account the highly efficient conversion of hydrogen and the fact that a relatively small amount of fuel is needed to travel a given distance [18].

Acceptable compromises need to be found regarding hydrogen storage systems which guarantee a successful introduction of hydrogen technology. In order to provide a framework for the development of hydrogen storage technology, governmental institutions and other funding bodies established a number of targets and milestones. These targets set limits to, for example, the refilling time, the cycle lifetime, the costs, and the densities of the storage system [22, 39, 40]. Usually, in the research of materials for hydrogen storage, special attention is drawn to the gravimetric and volumetric densities. In 2004, the DOE introduced a number of milestones, which also included targets concerning the storage

densities [39]. Ever since their introduction, these guidelines actuated as an important stimulation for research in this field. However, despite the worldwide effort of scientists and engineers, none of the current technologies meets all of these demands. In 2009, the DOE revised their system density targets which are now based on light-duty vehicles and reduced them to 4.5 wt.% and 5.4 MJ kg^{-1} (target for 2010), 5.5 wt.% and 6.48 MJ kg^{-1} (target for 2015), and 7.5 wt.% and 9 MJ kg^{-1} (ultimate target), respectively [41]. Taking into account the lower heating value of hydrogen (33.33 kWh kg^{-1}), as well as the fact that 1 kWh = 3.6 · 10^6 Ws = 3.6 MJ, the volumetric storage densities corresponded to 28 g$_{H_2}$ l^{-1}, 40 g$_{H_2}$ l^{-1}, and 70 g$_{H_2}$ l^{-1}, respectively (grams of H$_2$ per liter of storage volume) [41]. Some of the currently valid DOE key targets are listed in Table 3. Concerning the EU, the key research issue for volumetric storage density is 1.1 kWh l^{-1}, corresponding to 33 g$_{H_2}$ l^{-1} [42].

Hydrogen can be stored, either in an empty tank (e.g., in the case of high pressure hydrogen storage or liquefied hydrogen storage) or in a tank containing a solid (solid-state H$_2$ storage). In the latter case, the storage density is often

TABLE 3: DOE hydrogen storage targets for light-duty vehicles [41].

Storage parameter	Units	2010	2015	Ultimate target
Gravimetric system density	$kWh\,kg^{-1}$	1.5	1.8	2.5
	$MJ\,kg^{-1}$	5.4	6.48	9
	wt.%	4.5	5.5	7.5
Volumetric system density	$kWh\,l^{-1}$	0.9	1.3	2.3
	$MJ\,m^{-3}$	3.24	4.68	8.28
	$g_{H_2}\,l^{-1}$	28	40	70
Fuel cost at pump	$ GGE^{-1a}	3–7	2–6	2-3
System filling time for 5 kg H_2	min	4.2	3.3	2.5
	$kg_{H_2}\,min^{-1}$	1.2	1.5	2
Maximum loss of useable H_2	$g\,(h\,kg_{H_2})^{-1}$	0.1	0.05	0.05

[a]1 gasoline gallon equivalent (GGE) $\approx$ 1 kg hydrogen [43].

referred exclusively to the solid used, in order to facilitate the performance comparison of different materials.

Thus, it is extremely important to distinguish between storage densities on a material basis and those which are based on the whole storage system. It has to be pointed out that the technological requirements and targets, which were mentioned previously and which are listed in Table 3, refer to the *whole* storage system. This means that, apart from the fuel itself (and the storage material in the case of hydrogen storage in solids), also the tank shell, regulation, and system devices, as well as other auxiliaries, need to be taken into account. In the case of high pressure storage, suitable materials and sufficient dimensions need to be chosen for the tank shell, in order to withstand the high pressures. This reduces the effective storage density of the system [26]. Also in the case of liquid hydrogen storage, the storage density is reduced significantly, due to necessary adaptations like isolation, secondary devices, and so forth [26].

3.1. Overview of Hydrogen Storage Techniques. In the previous section, it was shown that the main problem for hydrogen storage is its extremely low density under normal conditions. In order to reduce the occupied volume by hydrogen gas, a number of different technologies are being investigated.

3.1.1. Compression. Compressing hydrogen up to high pressures is a relatively simple and cost-efficient technology [25]. This is why most of the current hydrogen car prototypes are based on storage tanks with high pressure vessels [26]. For the pressure vessels, adequate materials and dimensions are needed in order to withstand these high pressures, to accomplish safety issues, and to avoid hydrogen diffusion. In practice, this results in an important weight gain and, consequently, in a reduction of the system storage capacity. For pressurized vessels, spherical or cylindrical tank structures are necessary, in order to reduce the tank shell dimensions. According to the United Nations Economic Commission for

Europe (UNECE), pressure vessels for hydrogen storage can be classified into four types [44]:

Type 1: all metal cylinder,

Type 2: partly fiber-wrapped, load-bearing metal liner,

Type 3: fully fiber-wrapped, non-load-bearing metal liner,

Type 4: fully fiber-wrapped, non-load-bearing nonmetal liner.

From type to type, the weight of the vessel is successively reduced by substituting metals with other lighter materials. The two basic components of a state-of-the-art type 4 pressure vessel are (a) a liner which prevents hydrogen permeation and (b) a composite structure which accounts for the mechanical stability of the structure. In Figure 5, a schematic diagram of a type 4 pressure vessel and its components is shown.

