

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/264733812>

# Solid-state Materials and Methods for Hydrogen Storage: A Critical Review

ARTICLE in CHEMICAL ENGINEERING & TECHNOLOGY · FEBRUARY 2010

Impact Factor: 2.44 · DOI: 10.1002/ceat.200900376

CITATIONS

91

READS

489

## 4 AUTHORS:



[Kean Long Lim](#)

National University of Malaysia

8 PUBLICATIONS 112 CITATIONS

[SEE PROFILE](#)



[Hossein Kazemian](#)

University of Northern British Columbia

114 PUBLICATIONS 1,135 CITATIONS

[SEE PROFILE](#)



[Zahira Yaakob](#)

National University of Malaysia

129 PUBLICATIONS 975 CITATIONS

[SEE PROFILE](#)



[Wan Ramli Wan Daud](#)

National University of Malaysia

341 PUBLICATIONS 3,630 CITATIONS

[SEE PROFILE](#)

Kean Long Lim<sup>1</sup>  
Hossein Kazemian<sup>1,2</sup>  
Zahira Yaakob<sup>1</sup>  
Wan Ramli Wan Daud<sup>1</sup>

<sup>1</sup> Fuel Cell Institute, Universiti  
Kebangsaan Malaysia, Bangi,  
Selangor, Malaysia.

<sup>2</sup> Department of Chemical and  
Biochemical Engineering, The  
University of Western Ontario,  
London, Ontario, Canada.

## Review

# Solid-state Materials and Methods for Hydrogen Storage: A Critical Review

Hydrogen is important as a new source of energy for automotive applications. It is clear that the key challenge in developing this technology is hydrogen storage. Current methods for hydrogen storage have yet to meet all the demands for on-board applications. High-pressure gas storage or liquefaction cannot fulfill the storage criteria required for on-board storage. Solid-state materials have shown potential advantages for hydrogen storage in comparison to other storage methods. In this article, the most popular solid-state storage materials and methods including carbon based materials, metal hydrides, metal organic frameworks, hollow glass microspheres, capillary arrays, clathrate hydrates, metal nitrides and imides, doped polymer and zeolites, are critically reviewed. The survey shows that most of the materials available with high storage capacity have disadvantages associated with slow kinetics and those materials with fast kinetics have issues with low storage capacity. Most of the chemisorption-based materials are very expensive and in some cases, the hydrogen absorption/desorption phenomena is irreversible. Furthermore, a very high temperature is required to release the adsorbed hydrogen. On the other hand, the main drawback in the case of physisorption-based materials and methods is their lower capacity for hydrogen storage, especially under mild operating conditions. To accomplish the requisite goals, extensive research studies are still required to optimize the critical parameters of such systems, including the safety (to be improved), security (to be available for all), cost (to be lowered), storage capacity (to be increased), and the sorption-desorption kinetics (to be improved).

**Keywords:** Capillary array, Carbon nanotubes (CNT), Clathrates hydride, Doped polymers, Hollow Glass Microspheres (HGM), Hydrogen storage, Metal hydrides, Metal imides, Metal nitrides, Metal Organic Frameworks (MOF), Solid-state materials, Zeolites

*Received:* July 21, 2009; *revised:* November 5, 2009; *accepted:* November 9, 2009

**DOI:** 10.1002/ceat.200900376

## 1 Introduction

There is no doubt that global warming is a sign of serious environmental degradation. For centuries, humankind has utilized the natural resources without any consideration of their environmental impact and the results of their exhaustion. It is now becoming apparent that the combustion of fossil fuels, i.e., oil, gas and coal, is the main culprit contributing to the global

warming effects, which has already resulted in an increase in the number of natural disasters occurring worldwide.

Scientists are looking for alternative renewable resources to reduce the overall dependency on fossil fuels. Extensive research has recently been carried out on energy sources such as solar, geothermal, tidal, wind power, biomass, nuclear energy, etc. However, apart from some other technical and environmental concerns, the main problem with these technologies involves difficulties with the storage and/or transportation of these energies especially for automotive energy applications. Hydrogen has been identified as the ideal energy carrier to resolve the problem [1].

Hydrogen, which is a tasteless, colorless, odorless, and non-toxic molecule, is well known for its clean combustion creating neither air pollutants nor greenhouse gases. Due to the possibility for its unlimited supply, inherent pollution free nature,

---

**Correspondence:** Associate Prof. H. Kazemian (hossein.kazemian@uwo.ca and hosseinkazemian@gmail.com), Department of Chemical and Biochemical Engineering, Faculty of Engineering, The University of Western Ontario, London, Ontario, Canada N6A 5B9.

non-exclusive access around the globe, and provision of the highest energy efficiency; hydrogen appears to have the capacity to become the ultimate solution to energy security, resource availability, and environmental concerns. It is a convenient, safe, and versatile fuel source that is easily and efficiently converted to desirable forms of energy [2]. The amount of energy per unit mass produced by hydrogen is about three times higher than that generated from gasoline and almost seven times higher than the energy obtained from coal in an equal mass [3]. However, hydrogen storage is a major barrier in the development of hydrogen-based technologies, e.g., fuel cells. In order to use this energy, an effective, safe and stable storage medium is required, which is still the major obstacle in order for hydrogen to replace fossil fuels as a major power source. The search for a safe, and techno-economically viable hydrogen storage method is a crucial materials challenge for moving towards an energy economy based on hydrogen [4].

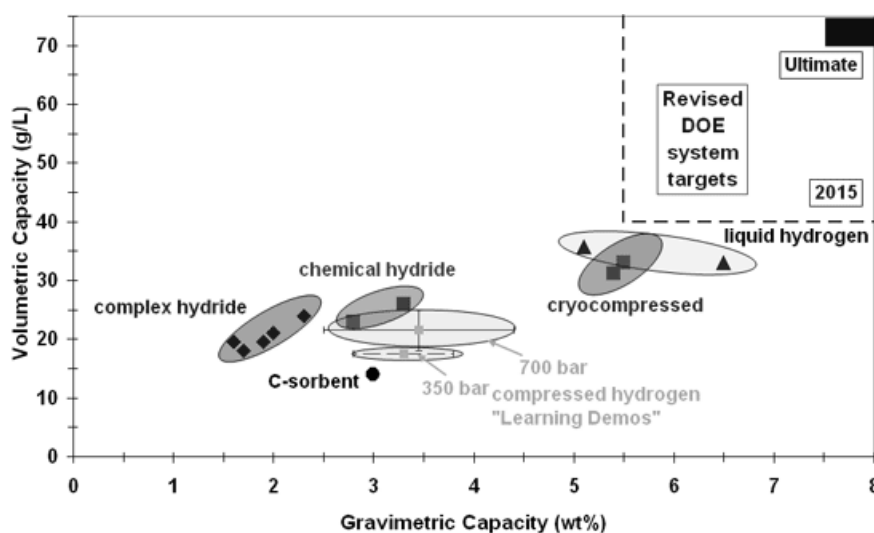
To date, several storage technologies for subsequent utilization of hydrogen have been studied and these are based on a variety of physicochemical approaches. However, due to the chemical nature of hydrogen, chemical materials that reversibly adsorb hydrogen by means of chemical reactions usually receive significant attention. Most of the research on hydrogen storage has focused on storing hydrogen in light weighted materials that can maintain hydrogen in a compact manner for mobile devices.

A comparison with hydrocarbon fuels can be useful to elaborate on the importance of hydrogen storage by means of chemical approaches. Liquid and gaseous hydrocarbon can be extensively stored locally at the point of use, whereas, in comparison, hydrogen is very difficult to store and/or transport with the currently available technologies. The reason is that hydrogen has a higher energy density by mass, while its energy density by volume is very poor. Thus, it requires larger (heavier) storage vessels in comparison to the smaller hydrocarbon storage tanks required to deliver the same amount of energy. However, the energy density by volume can be enhanced by increasing the gas pressure in order to achieve smaller (but not lighter) containers for storage. Furthermore, the compression of the hydrogen requires higher energy consumption to power the compressor. The liquefaction and conversion of hydrogen to the slush phase have also been considered as alternative physical approaches to achieve higher volumetric energy density, e.g., as used in space shuttles. However, due to the very low boiling temperature of hydrogen (20.268 K), a significant energy loss is encountered since cryogenic storage is required to maintain liquid or slush phase hydrogen. In order to prevent the liquefied hydrogen from boiling off, the cryogenic storage containers have to be well insulated, which is very expensive. It is worth noting that even though some of the techno-economical difficulties of the hydrogen storage have

been solved, the problem of the very low volumetric density of hydrogen remains unsolved. In this regard, the comparison of the hydrogen content of 1 L of gasoline (as the main fuel for vehicles) with the hydrogen content of the same amount of liquid hydrogen is useful. A quantity of 1 L of gasoline contains ca. 116 g hydrogen, whereas 1 L of pure liquid hydrogen contains only 71 g of hydrogen. This fact implies that the hydrogen content of 1 L of gasoline is ca. 64 % greater than the hydrogen content of the same volume of liquid hydrogen. The contribution from the carbon content of the hydrocarbon fuels to the energy production should also be taken into account.

According to the agreement on the Freedom CAR Partnership in 2002, between the United States Council for Automotive Research (USCAR) and the United State Department of Energy (U.S. DOE), the attainment of a 5 kg hydrogen storage system for on-board application by 2005 was defined as the target. However, because of some technical obstacles, this goal was not fulfilled by the deadline. Taking into account the weight of the tank and its accessories, the system storage densities are usually around half those of the material storage densities. In order to achieve the defined goal for a working system capable of storing 5 wt % of hydrogen, a candidate material for storage must be able to store at least 10 wt % of hydrogen [5].

The materials and methods for hydrogen storage that are available now have yet to meet all the criteria required for on-board applications [6]. The status of current hydrogen storage technologies for different materials and the U.S. DOE targets are shown in Fig. 1. The U.S. DOE has assessed some of the on-board hydrogen storage technical barriers for the multi-year hydrogen, fuel cells and infrastructure research, development and demonstration plan as follows: (i) cost, (ii) weight and volume, (iii) efficiency, (iv) durability, (v) refueling time, (vi) hydrogen capacity and reversibility, and (vii) lack of understanding of hydrogen physisorption and chemisorption phenomena. Chahine and Benard [7] reported that a 6.5 wt % hydrogen storage capacity is required to power a hydrogen-fueled car to achieve a range of 500 km.



**Figure 1.** A summary of available hydrogen storage technologies by the U.S. DOE ([www1.eere.energy.gov/hydrogenandfuelcells/storage/tech\\_status.html](http://www1.eere.energy.gov/hydrogenandfuelcells/storage/tech_status.html)).

