Materials for Hydrogen Mobile Storage Applications

Steven Zhang 1,a,*, Lok Him Lee 2,b, Yufan Sun 2,c and Yifei Liu 3,d

1 Experimental High School Affiliated to Beijing Normal University, Beijing 103302, China
2 Adcote Shanghai High School, Shanghai 200083, China
3 Beijing No. 8 High School, Beijing 100032, China

*,a Corresponding author email: 15311463460@163.com, b syntax.s@outlook.com,
c lyfdani2020@hotmail.com, d cl2004_0123@aliyun.com

Abstract. There are several attempts to achieve efficient hydrogen storage. In this article, we introduce four main methods: conventional tank storage, metal and alloys hydrides storage, polymeric materials storage and carbon nanomaterials storage. We illustrate the advantages, disadvantages and current research process of each methods.

Key words: Hydrogen storage, Hydrogen storage material, Storage efficiency.

1. Introduction

Hydrogen, as a clean, powerful and available resource, has raised significant attention. However, its storage is the major limitation. The improvements in the conventional type of storage have already made hydrogen fuel automobiles possible. But higher storage efficiency is required for future hydrogen use. There are notable developments in hydrogen storage by metals, organic polymeric materials, and carbon nanomaterials. These new materials provide opportunities to improve storage efficiency.

2. Conventional metal material

2.1. Introduction

Conventional hydrogen energy storage methods include high-pressure gaseous hydrogen storage and low-temperature liquid hydrogen storage. High-pressure gaseous hydrogen storage method compresses the hydrogen in the tank and then releases the pressure when hydrogen needs to be used. This method is used in the mobile field. Low-temperature liquid hydrogen method reduced the temperature of the hydrogen, turning the hydrogen gas into liquid and putting it in an adiabatic tank. This method is prevalent in aerospace field.

2.2. High-pressure Gaseous Hydrogen Storage

High-pressure gaseous hydrogen storage is the storage of hydrogen by compressing hydrogen in a high-pressure container under high pressure. The process is fast and controllable and can be carried out at room temperature, requiring a heavy resistance pressure vessel. Recently, new high-pressure gas cylinders use aluminum alloy or plastic as the inner tank to further reduce the weight of the tank, and carbon fiber is wrapped around the inner tank to increase the cylinder’s strength. However, the vessel’s
storage efficiency is low. The storage quality is less than 1% of the mass of the gas cylinder when hydrogen gas pressure is 150 atmospheres in the gas cylinder. [1] The key to the application of gaseous hydrogen storage is to develop a hydrogen storage container with excellent performance and high safety.[2]

![Image of hydrogen storage container](image_url)

**Figure 1.** Picture of a hydrogen storage

### 2.3. Low-temperature Liquid Hydrogen Storage

The mechanism of low temperature liquid hydrogen storage is that hydrogen is liquified under low temperature conditions (below -252.7°C) and stored in a highly insulated Dewar container. With a mass density of hydrogen reaching 5.5% (mass fraction), it achieves a high-volume density of liquid hydrogen. But the energy consumption of hydrogen liquefaction is high, and the energy consumption of hydrogen liquefaction is about 40% of that of hydrogen burning. Thus, a high adiabatic feature is required for storage tanks.

### 2.4. Future Expectation

Currently, these two ways of hydrogen storage have many limitations and disadvantages. The low-temperature liquid hydrogen storage is used in rocket engine liquid propeller. However, due to the high cost of hydrogen storage, it is difficult to achieve large-scale applications. There are some ways to improve this conventional hydrogen storage, such as combine these two methods and, use organic materials in the methods.

### 3. Metal and metal hydride

#### 3.1. Introduction

There are two possible ways of metal hydriding: direct dissociative chemisorption and electrochemical splitting of water[3] Hydrogen is stored in the form of metal hydrides after reaction. When needed, hydrogen could be released by raising the temperature or decreasing external temperature.

#### 3.2. Metals and Alloys for Hydrogen Storage

Magnesium has shown promise for onboard hydrogen storage especially for vehicular applications due to its high hydrogen storage concentration 7.6 wt% [4], non-toxicity, relative safety of operation and low cost. Although magnesium presents several advantages in hydrogen storage which dramatically draw people’s attention these years, Magnesium’s characteristics of thermodynamic instability, slow dehydrogenation kinetics, and easy oxidation in the air hinder its application. Mg-based systems can be modified to improve the sorption characteristics. The efforts have been made to reduce desorption
temperature and fasten the re/dehydrogenation reactions which can be influenced by 1) Improving surface and kinetic properties by ball milling 2) Alloying with other transition metal and their oxides 3) Using catalyst 4) Using thin film hydride. [5] With these efforts, magnesium and its alloys have great prospects.