An important concern regarding high pressure vessels is safety issues, especially in the case of mobile applications. Thus, pressure vessel has to be extensively tested regarding overpressure and accidental impacts. Another drawback of gaseous storage is the energy expenditure which is needed for the compression process. Thus, around 12% of the stored hydrogen energy is consumed for reaching 35 MPa and 15% for 70 MPa, respectively [26].

In order to determine gas densities at given pressure-temperature conditions, adequate models are needed. In general, the ideal gas equation (1) becomes invalid at elevated pressures:

$$p \cdot V = n \cdot R \cdot T \tag{1}$$

p: absolute gas pressure (Pa)

V: volume occupied by gas (m^3)

n: number of moles of gas (mol)

R: universal gas constant (8.3145 J(K mol)$^{-1}$)

T: absolute temperature (K).

A better approximation for describing the thermodynamic behavior of real gases can be made by the van der Waals equation (see (2)). This approach is a modification of the ideal gas law which introduces two correction factors a and b:

$$\left(p + a \cdot \left(\frac{n}{V} \right)^2 \right) \cdot (V - n \cdot b) = n \cdot R \cdot T \tag{2}$$

a: van der Waals correction for finite gas molecule size

b: van der Waals correction for volume of one mole of gas.

In Table 4, the van der Waals constants for hydrogen are given. The term $n \cdot b$ implements the volume occupied by the gas molecules, which has to be subtracted from the total volume available V. On the other hand, the term $a \cdot (n/V)^2$ represents the attraction due to van der Waals forces. It is
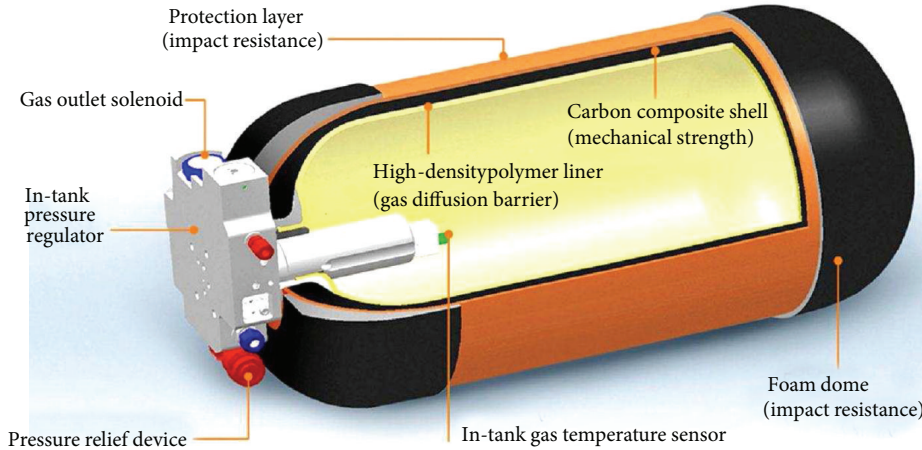
FIGURE 5: Schematic diagram of a type 4 pressure vessel and its components for gaseous hydrogen storage (Quantum Technologies, Inc., Irvine). Reprinted from [26], with permission from Elsevier.

TABLE 4: Van der Waals constants for hydrogen.

Description	Symbol	Value	Unit	Reference
VdW correction	a	0.2484	$(\mathrm{l}^2\mathrm{bar})\,\mathrm{mol}^{-1}$	[27]
VdW correction	b	0.02651	$\mathrm{l}\,\mathrm{mol}^{-1}$	[27]

added to the pressure component p, in order to account for the increasing attraction between the gas molecules, for increasing number of molecules n, or reduction of the available volume V.
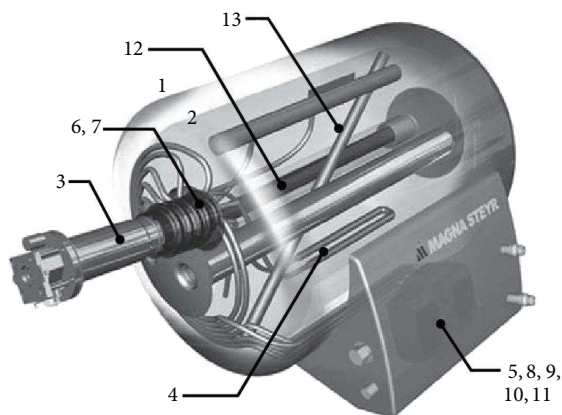
Despite its descriptive character, the van der Waals equation turns out to be relatively imprecise if it is applied to hydrogen gas [45]. Hence, more precise equations of state (EOS) have to be used in order to estimate the density of hydrogen under given thermodynamic conditions [45]. Modifications of the van der Waals EOS have been proposed by Redlich-Kwong [46], Soave [47], and Peng-Robinson [48]. A different approach is done by empirical (virial) equations of state, based on the Benedict-Webb-Rubin (BWR) equation [49]. A comparison with the Peng-Robinson approach reveals that modified BWR (MBWR) equations give more precise values for hydrogen [50, 51]. Some common examples for MBWR equations are the Lee-Kesler equation [52] and the 32-term MBWR equation introduced by Younglove [53]. The latter is the basis of the NIST database of thermophysical properties of fluids which has been used throughout this study [36]. More recently, another approach was introduced by Leachman et al. [54] which claims to have an uncertainty in density of only 0.04% in the region between 250 and 450 K and for pressures up to 300 MPa [54].