There are a few methods commonly available to store hydrogen. Conventionally, it is stored in high-pressure gas cylinders (up to 800 bar) and as liquid hydrogen in cryogenic tanks (at 21 K). However, hydrogen storage by these two methods is very inefficient and not particularly safe for transport applications. In order to find more efficient and safer methods for hydrogen storage, hydrogen adsorption on materials with high specific surface area and chemically bonded in covalent and ionic compounds is becoming more attractive [8]. Materials such as metal hydrides, alloys, complex hydrides and high surface porous materials are showing tremendous affinity for absorbing large amounts of hydrogen. However, each method suffers from some particular drawbacks.

This review intends to discuss and highlight the potential of a wide range of solid-state storage materials and methods that can be utilized as hydrogen storage candidates for on-board applications.

## 2 Solid-state Storage

The storage of hydrogen by absorption as chemical compounds or by adsorption on carbon materials have definite advantages from a safety perspective, in which some form of conversion or energy input is required to release the hydrogen for subsequent use. Extensive efforts have been made on new hydrogen-storage systems, including metal organic frameworks (MOF), zeolites, metal hydrides, metal nitrides, metal imides, doped polymers, clathrate hydrates, hollow glass microspheres and capillary arrays, and carbon based materials.

In solid-state storage, hydrogen is bonded by either physical, e.g., MOF and carbon based materials, or chemical forces, e.g., hydrides, imides and nitrides. Physisorption has the advantages of higher energy efficiency and faster adsorption/desorption cycles, whereas chemisorption results in the adsorption of larger amounts of gas but in some cases, is not reversible and requires a higher temperature to release the adsorbed gas.

### 2.1 Carbon-based Materials

Carbon, one of the most common elements found in both living and non-living creatures in the earth, is well known for its great ability to adsorb gases. For decades, it has been used as a purifier, detoxifier, etc., because of its ability to be prepared in a very fine powdered form with a highly porous structure and the propensity of the carbon atom to undergo certain interactions with some gaseous molecules.

Carbon-based materials have been extensively studied as hydrogen storage media. Dillon et al. [9] and Chambers et al. [10] have reported that carbon nanotubes (CNT) and graphite nanofibers exhibit high hydrogen storage capacities. Carbon materials with higher microporosity have extremely enhanced adsorbing properties toward gaseous molecules. Investigations have shown that macropores have no practical influence on the adsorption capacity. In fact, they are only important for gas compression and for the kinetic reaction rate [6]. In general, the storage capacity of carbon based materials is linearly proportional to the BET surface area [11–13]. The nature of hydrogen

adsorption on carbon porous materials at moderate temperature is a result of molecular physisorption [14, 15]. Since the molecular interaction in a physisorption process is very weak, only a very small amount of hydrogen can be adsorbed [16] even at a pressure of 90 bar [17]. Temperature also seems to be a key factor for hydrogen storage in pure carbon materials.

#### 2.1.1 Activated Carbon (AC)

Activated carbon (AC) is a high porosity, modified synthetic carbon containing crystallized graphite and amorphous carbon with a high specific surface area, which can be prepared using either thermal or chemical procedures [18]. AC has been considered as a potential candidate for hydrogen storage purposes because it is relatively cheap and accessible on a commercial scale. The hydrogen storage rate and capacity of the activated carbon can be influenced by its morphology and shape, i.e., powder, fiber and granular. It is shown that the hydrogen adsorption rate in fiber form is 2–50 times faster than in the granular form [19].

For conventional AC, the hydrogen uptake is proportional to its surface area and pore volume; and is fitted well with the Langmuir isotherm model (monolayer adsorption). High adsorption capacity is only obtained at extremely low cryogenic temperature and high pressure [20]. Hydrogen adsorption on various types of commercial and modified activated carbon products has been extensively studied [6]. Experimental results show that products with micropore volumes greater than 1 mL/g are able to store ca. 2.2 wt % of hydrogen due to physisorption and it is expected that optimization of the adsorbent and sorption conditions could lead to a storage capacity of 4.5–5.3 wt %.

Agricultural waste such as coconut shell, coconut fibers, jute fibers, nut shells and oil seeds, etc. [19, 21–28], are popular raw materials for producing AC. Jin et al. [12] prepared AC with different porosities using chemically activated coconut shell. They reported a maximum hydrogen adsorption capacity of 0.85 wt % at 100 bar and 298 K. Sharon et al. [22] produced activated carbon fibers (ACF) using soybean and bagasse. The authors measured hydrogen storage capacities of 1.09–2.05 wt % at a pressure of 11 Pa and room temperature. Another form of AC, the advanced AC monoliths, with good mechanical strength (maximum compression strength of 22 MPa), high volume of micropores (up to 1.04 cm<sup>3</sup>/g) and high density (up to 0.7 g/cm<sup>3</sup>) have been shown to adsorb 29.7 g/L of hydrogen at 77 K and 4 MPa [21, 29]. The morphology of chemically activated carbon obtained from coconut fiber is illustrated in Fig. 2.

Mechanically milled AC consists of some form of defective nanostructure, which increases the specific surface area. Research findings have revealed that after 10 h of milling, the hydrogen storage capacity increases from 0.90 wt % to ca. 1.7 wt % [31]. Studies have shown that loading of precious metals, e.g., Pt, on to AC increases the adsorption capacity [32]. The merging of the two adsorption phenomena, i.e. chemisorption (on the Pt surface) and physisorption (on the carbon surface) gives rise to a significant amount of spillover hydrogen.

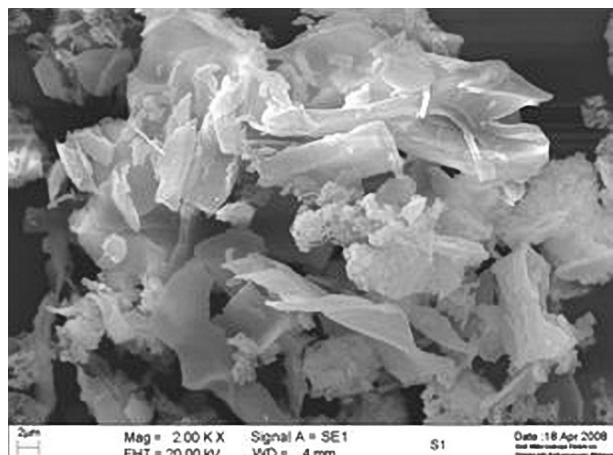


Figure 2. Activated carbon from coconut fiber [30].

### 2.1.2 Carbon Nanotubes (CNT)

Ever since the world's first carbon nanotubes (CNT) were discovered in 1991 [33], there has been significant interest in their potential capability as a hydrogen storage candidate. Nanocarbon materials may be able to store more hydrogen since they contain defective structures that act as trapping sites [31]. Dillon et al. [9], who were the first group that discovered the hydrogen storage capacity of CNTs, presented promising results, which has triggered a worldwide tide of research in the area. There are two main different species of CNTs characterized by the structure of their wall, i.e., the single-walled nanotubes (SWNT) and the multi walled nanotubes (MWNT) [34]. As summarized in Tab. 1, very different hydrogen storage values between 0.25 and 56 wt % have been reported in various experimental conditions for these materials. According to a technical report from the International Energy Agency (IEA), the consensus is that the very high hydrogen storage capacities,

**Table 1.** Summary of the reports of hydrogen storage capacity in carbon nanotubes.

Sample	<i>T</i> (K)	<i>P</i> (MPa)	H <sub>2</sub> (wt %)	Literature Ref.
SWNT	133	0.04	5–10	Dillon et al. [9]
SWNT	A <sup>a</sup>	0.067	3.5–4.5	Dillon et al. [36]
SWNT	77–300	8	1–15	Chen et al. [37]
SWNT	80	7	8.25	Ye et al. [38]
SWNT	A <sup>a</sup>	4.8	1.2	Smith Jr. et al. [39]
MWNT	298	12.16	56	Chambers et al. [10]
MWNT	300–700	A <sup>a</sup>	0.25	Wu et al. [40]
MWNT	A	10	0.68	Zhu et al. [41]
MWNT	300	1.0	13.8	Chen et al. [42]
MWNT	300	7.0	0.7–0.8	Badzian et al. [43]

<sup>a</sup> A: ambient temperature or pressure.

i.e., ca. 30–60 wt %) reported a few years ago, are practically impossible to achieve and were possibly the result of measurement errors. However, the storage capacity (up to 6 wt %) is still useful at cryogenic temperatures and with extremely high surface area carbons [35]. A typical SEM micrograph of a CNT at 10000x magnification is illustrated in Fig. 3.

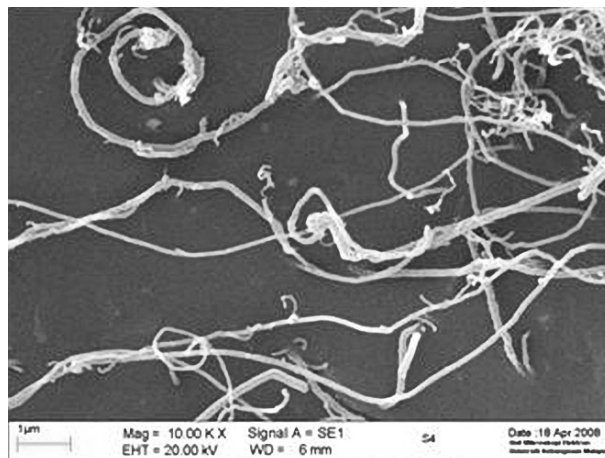


Figure 3. SEM micrograph of a typical carbon nanotube at 10000x magnification [30].

### 2.1.3 Graphite Nanofiber (GNF)

Graphite nanofibers (GNF) are grown with a chemical deposition method (CVD) where the carbon-containing gases are decomposed over a catalyst surface, e.g., metal or alloy, to form carbon sheets. The carbon atoms precipitate at one or more surfaces forming successive sheets that stack on one another to form GNFs [44]. A schematic diagram of the GNF formation process is shown in Fig. 4.

The findings of Chambers et al. [10] have suggested that the GNF structure shows great potential as a hydrogen storage material and the group have claimed that a cross-linked GNF was able to store up to 67.55 wt % hydrogen. However, it was not possible to reproduce the results elsewhere.

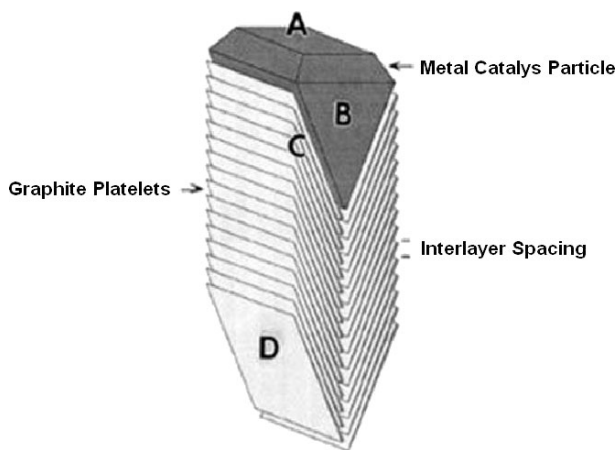


Figure 4. Scheme of GNF growth on a catalyst particle [45].