Alloys derived from LaNi$_5$ show some very promising properties, including fast and reversible sorption with small hysteresis and plateau pressure of a few bars at room temperature. [6] LaNi$_5$’s properties make them perform relatively good among metal materials. However, their rarity, cost, cycle degradation, pulverization and high density hinder their developments. A possible solution to the issue is to substitute lanthanum with mischmetals (MmNi$_5$-based alloys). The alloy MmNi$_{5.3}$Co$_{0.7}$Al$_{0.8}$ shows an extremely long cycle life (capacity decay of less than 10% after 300 cycles) with reasonable discharge capacity (250 mAhg$^{-1}$) and rate capability. [7] The use of mischmetals reduces cost. Also, the replacement of Ni with other metals (Al, Mn, Si, Sn, Fe) can mitigate the problem of pulverization. MmNi$_5$-based alloys, with all features above, become one of the most promising materials for hydrogen storage.

People noticed that FeTi would react directly with hydrogen to form an easily decomposed hydride which may be useful as a hydrogen storage medium.[8] However, FeTi usually requires exposure to H$_2$ atmosphere under high pressures as several Mega-Pascals at elevated temperatures as 673 K for the activation before hydrogenation because it has surface oxidation.[9] There are some methods to remove the oxidation and enable hydronation. When metals alloyed with others, their properties will change and improve the material’s performance. (Ti$_{0.85}$Zr$_{0.15}$)$_{1.05}$Mn$_1.2$Cr$_{0.6}$V$_{0.1}$M$_{0.1}$ (M=Ni, Fe, Cu) alloys have been found easily activated at room temperature and could uptake 1.96 wt% hydrogen and release 97% of the hydrogen absorbed at room temperature.[10] Also, ball millings can solve the oxidation issue by milling the FeTi in inert gases atmosphere to create new surfaces without oxidation layer.[11] The two methods mentioned both need activation before hydrogenation. A new technique called high-pressure torsion (HPT), however, can deform FeTi and the storage performance was verified without activation before hydrogenation. FeTi processed by HPT absorbed and desorbed 1.7 wt.% hydrogen at room temperature for several cycles without any activation process.[9] FeTi has high storage efficiency and low cost but suffers from the oxidation problem which required further solutions.

3.3. Future Expectation
The current mainstream material of hydrogen storage applied is conventional types. However, solid metal storages will provide great hydrogen storage efficiency. Under STP, per unit volume of metal can store 1300 units volume hydrogen.[12] Hydrogen storage metals can perfectly solve the problem of hydrogen storage and transportation. There is still a long way to go for metal hydrogen storage since the required efficiency for real-life mobile applications can still not be met.

4. Organic polymeric materials
A method is to store hydrogen in porous organic polymers. This technology primarily relies on physiosorption of hydrogen on the pores. Thus, the surface area of the material is an important factor on its performance. An example is hyper-crosslinked polystyrene, which has an area-to-mass ratio of 1930 m$^2$/g and is able to contain hydrogen at 1.5 wt% at condition of 77K and 0.1MPa. Increasing the pressure to 8MPa, its hydrogen storage capacity becomes 5.4 wt%. [17]
Figure 2. Porous polymers and their hydrogen storage capability

However, its capacity relies largely on temperature. At 273K the capacity drops sharply, even at a higher pressure. The clear downside of this material is that super low temperature is required and might not be very practical for current real-life applications. Increasing enthalpy in hydrogen absorption reaction and decreasing pore size could make porous materials more practical, but might sacrifice capacity due to a lower possible volume and smaller surface area.

Another simple method of storing hydrogen utilize reversible reactions of hydrogen with liquid organic compound. In other words, this kind of compound can be hydrogenated and dehydrogenated, making it possible to store hydrogen at good stability by forming chemical bonds. The reactions could happen at a normal temperature and pressure. For example, toluene and methylcyclohexane is a combination possible for hydrogen storage. Methylcyclohexane can be dehydrogenated to yield toluene, and toluene can be hydrogenated to yield methylcyclohexane. It has been tested on a scale of 1 kiloliter with a hydrogen density of 6.1 wt% [16]. The figure on the left lists other possible reactions. The compounds are highly stable. On average, the hydrogen density in this method excel over the porous method even under mild conditions.

Figure 3. Four examples of organic compound reaction cycle [17]

Yet, there are a few downsides of this method. Although the compounds could be stored at normal conditions, the process of hydrogenation often requires high pressure or temperature to happen. In addition, high temperature leads to the evaporation of the liquids, and the separation of hydrogen gas from the gaseous mixture can be troublesome. On the other hand, liquid state means higher chance of accidental ignitions. The safety of liquid hydrogen carriers is doubtful.