3.1.2. Liquefaction. Another possibility is to store hydrogen in liquid form. However, hydrogen only condensates at very low temperature (20.4 K). The liquefaction process is based on the Joule-Thomson effect, which explains the temperature change of a pressurized real gas when it is throttled [25]. The work of liquefaction of an idealized process takes into account an isothermal compression followed by reversible

isentropic expansion [25]. Furthermore, also the nuclear spin of hydrogen becomes important for the liquefaction process. The H_2 molecule occurs in two forms: orthohydrogen (parallel spin) and parahydrogen (antiparallel spin). Under normal conditions, hydrogen gas is a mixture of 75% ortho- and 25% parahydrogen ("normal hydrogen"). With decreasing temperature, the amount of parahydrogen increases, reaching 99.8% at its liquid state [25]. The transformation of the ortho- to the parastate is accompanied by a heat release which prejudices the cooling process [25].

Taking into account the transformation from the ortho- to the para-state, the ideal work of liquefaction of hydrogen is 11.88 MJ kg^{-1} [25, 55]. This is about 15 times more than for nitrogen liquefaction [25, 55]. Industrial liquefaction plants are based on the Linde cycle or the Claude cycle which use prestage cooling with liquid nitrogen and subsequent recirculation of precooled hydrogen gas in a counterflow heat exchanger [25]. Their efficiency is significantly lower than the ideal process, consuming approximately 30% of the chemical energy stored inside the liquefied hydrogen which is an important disadvantage of this technology [26, 39, 56].

In Figure 6, a schematic diagram of a system for liquid hydrogen storage, designed for application in vehicles, is shown. Its main purpose is to thermally isolate the cryogenic hydrogen from ambient conditions. The tank consists of a double-walled metallic vessel whose interspace is evacuated and contains a multilayered isolation [57, 58]. Also in the case of liquid hydrogen storage, spherical or cylindrical tank structures are beneficial. Here, these configurations help to optimize the surface/volume ratio and to reduce heat transfer between the interior and exterior of the tank. In spite of the very complex and costly insulation, heat flow to the inside of the tank is unavoidable. This causes the constant evaporation of some of the liquid hydrogen, which leads to a pressure rise inside the tank. When about 1 MPa is reached, the hydrogen has to be released in order to avoid that the tank is damaged [26]. If not captured, this so-called hydrogen boil-off is lost to the environment. Hence, it cannot be used for propulsion anymore. Also, additional hydrogen is lost due

(1) Outer tank
(2) Inner tank
(3) Coupling (Johnston-Cox)
(4) Heater
(5) Heat exchanger
(6) Cryogenic filling valve
(7) Cryogenic return valve

(8) Pressure regulation valve
(9) Shut-off valve
(10) Boil-off valve
(11) Safety relief valve
(12) Support post
(13) Liquid level sensor

FIGURE 6: Schematic diagram of a liquid hydrogen tank and its components (Magna Steyr, BMW). Reprinted from [57], with permission from International Association of Hydrogen Energy.

to heat transfer in the course of the fueling process. Furthermore, it is claimed that large amounts of escaping hydrogen may contribute to global warming [59].
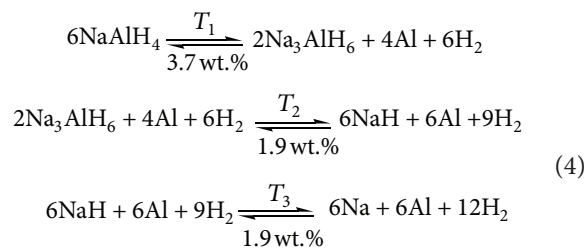
Among the car manufacturers, opinions regarding liquid hydrogen storage are contradictory. Thus, BMW equipped a number of hydrogen prototypes with such systems [58]. According to General Motors Company, on the other hand, liquid hydrogen storage is not favorable over compressed gas storage [26]. Despite its disadvantages, liquid hydrogen is used as a fuel for spacecraft rocket propulsion. For this application, gravimetric and volumetric energy contents are the most critical parameters, and, because of the fast fuel consumption, isolation can be reduced to a minimum [60].

3.1.3. Chemisorption in Metal Hydrides. A third possibility is to store hydrogen through dissociative chemisorption, followed by the formation of a new compound. Among them, metallic hydrides are being widely studied. During chemisorption in metal hydrides, the hydrogen molecule is first dissociated on the surface, and then its atoms diffuse into the metal host [61]. Inside the bulk, chemical bonds are formed, resulting in the hydride phase. With respect to the bonding mechanism between the hydrogen and the host material, metal hydrides can be categorized, at a first glance, as saline hydrides (ionic bonding), covalent hydrides (covalent bonding), and interstitial hydrides (metallic bonding). Usually, the hydrogen compounds are formed and decomposed under determined pressure-temperature conditions. Thus, formation takes place under elevated hydrogen pressure whereby heat is generated due to the exothermic reaction (3). For releasing the hydrogen, the pressure is reduced and the

material is heated. For reversible hydrides, these cycles can be repeated several times.