Other researchers have synthesized GNF at ca. 500–600 °C by passing ethylene (in an optimum ratio with or without a carrier) over some solid catalyst [46, 47]. It has been reported that the storage at room temperature and 12.16 MPa is ca. 4.00–6.50 wt % [46]. However, mass production of nanomaterials with this procedure would be slow and costly. Gupta et al. [48] managed to grow GNF on the gram scale per run by a spray pyrolysis method involving benzene. They also measured the hydrogen storage capacity on carbon nanostructured materials such as Li- and K- doped CNT and GNF, and the best result was obtained on GNF was 10 wt % at 27 °C and 12.16 MPa. On the other hand, the storage capacity reported by Tibbets et al. [49] over GNF produced by the CVD method, measured at 3.5–11 MPa and room temperature, was less than 1 wt %.

One of the interesting findings from Kim et al. [50] involved the coating of activated carbon fibers (ACF) with GNF, which combined two adsorbent materials homogeneously without seriously diminishing the pore structures of the ACF. It was believed that this method might increase the storage capacity but no further investigation was performed on the storage characteristics in that particular study. However, Kim et al. [51] have utilized this concept to coat Ni nanoparticles in another study, which showed 2.2 wt % storage at 298 K and 100 bar. New carbon materials such as honeycomb graphite structures, as shown in Fig. 5, also show very promising results. Due to their mechanical and structural properties, carbon nanostructures are promising candidates for future automotive hydrogen storage applications [52].

#### 2.1.4 Graphene

It seems that a nanostructure with optimized pore size to adsorb hydrogen is not sufficient, since most of the abundant contaminant gases, i.e.,  $N_2$ ,  $O_2$ , and  $CO_2$ , are more polarizable than hydrogen, they are usually more strongly bound to the adsorbent than hydrogen, causing adsorbent poisoning. A desirable storage material design would not only maximize the hydrogen uptake, but also resist poisoning by larger and polarizable molecules present in the atmosphere. Graphene, a structure made from carbon has shown promising behavior. Zhechkov et al. have calculated that the graphene binding energy with the most abundant atmospheric gas,  $N_2$ , is  $18 \text{ kJ mol}^{-1}$  [53].

Graphene has a huge hydrogen storage density, which has been exploited in order to store hydrogen for hydrogen fuel technologies. Elias et al. have used a stream of hydrogen atoms to convert graphene reversibly into graphane, as shown in Fig. 6 [54]. The authors found that graphane can also release the stored hydrogen easily by heating at 450 °C [54].

#### 2.2 Metal-organic Frameworks (MOFs)

The storage of hydrogen in porous materials is one of the most promising strategies for on-board

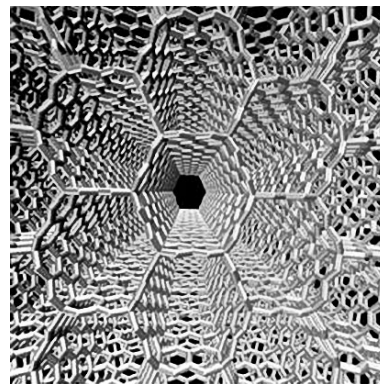


Figure 5. Structure of carbon foam (honeycomb graphite) [52].

hydrogen storage due to their tunable pore size and functionality. Metal-organic frameworks (MOFs) represent a new category of synthetic nanoporous material with a very high capacity for hydrogen storage. The main characteristics of MOF structures are their low density, high surface area, high enthalpy and large porous volume. In recent times, the design and synthesis of porous metal-organic frameworks with nanometer scale pores has expanded, and the number of available MOFs has increased dramatically. MOFs show potential characteristics in various fields from catalysis to drug synthesis and delivery, separation sciences, adsorption and many other fields [55].

The use of MOF materials as a medium for hydrogen storage was first reported in 1999 by Li et al. [56]. The authors indicated that MOF-5 shows a high hydrogen storage capacity of 4.5 wt % at 77 K and 0.8 bar, whereas its capacity at room temperature and at a pressure of 20 bar was almost 1 wt % [56]. However, in 2004, a research group observed that the maximum hydrogen uptake of MOF-5 was 1.32 wt % at 1 bar and 77 K [57]. In 2005, a hydrogen storage value of 1.6 wt % was reported for MOF-5 at pressures above 10 bar, but the adsorption capacity of MOF-5 was very low at room temperature, with values of less than 0.2 wt % at pressures up to 67 bar [58].

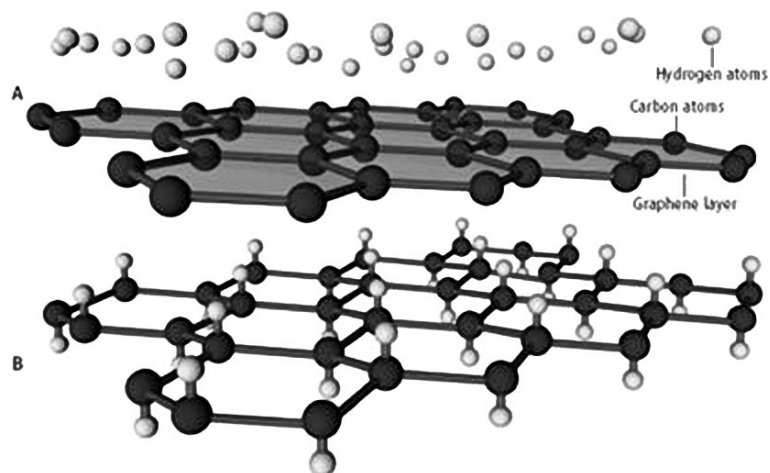
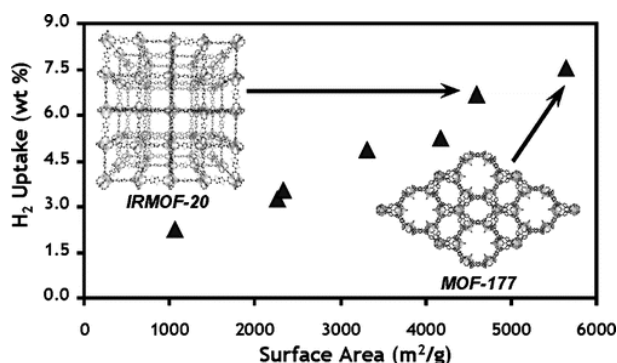


Figure 6. Hydrogen addition converting graphene (top) into graphane (bottom) [54].

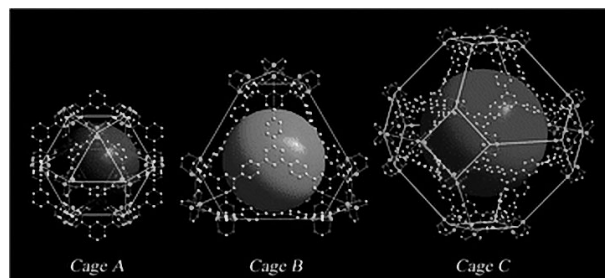
In 2006, hydrogen storage of 7.5 wt % in MOF-177 material was reported by Wong-Foy et al. [59]. The authors measured the saturation hydrogen uptake in a series of MOFs at 77 K. Saturation pressures in the range 25–80 bar were examined, and the results revealed that MOF-177 shows the highest uptake on a gravimetric basis (7.5 wt %) and IRMOF-20 shows the highest uptake on a volumetric basis at 34 g/L. These results are summarized in Fig. 7 and demonstrate that maximum hydrogen storage capacity in MOFs correlates to surface area [59].



**Figure 7.** The top-performing MOFs for hydrogen storage: Hydrogen uptake of MOF-177 and IRMOF-20 [59].

A new porous metal-organic framework of  $\text{Mn}(\text{DMF})_6]_3[(\text{Mn}_4\text{Cl})_3(\text{BTT})_8(\text{H}_2\text{O})_{12}]_2 \cdot 42\text{DMF} \cdot 11\text{H}_2\text{O} \cdot 20\text{CH}_3\text{OH}$  with a previously unknown cubic topology has been synthesized using the tritopic bridging ligand of 1,3,5-benzenetristetrazolate ( $\text{BTT}^{3-}$ ). Crystals of the compound remain intact upon desolvation and show a total hydrogen uptake of 6.9 wt % at 77 K and 90 bar, which at 60 g  $\text{H}_2$ /L provides a liquid hydrogen storage density of 85 %. The material exhibits a maximum iso-steric heat of adsorption of 10.1 kJ/mol [60]. A theoretical study has shown that there is a strong correlation between the exposed and coordinative unsaturated metal centers. The results show that the hydrogen surface density can be enhanced in many framework structures. The authors have also shown that the MOF-74 framework structure with open  $\text{Zn}^{2+}$  sites displays the highest surface density for physisorbed hydrogen in framework structures. Isotherm and neutron scattering methods were used to elucidate the strength of the guest-host interactions and to demonstrate the atomic-scale bonding of hydrogen in this material [61].

An improved synthesis of a high quality MOF-5 material has been developed recently in order to increase the hydrogen storage capacity. As a result, the hydrogen storage capacity of MOF-5 synthesized in the presence of  $\text{H}_2\text{O}_2$  was shown to be higher than a sample synthesized without  $\text{H}_2\text{O}_2$ . The synthesized MOF-5 exhibited a high hydrogen storage capacity of 2.96 wt % at 77 K and 1.45 MPa [62]. However, the most promising results regarding MOFs have been reported by Yan et al. for the NOTT-112 structure [63]. The authors achieved 10 wt % hydrogen storage capacity for NOTT-112 at 77 bar and 77 K. They also developed a new metal-organic polyhedral framework, as outlined in Fig. 8, that shows an excess hydrogen uptake of 7.07 wt % between 35 and 40 bar at 77 K. The



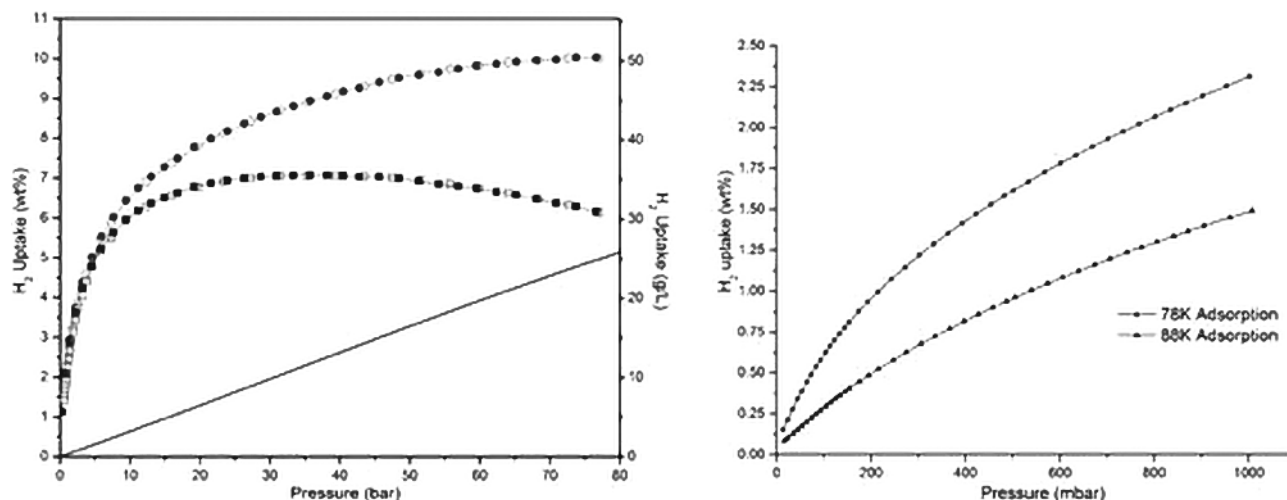
**Figure 8.** Different cages in the crystal structure of NOTT-112. The network in NOTT-112 is constructed by the packing of Cage A, Cage B and Cage C in a ratio of 1:2:1, respectively [63].

highest hydrogen uptake of 10 wt % was achieved at 77 bar and 77 K, and the results are shown in Fig. 9 [63].