The downsides can be solved by a tradeoff of capacity. The cycle of reaction of fluorenol and fluorene is shown on the righthand side. The hydrogen evolution reaction happens efficiently in mild condition in presence of iridium catalyst. The protonation step could even use water as a hydrogen source. The
fluorenol group has a hydrogen density of only 1.1 wt%, lower than other compounds. The polymer of this group has even lower density. Nevertheless, its low requirement of hydrogenation and higher safety coefficient makes it a potential material. Some other materials such as polystyrene exhibits high safeness too.

In conclusion, organic polymeric material has a great potential to be the ideal hydrogen storing material, and there are various derivatives to be investigated. It can be asserted that in future there will be a polymer that does this task better than any material mentioned in this article [17].

Figure 4. The reaction cycle of fluorene

5. Carbon nanotube

5.1. Introduction
Carbon nanomaterial, especially the carbon nanotubes (CNTs), has been an interest of many researchers for hydrogen storage. However, most experiments at present show that it is not practical. The low feasibility will be discussed in this section.

5.2. Two Possible Ways or Pure CNT to Store Hydrogen
First, it can simply store hydrogen as conventional metal materials do. However, since each two carbons are connected by strong covalent bond, we cannot open and close the nanotube freely. This means even if we put in hydrogen successfully, we cannot release them in an economical way. The second is to use it as adsorbent. In another word, CNTs can collect hydrogen through adsorption. This technology is potential but experimentally not feasible at present time.

5.3. Possible Principles for Hydrogen Storage
It is known that each two atoms can have induced dipole-dipole force—Van der Waal’s force (VDWs). When a ring of carbon is formed, attraction force from each carbon atom will overlap and strengthen in the middle, forming the trap. Hydrogen can be trapped by the force and tied at the central space. However, this capacity cannot be large, because when more hydrogen molecules fall into the trap, the repulsion between hydrogen molecules will become very large. In comparison, VDWs is much less. Chemical reaction forms hydride compounds, CHx. The disadvantage is that the speed of reaction is fairly low, and it may hard dissociate hydrogen. Many researchers assume that chemical adsorption is not the leading one, and it almost happens because of impurities.

5.4. History Experiments
Dillon and co-workers showed that soots containing SWCNT can absorb H2 molecules of 0.01 wt% at 300 torr and room temperature.[18] In experiments using highly purified SWCNTs and H2, the amount of adsorbed H2 was found to be 8.25 wt% at 80 K and 100 bars,[19] while other measured value of H2 is 4.2 wt% at room temperature and about 10 MPa.[20] In addition, it was reported that the amount of hydrogen stored electrochemically in SWNTs is 0.39 wt%. [21]
Even an inspired research indicates that in Li- or K-doped carbon nanotubes, it was demonstrated that H2 can be absorbed as much as 14–20 wt % under ambient pressure, while pristine carbon nanotubes only absorb H2 molecules of 0.4 wt% at similar conditions.[22] However, Ralph.T.Yang indicates in his rigorous comparison experiments that large component in that big proportion is water vapor, and the true value is only 2.5wt% which is not a desired amount.[23]

5.5. Future Expectation
The capacity of CNTs measured declined with time as the graph shows. One reason is the development of measuring techniques and technical methods. According to estimations from the US Department of Energy, the adsorption rate of H2 should achieve at least 6wt% at room temperature, in order to achieve economic significance. In conclusion, the present technologies are still not effective enough to turn those carbon nanomaterials into practice for storing hydrogen. However, to look forward, the excellent mechanical property and geometric structure of CNTs give possibility to combine other materials to give good results, for example, doped with alkaline metal or composite materials, etc.

6. Conclusion
There are four major types of mobile hydrogen storage mentioned in the review. The conventional type is the most mature one, thus already having widespread applications. The high-pressure gas tank can effectively condense hydrogen gas which has low energy density but high energy content and can provide available hydrogen. However, there is relatively low performance for the conventional type, so other storage types must be developed. The metal hydride storage is a possible alternative solution. Theoretically, it can provide a high storage efficiency. But there are still some issues: cost, efficiency, and stability, which hinder the application of metal hydride storage. Similarly, organic polymeric materials are advanced in storage efficiency but also have problems of the process of (de)hydroamination. There are several solutions offered to solve the storage issue among metal and polymeric materials. These two types of storage have promising prospects but still cannot meet the standard of real-life mobile applications. With the development of nanotechnology, carbon nanomaterials are also considered possible for hydrogen storage under particular conditions. But discussion remains on whether carbon nanomaterials could be suitable for applying storage. The current situation of mobile hydrogen storage is promising. Unlike conventional types, new types offer higher storage efficiency. But further researches are needed to reach the standard of 6.5wt% for commercial storage.