$$\mathrm{MH}_n\,(s) + \text{heat} \rightleftharpoons \mathrm{M}(s) + \frac{n}{2}\mathrm{H}_n\,(g) \tag{3}$$
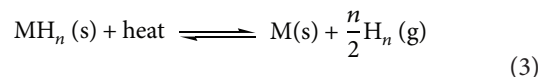
Materials which have been investigated for storing chemically bonded hydrogen include numerous compounds. Although often more sophisticated alloys are investigated, some basic metal hydride systems are usually classified as AB_5 (e.g., $LaNi_5$), AB (e.g., FeTi), A_2B (e.g., Mg_2Ni), AB_2 (e.g., ZrV_2), and so forth [62–65]. Other candidates include simple hydrides which contain only one element different from hydrogen, for example, MgH_2 [61, 66] or AlH_3 [67]; complex metal hydrides such as alanates ($NaAlH_4$, $LiAlH_4$, $MgAlH_4$, etc.) [68–72] or borohydrides ($NaBH_4$, $LiBH_4$, etc.) [72], and alloyed combinations of them; amides and imides (metal-N-H systems) [73–76]; reactive hydride composites [77–79]; as well as other chemical storage media like methanol (CH_4O), ammonia (NH_3), or B-N compounds in combination with on- or off-board reforming [72, 80–83]. Some of the classic metal hydride materials can be reversibly operated close to room temperature. However, these materials usually have very low gravimetric storage capacities of less than 3 wt.% [84]. On the contrary, light metal hydrides achieve promising gravimetric capacities (e.g., 18 wt.% in the case of $LiBH_4$); yet, they lack reversibility and/or need to be operated at high temperatures (e.g., around 573 K for MgH_2) [84]. In addition, some of the materials, like, for example, $NaAlH_4$, decompose by multistep reactions (see (4)) [69, 71, 72]:

$$6\mathrm{NaAlH_4} \underset{3.7\,\text{wt.\%}}{\overset{T_1}{\rightleftharpoons}} 2\mathrm{Na_3AlH_6} + 4\mathrm{Al} + 6\mathrm{H_2}$$

$$2\mathrm{Na_3AlH_6} + 4\mathrm{Al} + 6\mathrm{H_2} \underset{1.9\,\text{wt.\%}}{\overset{T_2}{\rightleftharpoons}} 6\mathrm{NaH} + 6\mathrm{Al} + 9\mathrm{H_2}$$

$$6\mathrm{NaH} + 6\mathrm{Al} + 9\mathrm{H_2} \underset{1.9\,\text{wt.\%}}{\overset{T_3}{\rightleftharpoons}} 6\mathrm{Na} + 6\mathrm{Al} + 12\mathrm{H_2} \tag{4}$$

The fact that the intermediate compounds decompose at different temperatures $T_3 > T_2 > T_1$ further complicates the heat management of the storage system. Currently, research is focused on improving kinetics and thermodynamics of the investigated materials and on finding new compounds and catalysts in order to obtain high capacities at lower temperatures [85].

Due to the Westlake Criterion, the H-H distance in stable hydrides can reach values of 2.1 Å [86, 87], and even lower distances have been reported [88, 89]. Thus, on a materials basis, very high volumetric storage capacities can be achieved with metal hydrides, when their crystal densities are taken into account. For example, $115\,\mathrm{g\,l^{-1}}$ are reached in the case of $LaNi_5H_6$ and $150\,\mathrm{g\,l^{-1}}$ for Mg_2FeH_6 or $Al(BH_4)_3$ [84]. In Figure 7, the volumetric hydrogen densities of different

technologies are compared. It can be seen that metal hydrides reach higher values than gaseous and even liquid hydrogen. This means that, in a determined volume, more hydrogen can be stored in form of a metal hydride than in form of compressed or liquefied hydrogen.

For hydrogen storage application, however, the hydride is usually available in powder form, in order to minimise diffusion paths and to increase reaction kinetics. Therefore, the value for the crystal density of the hydride should not be confused with the volumetric storage density, which is expected to be considerably lower. Furthermore, the material density changes in the course of the metal-hydride reaction. By continuously being loaded and discharged with hydrogen, the material matrix periodically expands and contracts for every hydrogen cycle, leading to a sintering of the material. Those density changes represent a major challenge for the practical implementation of this technique. In the case of AB_5-type metal hydrides this expansion can exceed 12% [90, 91]. Another problem with metal hydrides is their cycling stability due to segregation effects of their components or catalysts [92–99].

On a gravimetric basis, only very low values are reached with room temperature hydrides. Light metal hydrides perform much better. However, these materials involve high binding enthalpies which lead to a considerable amount of heat that needs to be transferred during hydrogen charging and discharging [26, 100, 101]. As chemisorption is based on an exothermal reaction, a considerable amount of heat is generated upon hydrogenation. This heat has to be removed by an active cooling device. On the other hand, for utilizing the hydrogen, and in order to release it from the material, the tank needs to be heated up. Thus, a number of secondary devices are needed, which again occupy precious space and lead to low storage capacities, when the complete tank design is taken into account. For a typical heat of formation of $25\,MJ\,kg_{H_2}^{-1}$, a heat exchanger of several hundreds of kW would be necessary [26]. This significantly reduces the energy efficiency of the whole process, for example, in the case of MgH_2 by 30% [96].