The corresponding total volumetric storage density for NOTT-112 is  $50.3 \text{ g L}^{-1}$ , similar to that reported for MOF-177 ( $48 \text{ g L}^{-1}$  at 72 bar) with both structures ( $0.477 \text{ g cm}^{-3}$ ) sharing similar crystallographic densities. At 1 bar, NOTT-112 has a similar total hydrogen uptake (2.3 %) to previously reported materials incorporating Cu(II) paddlewheel nodes (2.24–2.59 %). However, NOTT-112 goes on to out-perform these phases at higher pressures of hydrogen and shows a total uptake of 7.8 wt % at 20 bar and 77 K. Interestingly, MOF-5, NOTT-112, and MOF-177 have similar BET surface areas of ca.  $3800 \text{ m}^2 \text{ g}^{-1}$  with the latter two compounds also having similar pore volumes ( $1.6 \text{ cm}^3 \text{ g}^{-1}$ ). Thus, it appears that this combination of high surface area and pore volume is necessary to achieve this high level of hydrogen storage capacity [63]. Michel et al. [64] have synthesized several giant-pore MOFs and further confirmed that small pores plays a major role, as well as specific surface area, in determining hydrogen storage capacity.

Yang and co-workers extensively studied the hydrogen spillover effect of hydrogen storage in MOFs [65, 66] as well as for carbon materials [67, 68] and zeolites [69]. They observed that the hydrogen storage capacity of porous materials could be remarkably improved by modification with metal supported catalysts through a carbon bridge. The metal doping process is believed to modify the chemical nature of the porous materials in order to strengthen subsequent hydrogen adsorption [70].

Liu et al. have studied the hydrogen storage behavior of Pt (20 wt %)/C doped and carbon bridged Pt (20 wt %)/C modified MIL-101 and MIL-53 (chromium based MOF) under mild conditions [71]. At 293 K, the hydrogen storage capacity of modified MIL-101 and modified MIL-53 were 1.14 and 0.63 wt %, respectively, while doped MIL-101 and doped MIL-53 attained a hydrogen uptake of 0.75 and 0.43 wt %, respectively. The comparison of the gravimetric storage capacity of the modified and doped MIL-101 and MIL-53 with that of parent MOFs (0.37 wt % and none, respectively), indicate that both techniques have greatly enhanced the hydrogen storage capacity of the MOFs. In addition, the modified MOFs exhibit greater hydrogen uptake than the doped MOFs, which shows that the secondary spillover does take affect hydrogen adsorption. The effect of doping and the modification technique on the hydrogen storage is to help hydrogen molecules to dissoci-



**Figure 9.** Hydrogen sorption isotherms for NOTT-112. Left: High pressure excess hydrogen adsorption isotherms at 77 K (by volumetric method) are shown as red circles (total uptake) and blue squares (excess uptake). The solid olive line indicates the density of hydrogen gas at different pressures (right-hand scale). Filled symbols indicate adsorption and open symbols indicate desorption; Right: Gravimetric total hydrogen uptakes at 78 K and 88 K up to 1 bar [63].

ate and spillover effectively onto the outer and inner surface of the original MOFs. Therefore, it should be noted that a good dispersion of the metal supported catalyst on the MOFs helps to effectively diffuse the material, which plays a key role in the final hydrogen storage capacity of doped and modified MOFs [71].

### 2.3 Zeolites

Zeolites are hydrated microporous crystalline aluminosilicates having infinite, open and rigid 3D structures with high-internal-surface-area (up to 1000 m<sup>2</sup>/g). Synthetic zeolites were introduced by the Union Carbide Company (U.S.A.) as a new class of industrial adsorbents in 1954. The adsorption characteristics of zeolites make them attractive candidates for gas storage, and therefore, taking this property into account, zeolites have been studied as potential hydrogen storage materials. A study by Dong et al. [72] has shown a similar conclusion for storage capacity as seen for MOFs [64], where a physisorption storage method is observed that is highly dependent on a large volume of micropores. It was reported that in operational conditions of 77 K and 1 bar, a typical high silica zeolite of the MFI group (ZSM-5) with a surface area of 430 m<sup>2</sup>/g could adsorb up to 0.7 wt % of hydrogen, which is far lower than a typical activated carbon with a surface area of 2030 m<sup>2</sup>/g that adsorbs up to 2.1 wt % of hydrogen [73]. A modeling study on zeolite hydrogen storage suggests that zeolite A (LTA) can store at least 2 wt % hydrogen if all cage sites are filled [34].

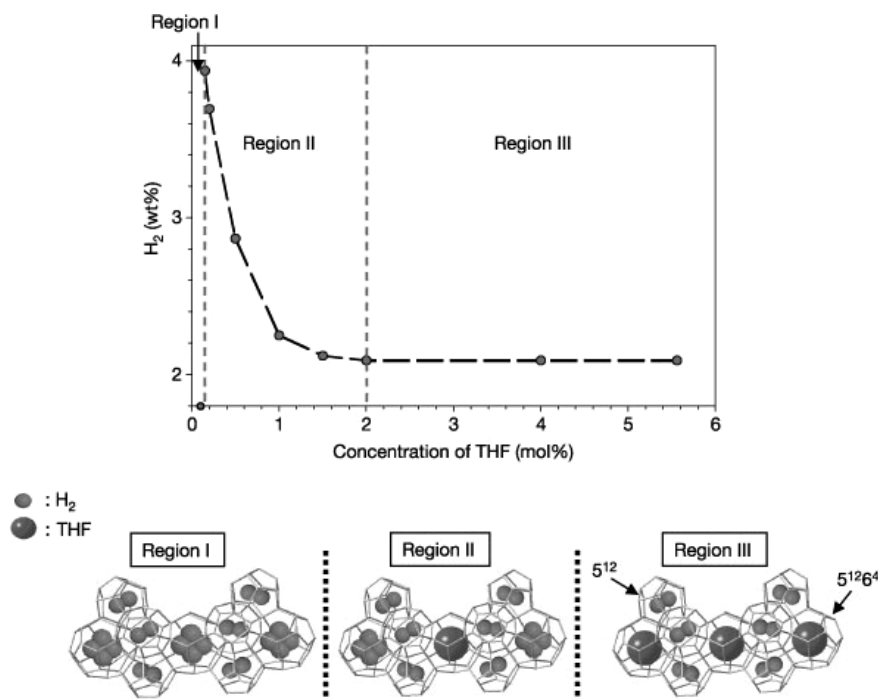
Recently, a method that demonstrates the potential of hydrogen storage at high pressures in small pellets coated with a thin zeolite layer has been reported by Lachawiec et al. [67]. The authors made a SAPO-34 zeolite membrane, which was impermeable to high-pressure hydrogen at room temperature by adsorbing methanol in the SAPO-34 layer. The hydrogen permeance decreased by three orders of magnitude when the

methanol feed activity was  $\sim 0.1$ , and it decreased by more than six orders of magnitude when the methanol feed activity was higher than 0.85 at 293 K. The hydrogen permeance at 293 K was less than  $\sim 10^{-14}$  mol/m<sup>2</sup> s Pa for at least five days with a hydrogen feed pressure of 6.6 MPa. At higher temperatures, methanol desorbed and the hydrogen flux increased. The hydrogen permeance could be controlled by the activity of the methanol on the feed side. These results also demonstrated that the SAPO-34 membrane had low fluxes through defects, and that hydrogen flow through these defects was blocked by capillary condensation of methanol at high methanol activities. For a 1  $\mu$ m thick SAPO-34 layer on a 1 cm spherical pellet, the zeolite represents only ca. 0.006 % of the total material mass. Thus, the amount of methanol would be  $\sim 0.1$  mol-% of the amount of hydrogen at 7 MPa pressure and 298 K and the percentages would be even lower for higher hydrogen pressures. For a hydrogen permeance of  $\sim 1 \cdot 10^{-14}$  mol/m<sup>2</sup> s Pa, < 1 % of the hydrogen would leak in a week [74].

### 2.4 Clathrate Hydrates

Clathrate hydrates are a class of solid inclusion compounds in which guest molecules occupy cages formed from a hydrogen-bonded water molecule network. The empty cages are unstable, and often collapse into conventional ice crystal structures. However, inclusion of appropriately sized molecules helps to stabilize them [75, 76]. Clathrate hydrates of hydrogen often possess two different cages to meet the necessary storage requirements. However, higher pressures of ca. 2 kbar are required to produce the material, which makes them impractical. The synthesis pressure can be decreased by filling the larger cavity with tetrahydrofuran (THF) to stabilize the material. [77–79]. The hydrogen gas content as a function of THF concentration, and a schematic diagram of hydrogen distribution in the cages of THF + H<sub>2</sub> hydrate, are shown in Fig. 10.





**Figure 10.** Hydrogen gas content as a function of THF concentration, and a schematic diagram of hydrogen distribution in the cages of THF + H<sub>2</sub> hydrate (hydrogen gas content is calculated from g of hydrogen per g of hydrate, and expressed as wt %). In region III, hydrogen molecules are only stored in small cages, while in region II both small and large cages can store hydrogen molecules. At the highly dilute THF concentrations in region I, hydrogen molecules can still be stored in both cages, but extreme pressures (~2 kbar) are required to form the hydrates. Pure H<sub>2</sub> clathrate (2H<sub>2</sub>)<sub>2</sub>·(4H<sub>2</sub>)·17H<sub>2</sub>O would have a 5.002 wt % hydrogen content [80].

