



Progress and problems in hydrogen storage methods

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Abstract

A technique of hydrogen storage has to meet the DOE criterion for the volumetric and gravimetric density of the stored hydrogen and the reversibility criterion for the charging/discharging processes. There are basically five candidate methods that have attracted the common interest: compression, liquefaction, physisorption, metallic hydrides, and complex hydrides. An overview was given for the storage methods available today with respect to the progress made recently and problems still there. © 2004 Elsevier Ltd. All rights reserved.

Keywords: Hydrogen; Storage; State; Overview

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1. Introduction

Hydrogen is shown to be the future fuel from the point of view of human fuel evolution. The fuel evolution experienced the history from coal through petroleum to natural gas following the direction of increasing the content of hydrogen, therefore, it must finally reach the destination of pure hydrogen. Every step of the fuel evolution initiated a progress in human civilization, therefore, the large-scale utilization of hydrogen fuel will certainly elevate the human civilization to a higher horizon. Hydrogen is the cleanest fuel, and has a heating value three times higher than petroleum. However, it is not a natural source, but a man-made fuel; therefore, hydrogen bears a manufacture cost, which made it costing three times higher than the petroleum products. Therefore, any method of storage is not allowed to considerably increase the cost of hydrogen fuel. There are still problems in the realization of the renewed hydrogen from water, but the market supply and the cost of hydrogen do not constitute the bottleneck of hydrogen vehicles today although the hydrogen used presently may not be renewed. There is only one bottleneck for the hydrogen vehicle program, the storage of hydrogen. Just think about as large as 49 m³ that 4 kg hydrogen occupies, which is required for a practical driving distance, one can imagine how difficult is the job of hydrogen storage. Storage basically implies to reduce the enormous volume of the hydrogen gas. The reversibility of the hydrogen uptake and release excludes all covalent hydrocarbon compounds as hydrogen carriers because the hydrogen is only released from the compounds if being heated to temperatures above 800 °C. The methods of interest include compression, liquefaction, physisorption, metallic hydrides, and complex hydrides, which are commented with respect to the technical state and the viability in future application.

2. Compression

It might be the simplest way to store hydrogen in a cylinder of pressure up to 20 MPa, but the energy density is too low to satisfy the fuel demand of driving practice. About four times higher pressure is needed to meet the driving purpose, however, such industrial cylinders have not been commercially available. Industry sets up a goal to manufacture cylinders capable of withstanding pressure up to 70 MPa with a weight 110 kg to reach a gravimetric density 6%; and volumetric density 30 kg/m³. The hydrogen density as such is remarkably lower than the cryoadsorption method, and the high cost of compression and the cylinder might hinder the method to be accepted commercially. The isothermal

compression of hydrogen from 0.1 to 80 MPa consumes energy 2.21 kW h/kg, but much higher energy would be consumed in a real process as the case of liquefaction. A report from Linde Company estimates the cost of compressed H₂ is much higher than the cost of liquid hydrogen. It seems, therefore, this method is not likely to be used in the future. Furthermore, the safety of pressurized cylinders is of big concern especially in the densely populated regions.

3. Liquefaction

This method faces two challenges: the efficiency of the liquefaction process and the boil-off of the liquid. The theoretical work necessary to liquefy hydrogen gas of room temperature is 3.23 kW h/kg, but the technical work is about 15.2 kW h/kg, which is almost half of the lower heating value of hydrogen [1]. Gasification of liquid hydrogen inside the cryogenic (21.2 K) vessel is an inevitable loss even with a perfect insulation technique. The exothermic reaction of the conversion from ortho- to para-hydrogen provides a heat source of the gasification. The heat of conversion is 519 kJ/kg at 77 K, and 523 kJ/kg at temperatures lower than 77 K, which is greater than the latent heat of vaporization (451.9 kJ/kg) of normal hydrogen at the normal boiling point. The critical temperature of hydrogen is very low (33.2 K), above which liquid state cannot exist. Therefore, liquid hydrogen can only be stored in an open system otherwise the pressure in a closed system can be as high as 1000 MPa at room temperature. So, the boil-off of liquid means the emission of H₂ into the atmosphere. The relatively large amount of energy necessary for liquefaction and the continuous boil-off of liquid limit this storage system to utilizations where the cost of hydrogen is not an important issue and the hydrogen is consumed in a rather short time, e.g. air and space applications.