3.2. Hydrogen Storage by Physisorption. Physisorption (or *ad*sorption) fills the gap between the techniques described before. The H_2 molecule (adsorbate) is thereby bound by van der Waals forces on a porous material (the adsorbent) which has a high internal surface area. Physisorption is a non-activated process and the hydrogen-material-interactions are relatively weak (typically between 2 and $8\,kJ\,mol^{-1}$) [45, 102–105]. As a consequence, the sorption heat is much lower than for chemisorption, and no active cooling device is needed, nor does the material need to be heated up in order to release the major part of the stored hydrogen. On the other hand, the interaction is strong enough to enhance the amount of hydrogen stored in a given volume or to use cryogenic temperatures which are closer to ambient conditions (that means higher) than in the case of liquid hydrogen.

These relations among the different storage technologies are visualized in the thermophysical phase diagram in Figure 8 [106]. In this diagram, the volumetric density of
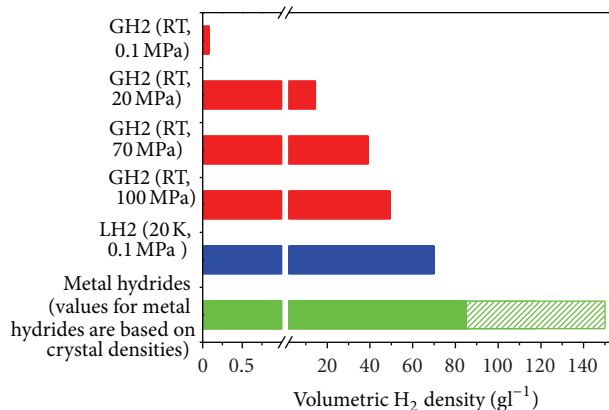

Figure 7: Comparison of volumetric fuel densities for different hydrogen storage technologies: compressed hydrogen (GH2) at room temperature for 0.1, 20, 70, and 100 MPa [36]; liquid hydrogen (LH2); and metal hydrides [22].

parahydrogen is plotted over the temperature for different pressures. A wide range of temperatures from zero to 400 K is covered, and the temperatures which are most interesting for studying hydrogen adsorption (liquid nitrogen and room temperature) are indicated. A tank device for cryogenic adsorption could be operated within the range of these two temperatures [107]. Also the critical point and the boiling point of hydrogen, which is important for liquid hydrogen storage, are marked. The DOE target values for the volumetric storage density (see Table 3) are visualized by horizontal lines. It has to be reminded that these values refer to the whole storage system and are included only for orientation. It can be seen that, in order to achieve the 2015 target by compression, pressures superior to 72 MPa and 13.9 MPa would be needed at RT and 77 K, respectively. The ultimate DOE target for the volumetric density would require pressures of more than 187.7 MPa at RT or 44.6 MPa at 77 K. The challenge for hydrogen storage by physisorption is the reduction of these high pressures.

3.2.1. Basic Concepts for Hydrogen Storage by Physisorption. In general, two different strategies are considered for utilizing adsorbents in hydrogen storage tanks. In the first case, the tank is maintained at low temperatures ("cryoadsorption") [108]. At cryogenic temperatures, the thermal vibration of the adsorbate molecules is relatively low in comparison with the van der Waals forces, thus increasing the adsorption potential [84]. By using a temperature which is higher than in the case of liquid hydrogen storage, costs and isolation efforts can be significantly reduced. Usually, liquid nitrogen is used for cooling the tank down to 77 K. At this temperature, the adsorption potential is sufficiently high, so that the tank can be operated at relatively moderate pressures. Thus, many adsorbents reach their maximum excess adsorption of hydrogen at pressures of around 4 MPa. In Figure 8, a schematic example for adsorption at 77 K is included which exemplifies that, for reaching the 2015 DOE target, the operating pressure could be drastically reduced from 13.9 MPa (for a tank using compressed hydrogen) to 4 MPa.
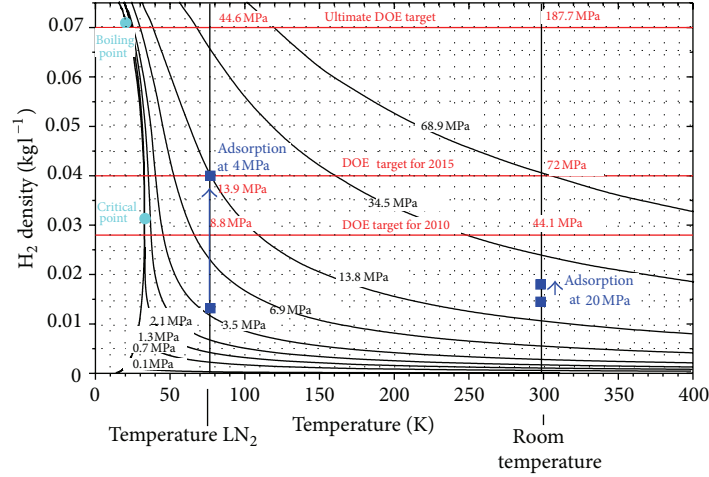
FIGURE 8: Density diagram for hydrogen, including the DOE targets for volumetric storage density. Thermo-physical data was obtained from NIST [106].

From an application point of view, it would be more interesting to operate the tank at room temperature. In this second scenario, costs for cooling could be avoided and no isolation would be needed, thus reducing weight and volume of the storage device. However, at increased temperature, the influence of the van der Waals forces decreases due to an increased thermal vibration of the adsorbate molecules. Due to the low adsorption potential under these conditions, high pressures are needed to reach sufficient storage capacities. However, also at room temperature it is possible to reduce the operating pressure for the storage of a determined amount of hydrogen by using an adsorbent, in comparison with an empty vessel [109, 110] (see Figure 8).