Reversible hydrogen storage capacities in THF-containing binary-clathrate hydrates have been increased to ~4 wt % at 270 K and modest pressures (12 MPa) by tuning their composition to allow the hydrogen guests to enter both the larger and the smaller cages, while retaining low-pressure stability. The tuning mechanism is quite general and convenient, using water-soluble hydrate promoters and various small gaseous guests [80].

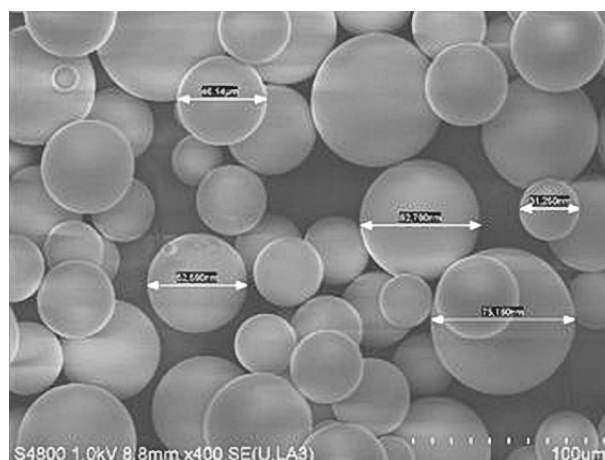
## 2.5 Hollow Glass Microspheres (HGM)

It has been believed for a considerable length of time that hollow glass microspheres (HGM) can be used as a solid medium for the controlled storage and release of hydrogen. The spraying of a glass frit inside a flame is one of the commercial procedures to make HGMs. Different chemical agents such as sulfur or urea must be added to the glass frit in order to cause the frit to blow outward and form the hollow spheres. In 1981, Teitel was the first person to propose the use of HGMs as hydrogen storage media [81, 82]. The characteristics of so-called super-high-strength micro-balloons towards hydrogen storage and extraction in comparison to other known methods have also been investigated [83].

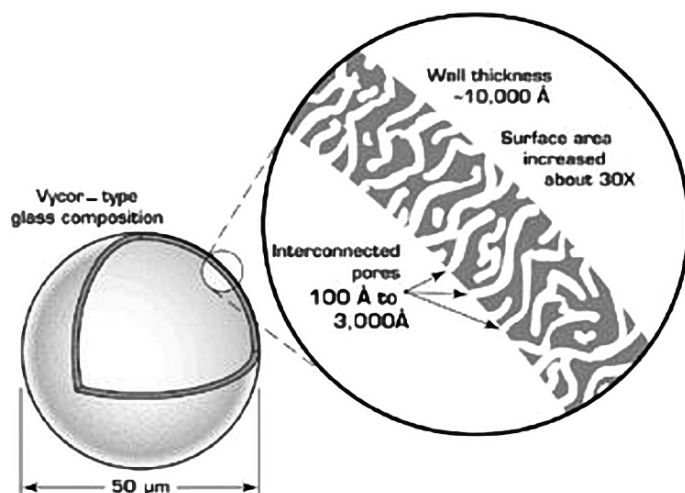
HGM with approximate diameters of 1–200 μm and wall thicknesses of 1.5 μm and below are considered as viable containers for transporting and storing hydrogen. However, one of the main concerns with regard to the use of HGM for hydrogen storage purposes is their strength. If the HGMs were made of engineered glass, which can be up to 50 times stronger than normal glasses, the amount of hydrogen capable of being stored in the microspheres can be increased remarkably. This would lead to an increase in the energy density per unit volume by over an order of magnitude resulting in the advancement of hydrogen energy technology and in the improvement of the hydrogen market as a renewable energy source via cheaper and safer hydrogen storage [4, 84].

Recently, researchers at the Savannah River National Laboratory (SRNL) reported a novel class of materials, i.e., the so-called Porous Walled-Hollow Glass Microspheres (PW-HGMs), for a variety of new applications. They consist of tiny micron sized glass balloons and a scanning electron microscope (SEM) image of a typical batch of 2–100 μm spheres with an average diameter of ~50 μm, are shown in Fig. 11. The distinguishing characteristic of the SRNL glass microspheres is

the interconnected porosity of their outer walls that can be produced on a scale of 100–3,000 Å, Fig. 12. The porosity results in some unique properties. These open channels can be used to fill the micro balloons with absorbents as well as other materials, thus providing a contained environment and a new



**Figure 11.** SEM image of a typical batch of 2–100 μm SRNL spheres with an average diameter of ~50 μm [85].



**Figure 12.** Schematic representation of a SRNL microsphere and its wall porosity [85].

type of glass-absorbent composite. Gaseous molecules such as hydrogen can enter the microspheres through the pores and be stored or cycled on absorbents inside, resulting in solid-state and contained storage. PW-HGMs, which are fluid like, recyclable and made from readily available resources, may be the ideal solution to hydrogen storage as well as for gas purification and targeted drug delivery [85].

In order to make HGMs more attractive for hydrogen storage purposes, researchers have been attempting to improve their fabrication procedures. The use of infra red (IR) irradiation has been suggested to accelerate the diffusion through the HGMs in order to reduce the temperature and time of hydrogen release [84]. The burst pressure,  $P_b$ , of the HGMs that governs the hydrogen storage capacity, depends on its wall strength. The value of  $P_b$  can be calculated as follows, using Eq. (1):

$$P_b = \frac{4\sigma_{\max} \Delta r}{D} \quad (1)$$

where  $\sigma_{\max}$  is the biaxial hoop stress at failure,  $\Delta r$  is the wall thickness and  $D$  is the outer diameter of the HGM [86].

A simple calculation for commercially available HGM reveals that the HGMs can endure higher pressures up to three times the pressure currently contained in typical metal composite cylinders that are in use today [87]. The filled microspheres can be reheated (at lower temperature than that required for filling) in a low-pressure vessel, to outgas the hydrogen from the microspheres. Unfortunately, the inherently poor thermal conductivity of inorganic glasses has limited the further development and implementation of this hydrogen storage method. This poor thermal conductivity results in slow release rates of encapsulated hydrogen.

The storage of high-pressure hydrogen in HGMs has also refocused the emphasis on enhancing the hydrogen release rates. Studies have shown that the slow outgassing at lower temperature can be accelerated with photo-enhanced diffusion. This possible solution can be realized by the discovery of

photo-induced outgassing, in which a high-intensity infrared (IR) irradiation is used to facilitate hydrogen release of selectively doped glasses. This process results in much faster response times for the release of hydrogen in glasses in comparison to the normal heating procedure and may provide a path to superior performance for hydrogen storage in HGMs.

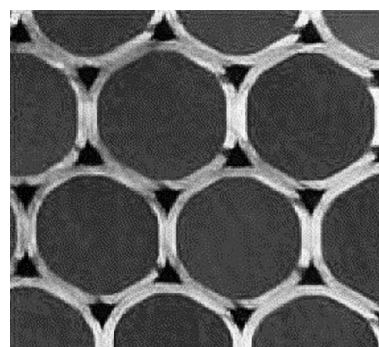
Specific dopants have been studied based on their optical absorption characteristics in order to ascertain the active spectral range responsible for the enhanced outgassing response [84]. In addition to glass host and dopant effects, the effect of light intensity on the outgassing response has also been investigated [84]. The results showed that addition of iron oxide to glasses with high permeability result in the most immediate photo-induced outgassing response, although NiO was the most effective on a per ion basis. The borosilicate glass, CGW 7070, exhibits the best hydrogen outgassing response. The amount of hydrogen released from a 0.5 wt %  $\text{Fe}_3\text{O}_4$  doped 7070 is proportional to the lamp intensity, as indicated by the voltage response.

In addition, at 20 V, no hydrogen is released, indicating a threshold intensity below which the radiation intensity is insufficient to cause hydrogen release. The reaction of hydrogen with iron-doped glass increases the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratio, which promotes infrared absorption and improves the hydrogen yield obtained from photo-induced outgassing [84]. Another disadvantage of HGMs is the difficulty in producing an ideal spherical shape of uniform diameter and wall thickness. Usually, eccentricity and diameter spread of HGMs, lead to the collapse of the spheres under the high external pressure applied during the hydrogen filling process [88].

## 2.6 Capillary Arrays

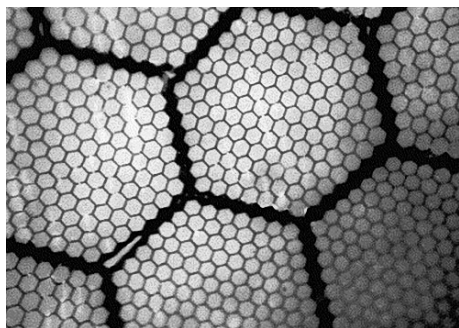
Capillary arrays have also been developed as a new technology for hydrogen storage. The technology can be used effectively for safe transportation and storage of highly pressurized hydrogen in mobile systems, ranging from domestic electronic devices to ground and sea vehicles. Two types of capillary arrays for hydrogen storage systems are under consideration:

- A bundle of cylinder capillaries sealed at both ends with semi-spherical caps and packed in a 2D hexagonal lattice, as shown in Fig. 13;



**Figure 13.** Cross-section of the array of closely packed cylinder capillaries. Dark regions represent the inter-tube space [88].

- An array of fused hexagonal capillaries sealed with a thin layer of a suitable substance, as demonstrated in Fig. 14.



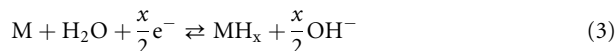
**Figure 14.** Honeycomb array of fused hexagonal capillaries. Dark stripes are the interfaces between the blocks [80].

The amount of stored hydrogen in each individual capillary is very small, which significantly reduces the possibility of explosions from improper handling or during accidents. Compared to HGMs, normal heating or IR radiation of the capillary arrays can be applied more easily to facilitate hydrogen release. The capillary arrays are very resistant to the external pressure, have a better packing ratio than the hollow spheres and can be produced with uniform diameter and wall thickness [88].

## 2.7 Metal Hydride

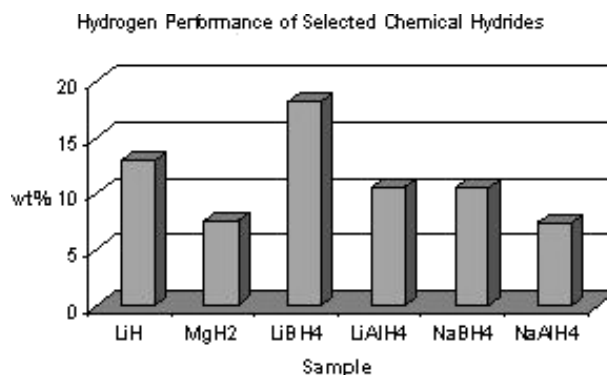
Metal hydrides are a category of promising materials that exhibit the potential to fulfill the defined targets for hydrogen storage. To date, simple metal hydrides, which contain magnesium, e.g.,  $\text{MgH}_2$ , and transition metals, as well as complex metal hydrides containing lithium, sodium, or calcium and boron or aluminum, e.g.,  $\text{NaAlH}_4$  and  $\text{LaNi}_5\text{H}_6$ , have been considered for this purpose. These materials have a good energy density by volume, although their energy density by weight is often worse than that of hydrocarbons. Some of the liquid hydrides are easy-to-fuel at room temperature and pressure, whereas solid hydrides, which could be formed as pellets and granules, require temperatures of ca.  $120^\circ\text{C}$  to release their hydrogen content.