4. Physisorption

4.1. The fundamentals

The storage of hydrogen can rely on physisorption because the adsorbed gas can be released reversibly. There are different mechanisms of adsorption depending on the geometry of the adsorbent and the temperature of adsorption. Multilayer mechanism functions if the adsorption happens on an open surface and volume filling would happen in a pore narrower than 2 nm. Capillary condensation could happen in a pore larger than 2 but smaller than 50 nm. Adsorption in a pore larger than 50 nm is the same as that on open surfaces. However, all the mechanisms here mentioned assume the possibility of condensation of the adsorbed adsorbates. Such possibility does not exist at above-critical temperatures; therefore, a different mechanism of adsorption must assume. There is only one mechanism for the adsorption of supercritical gases on any kind of adsorbents, that is the monolayer surface coverage. The single mechanism corresponds to the single type of isotherms of supercritical adsorption. This argument can be proved on considering the well-known BET theory of adsorption [2]. According to BET, the first molecular layer of

adsorbate is fixed on the solid surface due to the interaction between gas and solid. When the surface was completely covered with a layer of adsorbate, more gas molecules would be adsorbed above the first layer due to the interaction between the same species of adsorbate molecules forming the second layer, and so on for the subsequent layers. The interaction force received by the first layer molecules is, thus, different from that received by the second and subsequent layers. This difference must be reflected in the heat of adsorption of different layers. The experiment with nitrogen and carbon black [3] showed that the heat of adsorption of the first layer is 11–12 kJ/mol (0.11–0.12 eV) and it drops to the latent heat of condensation, 5.56 kJ/mol (0.058 eV) in the subsequent layers. Obviously, the subsequent layers from the second cannot exist at above-critical temperatures, otherwise a classical law of physics, i.e. gas cannot be liquefied at above-critical temperatures no matter how high pressure applied, would be false.

The monolayer adsorbate is itself fixed by a weak interaction; therefore, significant physisorption is only observed at relatively low temperatures. Shown in Fig. 1 is the linear variation of the logarithm of the saturation adsorption of hydrogen on activated carbon with temperature [4].

In summary, the physisorption of supercritical gases follows two basic rules: the monolayer adsorption mechanism, and the exponential decrease of adsorption with the increasing temperature. It follows that the adsorption capacity of hydrogen on a material depends on the specific surface area of the material and that higher temperatures will lower the adsorption capacity. The total storage capacity in a porous solid is, however, not only the adsorption capacity, but also the sum of contributions due to adsorption on solid surface and that due to compression in the void space [5].

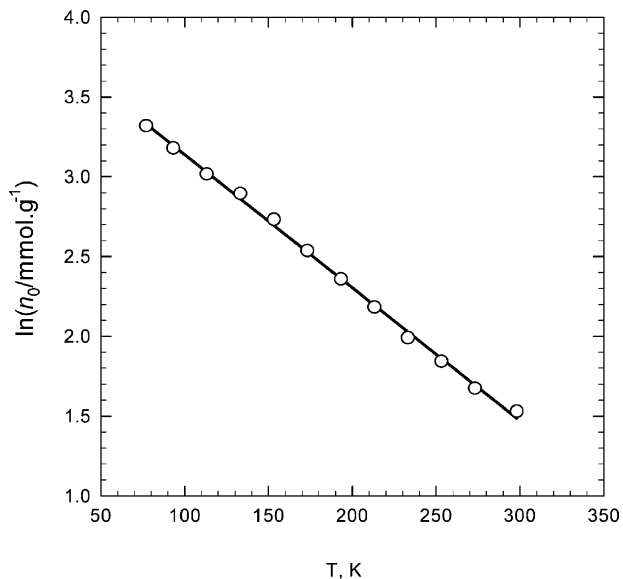


Fig. 1. Variation of the saturation adsorption with temperature [4].

4.2. Hydrogen storage in nanostructure carbons

Dillon et al. [6] presented the first report on hydrogen storage in carbon nano-tubes and triggered a world-wide tide of research on carbon nanotubes. However, their result was rebutted lately [7,8]. The succeeding experiments on carbon nano-tubes were carried out with different methods under various conditions. Samples are usually very small and often not well characterized. Some results of rather high storage capacity were later shown due to the faults of experiment. About 40 references reporting the hydrogen uptake capacity measured on nanostructure carbons have been looked up in CA until the end of 2003 [9–47]. The numbers are shown in Fig. 2, where the triangle dots are the data for low temperatures (around 80 K), and the circles are the data for ambient temperatures. The low temperature capacity is supposed to be one order of magnitude higher than that for ambient temperature, but the triangles are totally buried in the circles indicating a fact that serious uncertainty is involved in the data reported for the hydrogen uptake capacity of carbon nanotubes. The reports from GM and Sony companies [42,43] deserve special attention because they are the potential buyers of the technology. The former claimed that any reported capacity of higher than 1 wt% is due to experimental errors, and the latter reported a capacity of only 0.3 wt%.