Acknowledgments
Steven Zhang, Syntax Sun, Caleb Li and Yifei Liu conceive the ideas and write the manuscript together. Steven Zhang leads the cooperation. We thank Professor Daniel Prober from Yale University for the guidance and advice, Sal Elder and Yi Hu for advice and revising.

References
[1] Tongxiang Ma, Leizhang Gao, Mengjun Hu, "Research progress of solid hydrogen storage materials." Journal of Functional Materials (2018).
[2] Physical Hydrogen Storage, https://www.energy.gov/eere/fuelcells/physical-hydrogen-storage.
[3] Sakintuna, B. “Metal hydride materials for solid hydrogen storage: A review” International Journal of Hydrogen Energy, 32, (2007).
[4] Selvam, P. “Magnesium & magnesium alloy hydride” International Journal of Hydrogen Energy, 11, (1986).
[5] Jain, IP. “Hydrogen storage in Mg: A most promising material” International Journal of Hydrogen Energy
[6] Schlapbach, L “Hydrogen-storage materials for mobile applications”, Nature, 414, (2001).
[7] Sakai, T. “Rechargeable hydrogen batteries using rare-earth-based hydrogen storage alloys” Journal of Alloys and Compounds, 180, (1992).
[8] J. J. REILLY, R. H. WISWALL, Jr. “Formation and Properties of Iron Titanium Hydride”,

Inorganic Chemistry, 13, (1974).

[9] Edalati, K. “High-pressure torsion of TiFe intermetallics for activation of hydrogen storage at room temperature with heterogeneus” International Journal of Hydrogen Energy, 38, (2013).

[10] Liu, P. “Hydrogen storage properties of (Ti0.85Zr0.15)1.05Mn1.2Cr0.6V0.1M0.1 (M=Ni, Fe, Cu) alloys easily activated at room temperature” Progress in natural science-materials international, 27, (2017).

[11] Aoyagi, H. “Effect of ball milling on hydrogen absorption properties of FeTi, Mg2Ni and LaNi 5” Journal of Alloys and Compounds, 231, (1995).

[12] Min, L. “Why metal can store hydrogen”, Friends of Chemistry, 37, (2001).

[13] Germain, J., Hradil, J., Fréchet, J. M. J. & Svec, F. High surface area nanoporous polymers for reversible hydrogen storage. Chem. Mater. 18, 4430–4435 (2006).

[14] Lee, J.-Y., Wood, C. D., Bradshaw, D., Rosseinsky, M. J. & Cooper, A. I. Hydrogen adsorption in microporous hypercrosslinked polymers. Chem. Commun. 2670–2672 (2006).

[15] Germain, J., Fréchet, J. M. J. & Svec, F. Nanoporous polymers for hydrogen storage. Small 5, 1098–1111 (2009).

[16] Shukla, A. A., Gosavi, P. V., Pande, J. V., Kumar, V. P., Chary, K. V. R. & Biniwale, R. B. Efficient hydrogen supply through catalytic dehydrogenation of methylcyclohexane over Pt/metal oxide catalysts. Int. J. Hydrogen Energy 35, 4020–4026 (2010).

[17] Kato, R., Nishide, H. Polymers for carrying and storing hydrogen. Polym J 50, 77–82 (2018).

[18] Dillon, A. C., K. M. Jones, T. A. Bekkedahl, C. H. Kiang, D. S. Bethune, and M. J. Heben. "Storage of hydrogen in single-walled carbon nanotubes." Nature 386, no. 6623 (1997): 377-379.

[19] Ye, Y., C. C. Ahn, C. Witham, B. Fultz, J. Liu, A. G. Rinzler, D. Colbert, K. A. Smith, and R. E. Smalley. "Hydrogen adsorption and cohesive energy of single-walled carbon nanotubes." Applied physics letters 74, no. 16 (1999): 2307-2309.

[20] Liu, C., Y. Y. Fan, M. Liu, H. T. Conga, H. M. Cheng, and M. S. Dresselhaus. "Hydrogen in single-walled carbon nanotubes at room temperature." Science 286 (1999): 1127-1132.

[21] Nützenadel, Ch, A. Züttel, D. Chartouni, and Louis Schlapbach. "Electrochemical storage of hydrogen in nanotube materials." Electrochemical and Solid State Letters 2, no. 1 (1998): 30.

[22] Chen, P., X. Wu, J. Lin, and K. L. Tan. "High H2 uptake by alkali-doped carbon nanotubes under ambient pressure and moderate temperatures." Science 285, no. 5424 (1999): 91-93.

[23] Yang, Ralph T. "Hydrogen storage by alkali-doped carbon nanotubes–revisited." Carbon 38, no. 4 (2000): 623-626.