Metal hydrides show promising results in hydrogen storage, e.g.,  $\text{MgH}_2$  has been seen to store up to 7.60 wt % hydrogen [89], since they have higher hydrogen storage density (6.5 H atoms/ $\text{cm}^3$  for  $\text{MgH}_2$ ) as compared to compressed hydrogen gas (0.99 H atoms/ $\text{cm}^3$ ) or liquid hydrogen (4.2 H atoms/ $\text{cm}^3$ ) [90]. Hydrogen can easily attach to metals under moderate pressure and temperature, and hence, metal hydride storage is much safer and volume-efficient for on-board applications [91]. Two possible routes for the production of metal hydrides consist of direct dissociative chemisorption and the electrochemical splitting of water. The reactions involved are as follows, Eqs. (2) and (3):



where M represents the metal and  $x$  is its valence.

Light metals, e.g., lithium, beryllium, sodium, magnesium, boron and aluminium based storage materials are some of the popular substances used for storage purposes. The different hydrogen capacities of some selected metal hydrides are shown in Fig. 15.



**Figure 15.** Hydrogen performance of some selected chemical hydrides [83].

Prior to 1980, several compounds including complex borohydrides, or aluminohydrides, and ammonium salts were studied as potential hydrogen storage media. The maximum theoretical hydrogen yield of these hydrides is limited to ca. 8.5 wt %. Several B-N-H compounds such as amine boranes, boron hydride ammoniates, hydrazine-borane complexes, and ammonium octahydrotriborates or tetrahydroborates have been extensively investigated as hydrogen carriers [91].

### 2.7.1 Magnesium Based Hydride Materials

Theoretically,  $\text{MgH}_2$  contains 7.60 wt % of hydrogen. However, magnesium based materials have limited practical application because of slow adsorption and desorption reaction times, and consequently, they require higher temperatures to release hydrogen [4]. Furthermore, the formation of a highly stable magnesium oxide layer reduces the adsorption rates [88]. Generally, ball milling and the use of suitable catalysts can improve the sorption kinetics [92]. Recently, there has been another attempt to decrease the size into nanofibers by the hydriding chemical vapor deposition method [93], which has resulted in a significant increase the specific surface area.

Mechanical ball milling of  $\text{MgH}_2$  can pulverize the material into micron- and nano-sized particles, which greatly improves the hydrogen sorption energy [94]. Johnson et al. [95] reported that ball milling of  $\text{MgH}_2$  for 15 h under a hydrogen pressure of 10 bar at  $300^\circ\text{C}$ , improved the hydrogen capacity from 4.86 wt % to 6.01 wt %.

Other researchers have shown that the addition of some components may improve the capacity and the reaction kinetics (catalysis effect) of the magnesium hydrides. Johnson

et al. [95] reported that a mixture of  $\text{MgH}_2/\text{LiBH}_4$  materials could adsorb hydrogen faster than pure  $\text{MgH}_2$  for 15 h at a rate comparable to milled  $\text{MgH}_2$ . The hydrogen desorption rates of  $\text{MgH}_2/\text{LiBH}_4$  and  $\text{MgH}_2$  were  $0.28 \cdot 10^{-2}$  wt %/s and  $0.12 \cdot 10^{-2}$  wt %/s respectively. Wang et al. [96] lowered the hydrogen uptake and release temperature of  $\text{Mg}(\text{NH}_2)_2/2\text{LiH}$  to  $107^\circ\text{C}$  by introducing potassium to the system. Friedrichs et al. [97] attempted to mill  $\text{MgH}_2$  with niobium oxide ( $\text{Nb}_2\text{O}_5$ ), which currently provides one of the fastest sorption kinetics known [98, 99], but the storage capacity is reduced to ca. 1 wt % as a result of the heating effect. Although the  $\text{Nb}_2\text{O}_5$  effectively reduces the crystal growth, it has no significant influence on the kinetics for a size up to 144 nm. Palladium, Pd, has also been used to dope the magnesium surface due to its known characteristics as a good catalyst to dissociate hydrogen [89]. Palladium is easy to recover from the oxide during exposure to hydrogen [100] and it enhances the adsorption rates even at room temperature. However, the cost of using such an expensive material is still the main disadvantage of this route, especially for industrial applications [101].

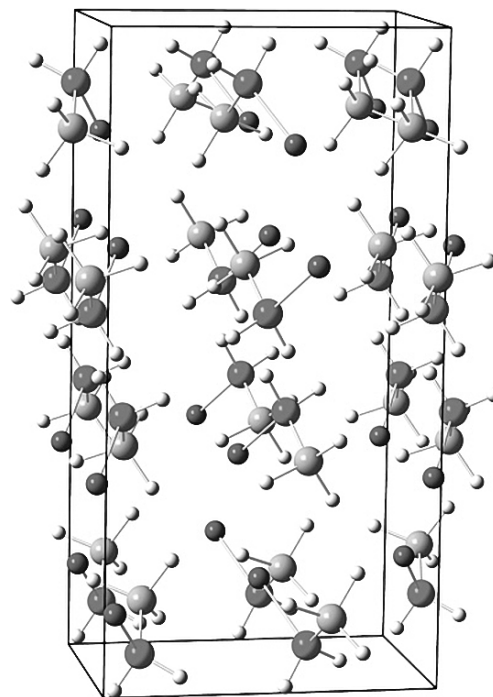
### 2.7.2 Boron Based Materials

In 1952, Schlesinger et al. [102] published a paper about the generation of hydrogen from sodium borohydride,  $\text{NaBH}_4$ . Aiello et al. [103] has performed a feasibility study on  $\text{NaBH}_4$  and  $\text{LiBH}_4$ , and concludes that both have a great potential as hydrogen storage materials. In fact,  $\text{NaBH}_4$  has already been commercialized by the Millennium Cells company. The waste product is borax,  $\text{NaBO}_2$ , which can be regenerated by just pumping hydrogen onto it or by hydrolysis using coke or methane.

Despite the fact that  $\text{LiBH}_4$  has a gravimetric hydrogen density of 18 wt %, which is a very high storage capacity, the desorption at low temperatures releases only a small amount of hydrogen (0.3 wt %) [102]. In addition to this,  $\text{LiBH}_4$  is an expensive compound [101]. In comparison to other non-boron-containing materials, the hydrolysis of boron-containing materials appears to have an obvious advantage in terms of capacity [1].

The boron nitride (BN) nanostructure in lightweight nano-balls and nanoforms is another candidate for hydrogen storage [104]. BN can store up to 2.6 wt %  $\text{H}_w$  after a milling process for 80 h and is able to desorb at 573 K, which is a relatively high temperature compared to other nanostructures [105]. BN fullerenes have also demonstrated a hydrogen storage capacity of 3 wt % [106].

Various studies have shown that the alkali-metal amidoboranes,  $\text{LiNH}_2\text{BH}_3$  and  $\text{NaNH}_2\text{BH}_3$ , as shown in Fig. 16, fulfill some of the principal criteria demanded for hydrogen-storage materials.  $\text{LiNH}_2\text{BH}_3$  and  $\text{NaNH}_2\text{BH}_3$  exhibit high storage capacities of 10.9 wt % and 7.5 wt %, respectively, with an easily accessible dehydrogenation temperature of ca.  $90^\circ\text{C}$  without the unwanted borazine by-product. These materials are environmentally friendly compounds, non-flammable, non-explosive and stable solids at room temperature and pressure. To date, the only disadvantage of these materials is their lack of easy reversibility. Nevertheless, thermal neutral dehydrogena-



**Figure 16.** Schematic diagram of the crystal structure of  $\text{LiNH}_2\text{BH}_3$  and  $\text{NaNH}_2\text{BH}_3$  determined from high-resolution X-ray powder diffraction data at room temperature (boron is represented by orange spheres, nitrogen by green spheres, hydrogen by white spheres and lithium by red spheres) [99].

tion of alkali-metal amidoboranes should facilitate on-board regeneration [107].

## 2.8 Metal Nitrides, Amides and Imides

Metal nitrides, amides and imides show high hydrogen capacity at low operating temperatures compared to other competitive chemisorption approaches. Light metal-nitride compounds have also shown potential as a solid-state hydrogen storage medium. Lithium nitride that is usually used as a starting material for the synthesis of binary or ternary nitrides can also reversibly uptake large amounts of hydrogen. However, the temperature required to release the hydrogen at usable pressures is too high for practical application of the present material [108].

Researchers from the National University of Singapore have made initial studies of Li-alkali earth metal imides as hydrogen storage materials. They have shown that lithium nitride is capable of storing 11.4 % of its own weight in hydrogen, which is 50 % more than for magnesium hydride. Other metal hydrides generally store only 2–4 % of their weight. Due to the high temperatures required to release the hydrogen, this novel material is not ready for practical applications yet, but it points the way to a practical hydrogen storage material. Metal imides have a maximum storage capacity of 7.0 wt %. However, the materials require relatively high operating temperatures, which could limit their real application [109]. Chen and co-workers have shown that the addition of alkali earth metals such as Mg or Ca

dramatically decreases the hydrogen storage temperatures, increases the desorption pressures, and allows high storage capacities to be achieved. This result takes the metal–N–H system a big step forward towards practical targets. Furthermore, by reacting different metal amides with hydrides, the possibility of developing a broad range of metal–N–H systems such as ternary imides, e.g., Mg–Na–N–H and Li–Mg–N–H systems [110, 111], and quaternary imides, e.g., the Mg–Ca–Li–N–H system [112] for hydrogen storage, has been developed.

Luo and co-workers investigated the hydrogen-storage properties and mechanisms of a novel Li–Al–N ternary system [113]. It is seen that ca. 5.2 wt % of hydrogen is reversibly stored in a  $\text{Li}_3\text{N–AlN}$  (1:1) system, and the hydrogenated product is composed of  $\text{LiNH}_2$ ,  $\text{LiH}$ , and  $\text{AlN}$ . A stepwise reaction is detailed for the dehydrogenation of the hydrogenated  $\text{Li}_3\text{N–AlN}$  sample. Further investigations have shown that the presence of  $\text{AlN}$  in the  $\text{LiNH}_2\text{–}2\text{LiH}$  system enhanced the kinetics of the first dehydrogenation step with a 10 % reduction in the activation energy. This was mainly due to the higher diffusivity of lithium and hydrogen within  $\text{AlN}$  [113].