Some authors explained their rather high hydrogen uptake capacity at ambient temperature with the possibility of hydrogen liquefaction inside nanotubes. There are two counter arguments against the explanation. First of all, hydrogen condensation at ambient temperature is absolutely impossible no matter where it locates. The fact that liquid

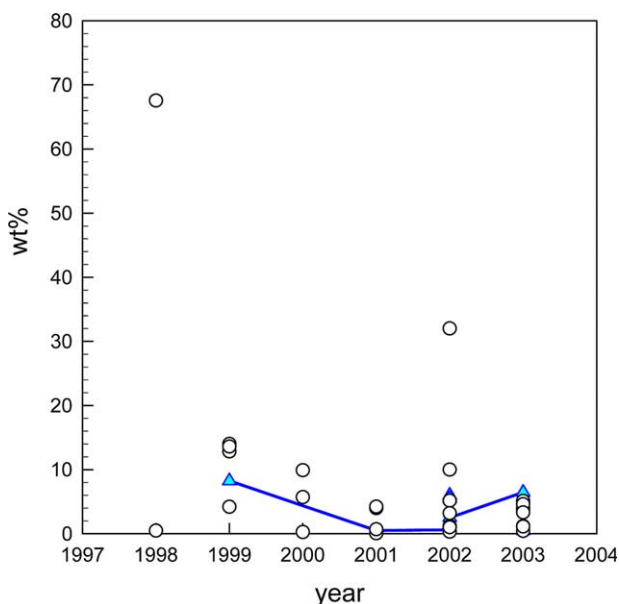


Fig. 2. The measured hydrogen uptake capacity of references until the end of 2003 [9–47].

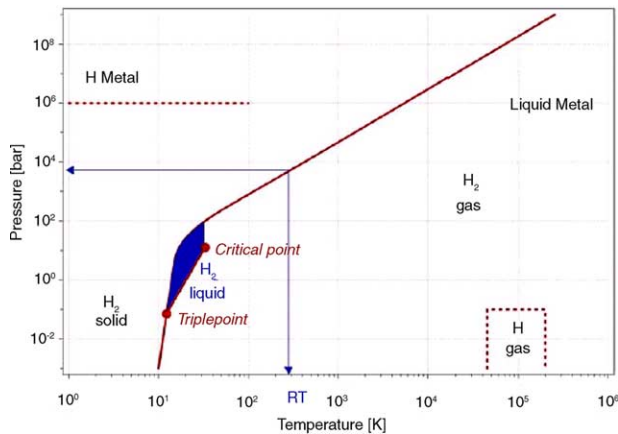


Fig. 3. Primitive phase diagram for hydrogen [48].

hydrogen can never exist beyond the narrow temperature range of 21.2–33 K is indicated in Fig. 3, which is the primitive phase diagram for hydrogen [48]. In addition, molecular dynamics simulation showed that condensation did not happen even for a pressure as high as 35 GPa inside a simulated single wall carbon nanotube with a diameter 0.683 nm [49]. Second, whether hydrogen molecules can or not enter the interior space of nanotubes is a question. Should the strengths of the adsorption potential at the ends and the exterior surface of a nanotube be equal, the ratio of the probabilities for a hydrogen molecule to enter the tube or to be adsorbed on the exterior surface must equal the ratio of areas of the tube openings to the exterior surfaces, which is usually very small. Besides, the adsorption potential of the exterior surface renders nanotubes interacting each other and form bundles, which together with the adsorption of hydrogen molecules on the exterior surfaces increase considerably the transportation resistance of hydrogen to the openings. Therefore, it is difficult for the hydrogen molecules to be adsorbed on the interior surface of carbon nanotubes unless there is a ‘black hole effect’ at the ends of nanotubes.