3.2.2. Physisorption Fundamentals. Three different kinds of van der Waals forces can contribute to the interaction between adsorbent and adsorbate [111]:

  (1) permanent dipole-permanent dipole forces (Keesom interaction),

  (2) permanent dipole-induced dipole forces (Debye interaction),

  (3) instantaneous induced dipole-induced dipole forces (London dispersion forces).

In the case of hydrogen adsorption on carbon surfaces, the first two contributions are usually not taken into account [103]. Mathematically, the van der Waals forces can be approximated by a Lennard-Jones potential (L-J potential) [112, 113]. Thereby, repulsion and attraction between adsorbent and adsorbate are represented as a function of their distance (see (5)):

$$L(r) = 4 \cdot \epsilon \left(\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right) \tag{5}$$

$L(r)$: L-J potential between adsorbent and adsorbate

r: distance between adsorbent and adsorbate

ϵ: minimum value of $L(r)$

σ: finite distance at which $L(r) = 0$.

In Figure 9, the Lennard-Jones potential between carbon and hydrogen is shown. The values for ϵ and σ, corresponding to the interaction between carbon and hydrogen, are listed in Table 5 and were calculated using the formulas and data from [114]. It can be seen that the potential has a minimum at a distance of around 0.35 nm.

3.2.3. Material Demands. Designing an optimized adsorbent for hydrogen storage is a challenging task. In general, there are two basic requirements which need to be taken into account [109, 115]. On the one hand, a large number of adsorption sites per weight and volume of adsorbate should be provided. This has to be done by developing a highly porous material with large surface areas and pore volumes. On the other hand, the heat of adsorption of the adsorbent should be increased. Thus, at room temperature, the optimum adsorption enthalpy of an adsorbent should be between 10 and 50 kJ mol^{-1} [102, 115], and theoretical calculations reveal a value of 15.1 kJ mol^{-1} [104].

In order to increase the adsorption enthalpy of adsorbents, three possibilities are generally considered [102, 109, 115]: hydrogen spillover, unsaturated adsorption centers, and adsorption in very small pores. For hydrogen spillover, transition metals like, for example, platinum or palladium are introduced into the porous host material. Thereby, it is intended that these metal sites act as catalysts, in order to break the H–H bond, so that the adsorbed species are hydrogen atoms rather than the molecule itself. While theoretical studies claim the feasibility of this method, experiments have not yet been crowned with success [109, 115]. In addition, the formation of chemical bonds to the host material has to be taken into account so that high temperatures could be necessary for releasing the hydrogen [102].

Also in the case of unsaturated adsorption centers, the chemical composition of the material host is changed by
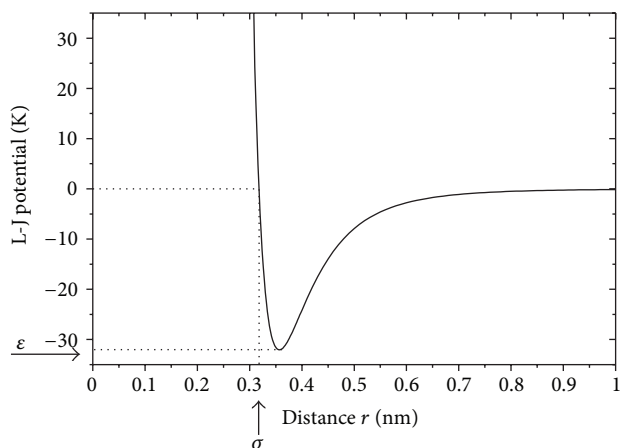
FIGURE 9: Lennard-Jones potential of the carbon-hydrogen interaction. Values for ϵ and σ were taken from [114].

TABLE 5: Lenard-Jones constants for the carbon-hydrogen interaction.

Description	Symbol	Value	Unit	Reference
Lenard-Jones constant	ϵ	32.06	K	[114]
Lenard-Jones constant	σ	0.318	nm	[114]

introducing other species like, for example, metals. However, their interaction with the hydrogen molecule is weaker and limited to increase the adsorption potential. This is accomplished by donation of charge between the molecules and the functionalized interaction sites [102]. This approach has been proven to be partially successful. Thus, heats of adsorption could be increased to around $10 \, \text{kJ} \, \text{mol}^{-1}$ and even up to $22 \, \text{kJ} \, \text{mol}^{-1}$ [115]. However, these high values may be caused by mechanisms different from the adsorption process. The main disadvantage of those first two methods is that additional (heavy) species are introduced into the porous material. This decreases the specific surface area and pore volumes, prejudicing the gravimetric storage capacity of the material.

The third method, decreasing the pore sizes of the material, manages without the introduction of additional species. Here, the concept is to build a very narrow porosity in which the hydrogen molecule can simultaneously interact with multiple pore walls. Due to their proximity, the adsorption potentials of opposed pore walls overlap, resulting in an amplified attraction.

At 77 K, a correlation of hydrogen adsorption with the BET surface area has been reported [22, 116]. However, such correlation was found to be more precise with the total volume of micropores [45, 117, 118]. This indicates that, under cryogenic temperature conditions, adsorbents with a high amount of micropores smaller than 2 nm are beneficial [115–118].