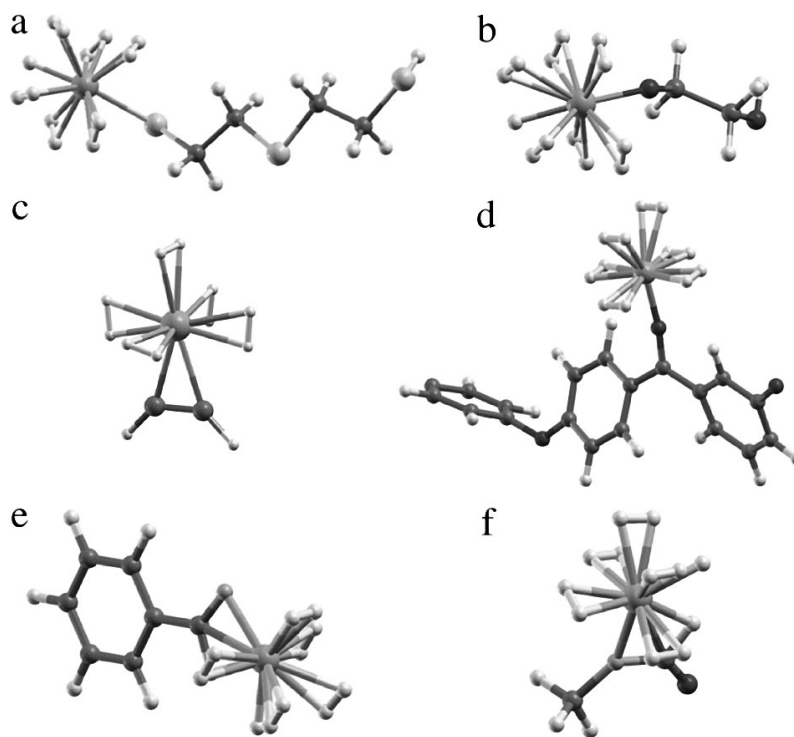
## 2.9 Doped Polymers

Incorporating metal nanoparticles (NPs) in polymer hosts has gained potential significance in technological applications, especially as advanced functional materials including optical sensors, hydrogen storage systems and microwave absorbers [114]. Recently, a group of Korean researchers proposed functionalized organic molecules doped with titanium atoms as high-capacity hydrogen storage materials. The authors have studied six types of functional groups that form complexes with Ti atoms and found that each complex is capable of binding up to six hydrogen molecules, Fig. 17. Among such complexes, Ti-decorated ethane-1,2-diol can store hydrogen with a maximum gravimetric density of 13 wt % and, under ambient conditions, a practically usable capacity of 5.5 wt %. They have also presented different forms of storage materials which are obtained by modifying some well-known nanomaterials using Ti-functional group complexes [115].

In this area, the DOE has also planned to investigate possible utilization of carbon doping with organo-metallic compounds that exhibit rigid planar configuration and are rich in electro-negative nitrogen atoms,  $[\text{CNH}]$ . From the results of Cabasso and Yuan [116], it is hoped that this class of materials will enable the DOE targeted temperature and moderate pressure hydrogen storage system to be realized.

## 3 Conclusions

In summary, in the journey towards a sustainable society, in which energy plays a very essential role, humankind has real-



**Figure 17.** Atomic structures of Ti-functional group complexes with the maximum number of hydrogen molecules attached. White, green, grey, red, yellow, and pink dots indicate the hydrogen, carbon, nitrogen, oxygen, sulfur, and titanium atoms, respectively. (a)–(f) Ti-functional group complexes with maximally adsorbed hydrogen's in 2-mercaptoethyl sulfide, ethane-1,2-diol, acetylene, PEEK, benzo-nitrile, and methyl-isocyanate, respectively [107].

ized the urgent need to substitute conventional fossil fuels, which are non-secure, pollution generating, and of limited resource, with more secure, cheap, endless, safe and environmentally friendly sources of energy. Among the several substitution candidates including wind, tidal, geothermal, solar, water, and hydrogen energies, the latter has received the most interest as the leading candidate to provide a secure energy future. Despite the technological issues involved in hydrogen production, its safe and economically viable storage, especially for on-board use, is still the largest obstacle to its widespread application as a power source. For researchers in the hydrogen energy sector, the first decade of the 21st century has been dedicated to resolving this technical barrier by finding a sophisticated storage strategy. Several physical and chemical scenarios have been considered and tremendous amounts of funding have been invested in this field resulting in several promising achievements, although most are still far from the defined targets.

In this article the most studied hydrogen solid-state storage materials and methods including carbon based materials, metal hydrides, metal organic frameworks, hollow glass microspheres and capillary arrays, clathrate hydrates, metal nitrides and imides, doped polymer and zeolites were critically reviewed.



Nevertheless, despite some promising achievements to date, both chemisorption and physisorption based solid storage materials and methods suffer from some essential drawbacks. For instance, most of the chemisorption materials, e.g., hydrides, nitrides, imides, etc., are very expensive and in some cases suffer from the irreversible nature of the hydrogen absorption/desorption process. In other cases very high temperatures are necessary for hydrogen release. On the other hand, in the case of physisorption based materials and methods, e.g., MOF, HGM, CNT, etc., the main drawback are their lower capacity especially under mild operating conditions.

Overall, as mentioned in the discussion and in most of the respected technical and scientific reports referenced, there are serious doubts that such huge values for hydrogen storage that were claimed some years ago are practical, and it is now believed that many can be attributed to some gross experimental measurement errors.

Nevertheless, the current authors believe that recent research on the modified and doped materials in order to enhance the share of spillover phenomena on hydrogen uptake can be converted into more promising achievements in the future.

With an optimistic vision, despite the relatively slow progress in the field of hydrogen storage, the reported results reveal that some of the studied materials will meet the defined targets in the near future. Among the investigated materials, MOFs seem to be the most encouraging candidates.

However, to accomplish the defined goals, extensive research studies are still required to optimize and improve the safety and accessibility for all, lower the production cost, increase the storage capacity, and enhance the sorption-desorption kinetics.

*The authors have declared no conflict of interest.*

## References

- [1] E. Fakioglu, Y. Yürüm, T. N. Veziroglu, *Int. J. Hydrogen Energy* **2003**, 29, 1371.
- [2] M. U. Niemann et al., *J. Nanomater.* **2008**, 9, DOI: 10.1155/2008/950967
- [3] M. S. Dresselhaus, I. L. Thomas, *Nature* **2001**, 414 (6861), 332.
- [4] L. Schlapbach, A. Züttel, *Nature* **2001**, 414 (6861), 353.
- [5] *Hydrogen Storage Technologies Roadmap*, U. S. C. f. A. R. (USCAR), **2005** (Available from: [www.uscar.org/commands/files\\_download.php?files\\_id=82](http://www.uscar.org/commands/files_download.php?files_id=82)).
- [6] L. L. Vasiliev et al., *Int. J. Hydrogen Energy* **2007**, 32, 5015.
- [7] R. Chahine, P. Benard, *Hydrogen Energy Program* **1998**, 12, 979.
- [8] A. Züttel, *Mater. Today* **2003**, 6 (9), 24.
- [9] A. C. Dillon et al., *Nature* **1997**, 386, 377.
- [10] A. Chambers, C. Park, R. T. K. Baker, N. M. Rodriguez, *J. Phys. Chem. B* **1998**, 102 (22), 4253.
- [11] M. Hirscher, B. Panella, *J. Alloys Compd.* **2005**, 404–406, 399.
- [12] H. Jin, Y. S. Lee, I. Hong, *Catal. Today* **2007**, 120, 399.
- [13] B. Panella, M. Hirscher, S. Roth, *Carbon* **2005**, 43, 2209.
- [14] H. G. Schimmel et al., *Mater. Sci. Eng., B* **2004**, 108, 124.
- [15] A. Züttel, P. Sudan, P. Mauron, P. Wenger, *Appl. Phys. A: Mater. Sci. Process.* **1998**, 78, 941.
- [16] M. Rzepka, P. Lamp, *J. Phys. Chem. B* **1998**, 102, 10894.
- [17] L. Zubizarreta, A. Arenillas, J. J. Pis, *Int. J. Hydrogen Energy* **2008**, 33, 4337. DOI: 10.1016/j.ijhydene.2008.07.112
- [18] *Introduction to Carbon Technologies* (Eds: H. Marsh, H. E. Heintz, F. Rodriguez-Reinoso), University of Alicante Press, Alicante **1997**, p. 35.
- [19] N. H. Phan et al., *Carbon* **2006**, 44, 2569.
- [20] S. Hynek, W. Fuller, J. Bentley, *Int. J. Hydrogen Energy* **1997**, 22 (6), 601.
- [21] M. Jordá-Beneyto et al., *Microporous Mesoporous Mater.* **2008**, 112 (1–3), 235.
- [22] M. Sharon et al., *Int. J. Hydrogen Energy* **2007**, 32 (17), 4238.
- [23] W. Su, L. Zhou, Y. Zhou, *Carbon* **2003**, 41 (4), 861.
- [24] W. Su, L. Zhou, Y. Zhou, *Chin. J. Chem. Eng.* **2006**, 14 (2), 266.
- [25] W. Su et al., *Chem. Ind. Forest Prod.* **2006**, 26 (2), 49.
- [26] S.-Q. Yao et al., *J. Yancheng Inst. Technol. Nat. Sci. Ed.* **2007**, 20 (2), 59.
- [27] F. Zhang et al., *Bioresour. Technol.* **2008**, 99 (11), 4803.
- [28] H.-P. Zhang, L.-Y. Ye, L.-C. Yang, *J. Xiamen Uni. (Nat. Sci.)* **2006**, 43 (6), 833.
- [29] M. Jordá-Beneyto et al., *Carbon* **2007**, 45 (2), 293.
- [30] K. L. Lim, *Hydrogen Storage on Activated Carbon Fibers and Carbon Nanotubes*, Universiti Kebangsaan Malaysia, Bangi, Malaysia **2008**.
- [31] K. Shindo, T. Kondo, M. Arakawa, Y. Sakurai, *J. Alloys Compd.* **2003**, 359 (1–2), 267.
- [32] H. Takagi, H. Hatori, Y. Yamada, *Chem. Lett.* **2004**, 33 (9), 1220.
- [33] S. Iijima, *Nature* **1991**, 354 (6348), 56.
- [34] F. Darkrim, A. Aoufi, P. Malbrunot, D. Levesque, *J. Chem. Phys.* **2000**, 112 (13), 5991.
- [35] *Hydrogen Production and Storage: R&D Priorities and Gaps*, International Energy Agency, Paris **2006** (Available from: <http://www.iea.org/Textbase/papers/2006/hydrogen.pdf>).
- [36] A. C. Dillon et al., *FY 1999 Progress Report*, DOE Hydrogen Program, U.S. DOE, Washington DC **1999**.
- [37] X. Chen et al., in *Proc. of the 3rd Materials Research Society Symp.*, Materials Research Society Press, Boston, MA **2002**.
- [38] Y. Ye et al., *Appl. Phys. Lett.* **1999**, 74 (16), 2307.
- [39] M. R. Smith Jr. et al., *J. Phys. Chem. B* **2003**, 107 (16), 3752.
- [40] X. B. Wu, P. Chen, J. Lin, K. L. Tan, *Int. J. Hydrogen Energy* **2000**, 25 (3), 261.
- [41] H. Zhu et al., *Appl. Surf. Sci.* **2001**, 178 (1–4), 50.
- [42] Y. Chen et al., *Appl. Phys. Lett.* **2001**, 78 (15), 2128.
- [43] A. Badzian, T. Badzian, E. Breval, A. Piotrowski, *Thin Solid Films* **2001**, 398–399, 170.
- [44] N. M. Rodriguez, A. Chambers, R. T. K. Baker, *Langmuir* **1995**, 11 (10), 3862.
- [45] R. T. K. Baker, *Encyclopedia of Materials: Science and Technology*, Elsevier, Amsterdam **2005**.
- [46] D. J. Browning et al., *Nano Lett.* **2002**, 2 (3), 201.
- [47] A. A. Volodin, P. V. Fursikov, B. P. Tarasov, *Mg<sub>2</sub>NiH<sub>x</sub> as Pro-catalyst of Synthesis of Carbon Nanofibers*, in *NATO Security through Science Series A: Chemistry and Biology*, Springer, New York **2007**.