Practical way to explore what really happens during the adsorption of hydrogen in nanotubes is to observe the behavior of the adsorption isotherms. Unfortunately, no much information about isotherms was available in literature. Therefore, five adsorption isotherms for 233–318 K [50] and three isotherms for 77 K [47] were collected by the author and are shown in Fig. 4. The isotherm 77 K-1 is for the powder sample without heat treatment, 77 K-2 is after the treatment of heating the powder at 400 °C for 1 h in nitrogen atmosphere, and 77 K-3 is for the pellets of nanotubes. It is shown that the uptake capacity at 77 K is remarkably higher than for higher temperatures, and all isotherms show typical feature of supercritical adsorption. The isotherm behaves like type-I if the adsorption is far ahead the saturation, and a maximum appears at some pressure, after which it drops down with the increasing pressure. The heat of adsorption was evaluated based on the isotherms for 233–318 K. It is -1.8 kJ/mol, only one-fourth of that on activated carbon [51]. The model for supercritical adsorption [52–54] was applied for the three isotherms at 77 K, and the adsorption predicted by the model was marked with curves. Apparently, the model fits the isotherms very well. It is concluded, therefore, the uptake of hydrogen by carbon

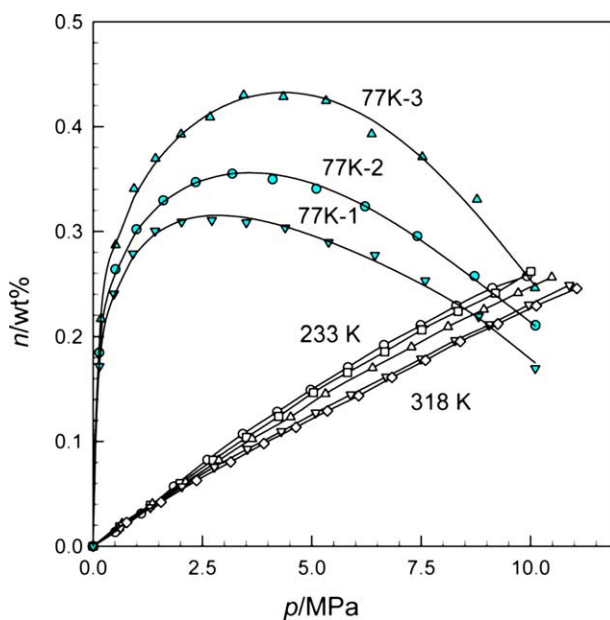


Fig. 4. Adsorption isotherms of H₂ on multiwalled carbon nanotubes [47,50].

nanotubes follows the rules of supercritical adsorption. Therefore, the specific surface area of carbon nanotubes and the temperature of adsorption control the hydrogen uptake capacity. Reports from Strobel et al. [55] and Nijkamp et al. [56] provided further experimental supports of the conclusion. Both of them observed the linear relationship between the uptake capacity and the specific surface area of carbon materials. The specific surface area of any carbon nanotubes or nanofibers cannot compete with super-activated carbon, and the storage at ambient temperature is too low to be practically utilized. That is why the storage of hydrogen in super-activated carbon cooled with liquid nitrogen is the only reasonable way to utilize the principle of physisorption. As shown in Figs. 5 and 6, the gravimetric density of the stored hydrogen is 10.8% (based on the weight of carbon) at 77 K and 6 MPa, and the volumetric density is 41 kg/m³ [5]. The cryoadsorption method of hydrogen storage seems economically competitive because the cost of cool provided by liquid nitrogen is cheap, and the activated carbon can be used for long, and the boiling-off of hydrogen is replaced by the boiling-off of nitrogen. In comparison with activated carbon, the enhancement effect of the carbon nanotubes for hydrogen storage [57] is shown in Fig. 7. Clearly, carbon nanotubes cannot enhance hydrogen storage.

Recently, hydrogen storage with nanotubes of other materials was reported [58–60]. However, as long as the interaction between hydrogen molecules and the surface atoms of the material remains the Van der Waals force, specific surface area of the material is still the decisive factor of the storage capacity. A metal-organic framework of Zn₄O(1,4-benzenedicarboxylate)₃ was proposed as hydrogen storage material [61], which might trigger another research tide on storing hydrogen in this group of compounds. It was reported that hydrogen was absorbed at 298 K and the amount absorbed is proportional to