At room temperature, the optimum pore size was found to be around 0.7 nm [102, 119]. This coincides with an overlapping of two carbon-hydrogen potentials, similar to the one shown in Figure 9. A pore of this size is sufficient for accommodating two layers of hydrogen molecules [119].

The amount of pores which are narrower than 0.7 nm can be obtained by calculating the DR micropore volume from CO_2 adsorption data, V_{DR} (CO_2) [120]. For hydrogen adsorption amounts at room temperature, a better correlation is achieved with this value than with the total micropore volume or the BET surface area [45, 116–118, 121–123].

3.2.4. Porous Materials for Hydrogen Storage. Numerous kinds of materials have been investigated as adsorbents for hydrogen. These include carbon-based materials (activated carbons, carbon nanotubes, nanofibers, fullerenes, carbons from templates, etc.), zeolites, silica, alumina, metal organic frameworks (MOFs), covalent organic frameworks (COFs), porous polymers, aerogels, and boron nitride materials. In the following, a brief overview of the different classes of materials as well as their performance for hydrogen storage is given.

Zeolites are aluminosilicates which can accommodate a wide variety of cations [112]. These materials can be found naturally or can be produced synthetically [112]. Due to their crystalline structure, zeolites have a very defined porous structure. However, they are composed of relatively heavy elements which limit their porosity, to maximum specific surface areas of less than $750 \, \text{m}^2 \, \text{g}^{-1}$ [109]. They are used in numerous industrial applications, for example as detergents, catalysts, desiccants, molecular sieves, or for water purification as well as gas separation and purification through pressure swing adsorption (PSA) [124–126]. Zeolites were among the first porous materials which have been investigated for hydrogen storage purposes [127–131]. However, due to their low porosity, hydrogen adsorption amounts are limited. Thus, less than 1.5 wt.% are adsorbed at 77 K and 0.1 MPa, and, for higher pressures, maximum adsorption amounts are lower than 2 wt.% [131, 132]. Theoretical calculations reveal that, even under ideal conditions, adsorption amounts are limited to 2.86 wt.% [131].

Some natural or synthetic oxides like silica and alumina can also reveal high porosity which often has a high contribution of mesopores. Due to this characteristic, these materials find a lot of applications in catalysis, separations, sensors, drug delivery, optical devices, and molecular sieves [133]. Silica gel, for example, reaches a high surface area of more than $1000 \, \text{m}^2 \, \text{g}^{-1}$ [132, 134], and some of them are commercially available, like, for instance, MCM-41 (with pore diameter limited to approximately 80 Å) [134–136], and SBA-15 (with pore sizes ranging from 20 to 300 Å) [137, 138]. However, their porous structure results inappropriate for hydrogen storage, and less than 0.6 wt.% were measured at 77 K and 0.1 MPa [132].

By means of sol-gel reaction, aerogels with large specific surface areas of more than $3000 \, \text{m}^2 \, \text{g}^{-1}$ can be prepared [139, 140]. Hydrogen adsorption was reported to reach over 5 wt.% at 77 K and 3.5 MPa [141, 142]. However, their low material density of typically around $0.1 \, \text{g} \, \text{cm}^{-3}$ leads to low volumetric storage densities. Together with their inappropriate pore size distribution, these materials can be regarded as unsuitable as hydrogen storage medium [139, 140].

More recently, also noncarbon nanotubes have been proposed for hydrogen storage [143]. Boron nitride (BN)

nanotubes, for instance, were claimed to have advantages over carbon nanotubes (CNTs) and to adsorb up to 2.6 wt.% at RT and 10 MPa [144, 145]. However, other studies reveal that BN nanotubes only show insignificant improvements over CNTs at RT [146]. Other boron-carbon-nitride (B-C-N) materials reach specific surface areas of more than $1500 \, \text{m}^2 \, \text{g}^{-1}$ and adsorb 1 wt.% hydrogen at 77 K and 0.1 MPa [147].

Another class of materials which recently were proposed for hydrogen storage application are porous polymers [148–150]. Thus, (hyper)crosslinked polymers can reach BET surface areas of up to $2000 \, \text{m}^2 \, \text{g}^{-1}$ and adsorb 1.5 wt.% at 77 K and 0.12 MPa and 3.8 wt.% at 77 K and 4.5 MPa [115, 150–152]. Polymers of intrinsic microporosity (PIM) are another approach to introduce porosity into polymers. These materials reach BET surface areas of more than $1000 \, \text{m}^2 \, \text{g}^{-1}$ and adsorb 1.7 wt.% at 77 K and 0.1 MPa [115, 148, 149].

Coordination polymers like metal-organic frameworks (MOFs) and covalent organic frameworks (COVs) are a different kind of porous polymer. Similar to zeolites, these materials are of highly crystalline nature. However, different from zeolites, the structure of these frameworks is composed of lighter elements, giving rise to higher specific porosity. Thus, MOF structures are built by metal ion clusters which are connected by organic linking groups. In the case of COFs, aromatic rings are the primary structural element [115]. The building blocks are linked by strong covalent bonds, resulting in a rigid structure which contains exclusively very light elements like H, B, C, N, or O. Coordination polymers can reach extremely high BET surface areas of more than $5000 \, \text{m}^2 \, \text{g}^{-1}$ [109, 153]. For MOF-177, which has a BET surface area of $4600 \, \text{m}^2 \, \text{g}^{-1}$, hydrogen uptake of 7.5 g(H_2)/g was reported at 77 K and 4 MPa [115]. The crystallinity of coordination polymers allows for an exact control of their porosity. A common strategy to achieve high surface areas in organic framework materials is to increase the size of the organic linkers [115]. However, this increases also the pore sizes of the structure which may be a problem for hydrogen adsorption at room temperature where small pores are advantageous. In addition, the low density of coordination polymers leads to relatively low volumetric storage density. Furthermore, MOFs are relatively sensitive to conditions of high temperature, mechanical pressure, and humidity which can lead to degradation of the material [115, 154].