- [48] B. K. Gupta, O. N. Srivastava, *Int. J. Hydrogen Energy* **2008**, 33 (12), 2975.
- [49] G. G. Tibbetts, G. P. Meisner, C. H. Olk, *Carbon* **2001**, 39 (15), 2291.
- [50] B. J. Kim, S. J. Park, *J. Colloid Interface Sci.* **2007**, 315 (2), 791.
- [51] B. J. Kim, Y. S. Lee, S. J. Park, *Int. J. Hydrogen Energy* **2008**, 33 (15), 4112.
- [52] T. Heine, L. Zhechkov, S. Patchkovskii, G. Seifert, *SPIE* **2007** (Available online: <http://spie.org/x13545.xml?ArticleID=x13545>). DOI: 10.1117/2.1200704.0714
- [53] L. Zhechkov, T. Heine, G. Seifert, *Int. J. Quantum Chem.* **2006**, 106 (6), 1375.
- [54] D. C. Elias et al., *Science* **2009**, 323 (5914), 610.
- [55] L. Pan et al., *Angew. Chem., Int. Ed.* **2003**, 42 (5), 542.
- [56] H. Li, M. Eddaoudi, M. O'Keeffe, O. M. Yaghi, *Nature* **1999**, 402 (6759), 276.
- [57] J. L. C. Rowsell, A. R. Millward, K. S. Park, O. M. Yaghi, *J. Am. Chem. Soc.* **2004**, 126 (18), 5666.
- [58] B. Panella, M. Hirscher, *Adv. Mater.* **2005**, 17 (5), 538.
- [59] A. G. Wong-Foy, A. J. Matzger, O. M. Yaghi, *J. Am. Chem. Soc.* **2006**, 128 (11), 3494.
- [60] M. Dinca et al., *J. Am. Chem. Soc.* **2006**, 128 (51), 16876.
- [61] Y. Liu et al., *Langmuir* **2008**, 24 (9), 4772.
- [62] S. Cheng, S. Liu, Q. Zhao, J. Li, *Energy Conversion Manage.* **2009**, 50 (5), 1314.
- [63] Y. Yan et al., *Chem. Commun.* **2009**, 9, 1025.
- [64] L. Michel et al., *Angew. Chem., Int. Ed.* **2006**, 45 (48), 8227.
- [65] Y. Li, R. T. Yang, *J. Am. Chem. Soc.* **2006**, 128 (25), 8136.
- [66] Y. Li, R. T. Yang, *J. Am. Chem. Soc.* **2006**, 128 (3), 726.
- [67] A. J. Lachawiec Jr., G. Qi, R. T. Yang, *Langmuir* **2005**, 21 (24), 11418.
- [68] A. D. Lueking, R. T. Yang, *Appl. Catal., A* **2004**, 265 (2), 259.
- [69] Y. Li, R. T. Yang, *J. Phys. Chem. B* **2006**, 110 (34), 17175.
- [70] U. Roland, T. Braunschweig, F. Roessner, *J. Mol. Catal. A: Chem.* **1997**, 127 (1–3), 61.
- [71] Y. Y. Liu et al., *Int. J. Hydrogen Energy* **2007**, 32 (16), 4005.
- [72] J. Dong et al., *Int. J. Hydrogen Energy* **2007**, 32 (18), 4998.
- [73] M. G. Nijkamp, J. E. M. J. Raaymakers, A. J. Van Dillen, K. P. De Jong, *Appl. Phys. A: Mater. Sci. Process.* **2001**, 72 (5), 619.
- [74] M. Yu, S. Li, J. L. Falconer, R. D. Noble, *Microporous Mesoporous Mater.* **2008**, 110 (2–3), 579.
- [75] L. J. Rovetto et al., *Molecular Hydrogen Storage in Novel Binary Clathrate Hydrates at Near-Ambient Temperatures and Pressures*, in Basic Energy Sciences, U.S. Department of Energy, Washington, DC **2006**, p. 629.
- [76] E. D. Sloan, *Clathrate Hydrates of Natural Gases*, 2nd ed., CRC Press, Boca Raton, FL **1998**.
- [77] W. L. Mao, H. K. Mao, *Proc. Natl. Acad. Sci. U. S. A.* **2004**, 101 (3), 708.
- [78] W. L. Mao et al., *Science* **2002**, 297 (5590), 2247.
- [79] S. Patchkovskii, J. S. Tse, *Proc. Natl. Acad. Sci. U. S. A.* **2003**, 100 (25), 14645.
- [80] H. Lee et al., *Nature* **2005**, 434 (7034), 743.
- [81] R. Teitel, *Hydrogen Storage in Glass Microspheres*, Report BNL 51439, Brookhaven National Laboratories, U.S. DOE, Suffolk County, NY **1981**.
- [82] R. J. Teitel, *US Patent 4 302 217*, **1981**.
- [83] A. A. Akunets et al., *Int. J. Hydrogen Energy* **1994**, 19 (8), 697.
- [84] D. B. Rapp, J. E. Shelby, *J. Non-Cryst. Solids.* **2004**, 349 (1–3), 254.
- [85] G. G. Wicks, L. K. Heung, R. F. Schumacher, *Am. Ceram. Soc. Bull.* **2008**, 87, 23–8.
- [86] R. C. Hibbeler, *Mechanics of Materials*, 5th ed., Prentice-Hall, Englewood Cliffs, NJ **2004**.
- [87] R. T. Tsugawa, I. Moen, P. E. Roberts, P. C. Souers, *J. Appl. Phys.* **1976**, 47 (5), 1987.
- [88] N. K. Zhevago, V. I. Glebov, *Energy Conversion Manage.* **2007**, 48 (5), 1554.
- [89] A. Zaluska, L. Zaluski, J. O. Ström-Olsen, *J. Alloys Compd.* **1999**, 288 (1–2), 217.
- [90] R. C. West, *CRC Handbook of Chemistry and Physics*, 62nd ed., CRC Press, Boca Raton FL **1982**.
- [91] F. Baitalow et al., *Thermochim. Acta* **2002**, 391 (1–2), 159.
- [92] H. Reule, M. Hirscher, A. Weißhardt, H. Kronmüller, *J. Alloys Compd.* **2000**, 305 (1–2), 246.
- [93] I. Saita, T. Toshima, S. Tanda, T. Akiyama, *Mater. Trans.* **2006**, 47 (3), 931.
- [94] J. Huot et al., *J. Alloys Compd.* **1999**, 293, 495.
- [95] S. R. Johnson et al., *Chem. Commun.* **2005**, 22, 2823.
- [96] J. Wang et al., *Angew. Chem., Int. Ed.* **2009**, 48 (32), 5828.
- [97] O. Friedrichs et al., *Acta Mater.* **2006**, 54 (1), 105.
- [98] G. Barkhordarian, T. Klassen, R. Bormann, *Scr. Mater.* **2003**, 49 (3), 213.
- [99] G. Barkhordarian, T. Klassen, R. U. Bormann, *J. Alloys Compd.* **2004**, 364 (1–2), 242.
- [100] L. Zaluski et al., *J. Alloys Compd.* **1995**, 217 (2), 295.
- [101] W. Grochala, P. P. Edwards, *Chem. Rev.* **2004**, 104 (3), 1283.
- [102] H. I. Schlesinger et al., *J. Am. Chem. Soc.* **1953**, 75 (1), 215.
- [103] R. Aiello, M. A. Matthews, D. L. Reger, J. E. Collins, *Int. J. Hydrogen Energy* **1998**, 23 (12), 1103.
- [104] T. Oku, M. Kuno, H. Kitahara, I. Narita, *Int. J. Inorg. Mater.* **2001**, 3 (7), 597.
- [105] P. Wang et al., *Appl. Phys. Lett.* **2002**, 80 (2), 318.
- [106] M. Oertel et al., *Int. J. Hydrogen Energy* **1987**, 12 (4), 211.
- [107] Z. Xiong et al., *Nat. Mater.* **2008**, 7 (2), 138.
- [108] P. Chen et al., *Nature* **2002**, 420 (6913), 302. DOI: 10.1038/nature01210
- [109] Z. T. Xiong, G. T. Wu, H. J. Hu, P. Chen, *Adv. Mater.* **2004**, 16 (17), 1522.
- [110] Z. T. Xiong, J. J. Hu, G. T. Wu, P. Chen, *J. Alloys Compd.* **2005**, 395 (1–2), 209. DOI: 10.1016/j.jallcom.2004.10.062
- [111] Z. T. Xiong et al., *J. Alloys Compd.* **2005**, 398 (1–2), 235. DOI: 10.1016/j.jallcom.2005.02.010
- [112] Y. F. Liu et al., *J. Power Sources* **2006**, 159 (1), 135. DOI: 10.1016/j.jpowsour.2006.04.006
- [113] K. Luo et al., *Int. J. Hydrogen Energy* **2009**, 34 (19), 8101.
- [114] B. Karthikeyan, *Chem. Phys. Lett.* **2006**, 432 (4–6), 513.
- [115] H. Lee, M. C. Nguyen, J. Ihm, *Solid State Commun.* **2008**, 146 (9–10), 431.
- [116] I. Cabasso, Y. Yuan, *FY 2008 Annual Progress Report*, U.S. DOE, Washington DC **2008** (Available from: [www.hydrogen.energy.gov/pdfs/progress08/iv\\_c\\_3\\_cabasso.pdf](http://www.hydrogen.energy.gov/pdfs/progress08/iv_c_3_cabasso.pdf)).