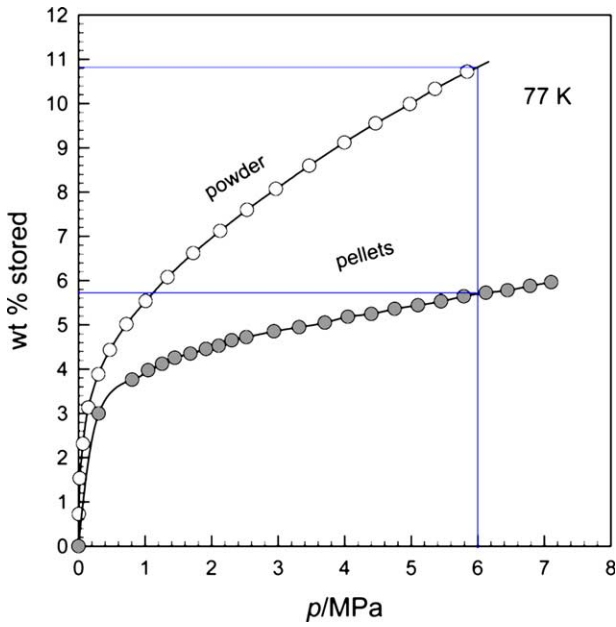


Fig. 5. Weight percentage of H₂ stored in activated carbon AX-21 powder and pellets [5].

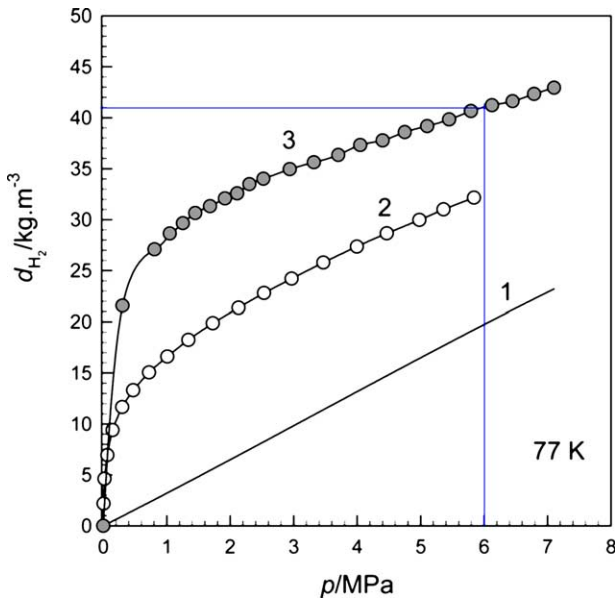


Fig. 6. Volumetric density of hydrogen in a vessel. 1, by compression only; 2, filled with carbon powder; 3, filled with carbon pellets [5].

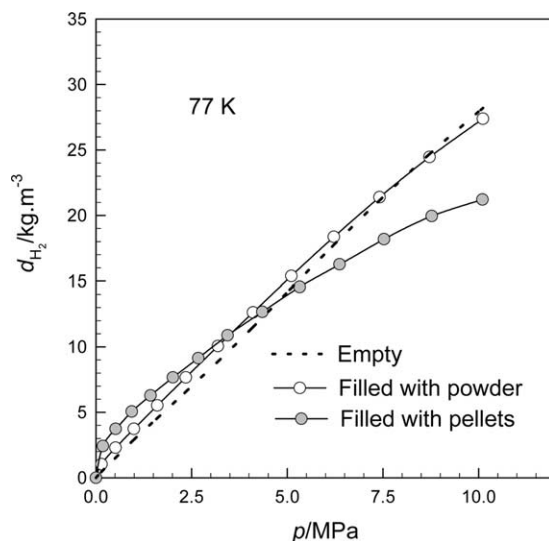


Fig. 7. Enhancement effect of carbon nanotube for hydrogen storage at 77 K [57].

the applied pressure. No saturation of absorption was found, which is very unlikely true for any kind of ab- or adsorption process. According to the lesson learnt from carbon nanotubes, such novel finding needs further verification, especially with the measurement in an expertised adsorption apparatus.

5. Metallic hydrides

Some metals and alloys absorb hydrogen and form hydrides. There are two classes of hydrides: metallic hydrides and complex hydrides. The main difference between them is the transition of metals to ionic or covalent compounds for the complex hydrides upon absorbing hydrogen. Some of the metallic hydrides of interest for the storage purpose are listed in Table 1 [7]. The prototype metallic hydrides are composed of two elements. The A element is usually a rare earth or an alkaline earth metal and tends to form a stable