Activated carbon (AC) is an interesting and well-known adsorbent with a highly adaptable porosity. Activated carbon materials are a form of carbon which does not occur naturally and which has to be synthesized technically. The technical process is called "activation" and can be performed utilizing different methods, as well as a large number of carbon-containing precursors. The porosity in ACs can cover a wide range of pore sizes and can be controlled by adjusting the activation parameters. Furthermore, the characteristics of the adsorbent can be adjusted by manipulating its surface chemistry. Activated carbon materials can be used in numerous applications, for example, in liquid and gas phase treatments (e.g., removal of volatile organic compounds (VOC) and SO_2 or for CO_2 and CH_4 separation and storage), energy

storage (as electrical double layer capacitors), as adsorbents in cryocoolers, and so forth [155].

Together with zeolites, carbon materials were among the first adsorbents studied for hydrogen storage [156, 157]. Thereby, research was focused on activated carbons (ACs) with high specific surface areas. Since the early days, a number of carbonaceous nanomaterials have been discovered, for example, fullerenes, multiwalled nanotubes (MWNTs), and single-walled nanotubes (SWNTs). In early studies, it was claimed that these fascinating materials would have a high potential for storing hydrogen, initializing a downright research "hype." To date, however, many of the early promises have not been fulfilled. What is more is that investigation of "classical" carbon adsorbents has suffered from this alteration of research focus. Currently, it is concluded that adsorption on nanomaterials is simply due to physisorption. Due to their low porosity in comparison with other carbon adsorbents like activated carbons, the latter perform better in terms of hydrogen storage [45]. Models for estimating the maximum hydrogen capacity of activated carbons often utilize graphene sheets. Such model has a surface area of $2630 \, \text{m}^2 \, \text{g}^{-1}$ and a maximum hydrogen capacity of around 6 wt.% [102, 104]. If the graphene planes are separated by slip pores of idealized size, up to 9.2 wt.% are reachable [104]. Nevertheless, real activated carbons are highly disordered, giving rise to other adsorption sites, for example, at graphene edges, and reveal a distribution of different pore sizes.

A lot of data can be found for commercial activated carbon materials [116, 117]. Some of the most studied materials are Maxsorb as well as AX-21, a KOH activated carbon with a BET surface area of around $2500 \, \text{m}^2 \, \text{g}^{-1}$ and a V_{DR} (CO_2) of $0.68 \, \text{cm}^3 \, \text{g}^{-1}$ [117]. For this material, diverse maximum adsorption amounts between 3 and 6 wt.% were reported for a temperature of 77 K [56, 117, 123, 158]. At room temperature, AX-21 adsorbs 1 wt.% at 5 MPa and 1.6 wt.% at 70 MPa [119, 123].

However, fewer studies have been carried out regarding synthesis and analysis of activated carbon materials that are specially tailored for hydrogen storage. Measurements of metal-carbide-derived activated carbons revealed 3 wt.% at 77 K and 0.1 MPa [115, 159, 160]. On zeolite-templated carbon 6.9 wt.% were measured at 77 K and 2 MPa (2.6 wt.% at 77 K and 0.1 MPa) [115, 161]. For KOH activated anthracite, surface areas of more than $3000 \, \text{m}^2 \, \text{g}^{-1}$ are obtained [123, 162]. At room temperature, maximum adsorption of almost 1.2 wt.% was measured for pressures of 20 MPa and 2.7 wt.% for 50 MPa [117, 119]. At 77 K, 5.3 wt.% were measured for 4 MPa [117] and around 6 wt.% for 8 MPa [123].

4. Conclusions

Strong efforts have been made in order to reach the targets for hydrogen storage in mobile applications which were established by bodies like the DOE. Yet, none of the investigated technologies currently fulfills all of the requirements. Today, the lion's share of hydrogen vehicles is based on pressure vessels with compressed hydrogen. However, this technology may not be appropriate for reaching the ambitious ultimate targets, and security concerns exist over the high pressures

involved. The use of liquid hydrogen is handicapped by the energy intensive liquefaction process as well as hydrogen boil-off.

The storage of hydrogen inside materials could be advantageous in a number of aspects. Metal hydrides and other compounds with chemisorbed hydrogen can reach high capacities. However, one has to bear in mind that storage capacities of the materials alone have to be significantly higher according to the established targets which are system-based. In addition, materials with chemically bonded hydrogen often present other difficulties like heat management problems, low kinetics, and/or irreversibility. A promising alternative could be hydrogen storage by physisorption in porous materials. The challenges for designing suitable adsorbents are (1) increasing their porosity, (2) tuning of pore sizes, (3) optimization of adsorption potentials, and (4) enhancement of the bulk material density in order to reach high volumetric capacities.

Conflict of Interests

The authors confirm that no conflict of interests exists and that they do not have any direct financial relation with any of the commercial identities mentioned in the paper.

Acknowledgments

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