Table 1
Most important families of hydrides forming in compounds

Intermetallic compound	Prototype	Hydrides	Structure
AB ₅	LaNi ₅	LaNi ₅ H ₆	Haucke phase, hexagonal
AB ₅	ZrV ₂ , ZrMn ₂ , TiMn ₂	ZrV ₂ H _{5.5}	Laves phase, hexagonal or cubic
AB ₃	CeNi ₃ , YFe ₃	CeNi ₃ H ₄	Hexagonal, PuNi ₃ -typ
A ₂ B ₇	Y ₂ Ni ₇ , Th ₂ Fe ₇	Y ₂ Ni ₇ H ₃	Hexagonal, Ce ₂ Ni ₇ -typ
A ₆ B ₂₃	Y ₆ Fe ₂₃	Ho ₆ Fe ₂₃ H ₁₂	Cubic, Th ₆ Mn ₂₃ -typ
AB	TiFe	TiFeH ₂	Cubic, CsCl-or Ti ₂ Ni-typ
A ₂ B	Mg Ni, Ti ₂ Ni	Mg ₂ NiH ₄	Cubic, MoSi ₂ -or Ti ₂ Ni-typ

hydride. The B element is often a transition metal and forms only unstable hydrides. Nickel is often used as B element since it is an excellent catalyst for the hydrogen dissociation.

Some metal hydrides absorb and desorb hydrogen at ambient temperature and near the atmospheric pressure, and the volumetric density of the hydrogen atoms present in the host lattice is extremely high. A volumetric density of 115 kg/m^3 was reached in LaNi_5H_6 . However, all the reversible hydrides working around ambient temperature and atmospheric pressure consist of transition metals; therefore, the gravimetric hydrogen density is limited to less than 3 wt%, for example, the gravimetric density of hydrogen in LaNi_5H_6 is only 1.4%. Recent attention turns to the hydrides formed by light metals, and Mg becomes the focus. The formation of metal hydrides is an exothermic reaction. Significant heat is released during absorbing hydrogen and the same amount of heat is required in order for hydrogen released from the hydrides. More stable the hydride is, more heat is needed to desorb hydrogen. An amount of energy approximately 25% higher than the heating value of hydrogen is needed for the release of hydrogen from MgH_2 . Although many efforts have been contributed to the Mg-based hydrides in recent years, it is still a challenge to find out an appropriate hydride of light metals.

6. Complex hydrides

Group I, II, and III elements, e.g. Li, Mg, B, Al, build a large variety of metal–hydrogen complexes. The number of hydrogen atoms per metal atom is 2 in many cases. This kind of complexes shows the highest volumetric density, 150 kg/m^3 , in Mg_2FeH_6 and $\text{Al}(\text{BH}_4)_3$, and the highest gravimetric density at room temperature known today in LiBH_4 (18 wt%). NaAlH_4 can reversibly absorb/desorb hydrogen at moderate temperatures; therefore, received more attention [62–71]. LiBH_4 and NaBH_4 are also on the list of candidates [72–76]. Some researchers thought complex hydrides as the promising solution of the hydrogen storage problem may be because this group of material has not been well studied with respect to the behavior as a hydrogen carrier. The low dynamics of the hydrogen releasing process is a major problem. Unlike the metallic hydrides, hydrogen is released via cascade decompositions from the complex hydrides, and the step reactions call for different conditions. Therefore, there is a large difference between the theoretical and the practically attainable hydrogen capacities. Besides, significant changes in the particle morphology and elemental distribution were induced by hydrogen desorption [77]. Repeated absorption/desorption cycles have to be tested before the conclusion regarding the potential application being made. $\text{Al}(\text{BH}_4)_3$ also has very high gravimetric hydrogen density (17 wt%). It has a melting point of -65°C and is liquid at room temperature. However, very little is known about it today.

7. Summary

Storage of hydrogen in a pressurized cylinder is not likely to be applied in the future due to the low density and high cost at high pressures. Liquid hydrogen could be applied if

the unit cost becomes comparable with gasoline, yet the inevitable boiling-off of liquid might be of concern. Metallic hydrides of heavy metals cannot get rid of the constraint of gravimetric density, and the relatively high temperature of ab- and desorption and the large amount of energy required for releasing hydrogen remain the barriers for the light metal hydrides. A confidential conclusion cannot be made for the complex hydrides before more works having been done. Physisorption of hydrogen on nanotubes/nanofibers of any materials seems hopeless for enhancing the hydrogen density due to the small surface area. Cryoadsorption of hydrogen on superactivated carbon of abundant slit-like micro-pores (< 2 nm) is presently promising because it reaches the gravimetric density of more than 10 wt% and a reasonable volumetric density of 41 kg/m^3 at relatively low cost. However, to find out better technique of hydrogen storage remains a challenge facing us.

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