Hydrogen Storage Methods, Systems and Materials

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Abstract. With the world energy crisis constantly developing and petrol resources reducing, hydrogen is recovered as an ideal substitute for its excellent characteristics. Despite its abundance, abilities for easy regeneration and less pollution emissions, hydrogen energy has lower energy density in standard conditions, which means hydrogen storage needs lots of space.Among all techniques,hydrogen storage technology is the hottest topic.High efficient hydrogen storage technology is highly wanted for the application in energy storage system.This paper reviews the hydrogen storage technology from varied main principles of hydrogen storage process. It makes concise comparison and analysis mainly on physical hydrogen storage (high pressure,high pressure with low temperature and liquid storage) and absorption storage (physical absorption,chemical absorption). This paper does some research on the main technical features of these two hydrogen storage technologies to find the most economic method. And the comparison shows advantages and disadvantages on each method. Physical hydrogen has weaknesses on high hydrogen storage conditions and poor security, meanwhile, chemical hydrogen storage is weak in the process of dehydrogenation.

Keywords: Physical hydrogen storage, chemical hydrogen storage, hydride.

1. Introduction

International Community has reached a consensus that human need to construct a low-carbon society, alleviate secondary crisis like global warming and tsunami which could be created by global energy crisis. Thus, clean and efficient new energy sources is wanted among worldwide for energy transformation. Scholars have taken renewable green energy like wind energy,solar energy,tide energy and biomass energy into consideration.Among all, hydrogen energy, as a kind of clean energy, is widely accepted because the product after combustion is water. In addition, hydrogen gets combustion easily and owns high massive calorific values, which proves hydrogen is great efficient alternative energy for most countries. Hydrogen can also be utilized variously, such as hydrogen fuel cell, hydrogen gas turbine, Hydrogen as raw material for chemical synthesis products and Hydrogen synthetic fuel.

All countries in the world attach importance to the development of hydrogen energy. America has invested $34 million since 2018 in innovation research and technology transfer for hydrogen-related superconductor magnetics energy storage. The EU plans to build 1,500 hydrogen filling stations by 2030, creating a value of 130 billion euros in the hydrogen industry;Japan plans to use hydrogen to generate nearly $2 trillion a year in economic growth by 2050 and to supply 20 million tons of hydrogen [1].

As an important industrial raw material and a possible major energy use in the future, the development of hydrogen energy faces a series of problems,including high production cost, difficulty of large-scale production and excessive loss in long distance carriage. In the whole process of using hydrogen, its storage is a key point. Actually, storage is the most important procedure to connect previous part of hydrogen production and later part of hydrogen use.According to IEA Global Hydrogen Review and Long-term plan for the development of China's hydrogen energy industry in 2021, annual output of hydrogen is about 9000×10^4 t globally, among which the annual output of hydrogen in China is 3300×10^4 t [2]. It means there is still high demand for hydrogen storage.

Hydrogen storage modes are classified in different aspects.

One method is put forward over the ideas of hydrogen storage behavioral characteristics. It is usually based on the common industrial method for storage. According to this method, there are three kinds to store hydrogen, which are high pressure gaseous hydrogen storage, low temperature liquid hydrogen storage and solid hydrogen storage [3]. High pressure gaseous hydrogen storage is usually to compress gaseous hydrogen through higher pressure and load it into storage tanks. It is a relatively mature and widely used technique. But when the gaseous hydrogen is stored only by pressure, the storage volume density is much lower, often 18~40 g/L [3]. The concept of low temperature liquid hydrogen storage is put forward to cope with the problems of high pressure.It needs to lower temperature of stand-by hydrogen so that it can be liquefied into super-critical state and well stored. However, less material could meet the standard of such a low temperature of, -250 °C and the cost for devices is much higher. So low temperature liquid hydrogen storage is used only for large-scale hydrogen storage. Solid hydrogen storage is realized by physisorption and chemisorption. It often uses metal hydride and nano materials as carrier to store the hydrogen.It gains advantages of low cost,convenient transportation,high security and high storage volume density,showing great potential.

The other classification mode is based on main principles of hydrogen storage process, as physical hydrogen storage and chemical hydrogen storage. Physical hydrogen storage is to compress hydrogen by only changing the physical conditions such as pressure and temperature. It includes broadly not only high-pressure gaseous hydrogen storage and low temperature liquid hydrogen storage. Chemical hydrogen storage is using carrier to store hydrogen. First the carrier reacts with hydrogen and produces stable compound. Then when changing conditions, Hydrogen is released.

In the following sections, the author will take the latter classification mode to overview the development of current hydrogen storage and give evaluations.

2. Physical Hydrogen Storage

This technique is a pure physical hydrogen storage method with no storage carrier. It has a low cost, an excellent ability to release hydrogen and large storage concentration. In common,it contains mainly high pressure gaseous hydrogen storage, hydrogen liquefaction and low temperature gaseous hydrogen storage.

2.1. High Pressure Gaseous Hydrogen Storage

High pressure gaseous hydrogen storage is often realized by gas cylinders or tanks, mostly in China.High-pressure hydrogen storage vessels operate at normal temperature. Design pressure is usually over 20 MPa. Carrier is 99 percents pure hydrogen. So, there is a high demand for the storage containers. When the hydrogen carrier is in high pressure and normal temperature, the permissible stress for container materials is being requested. Because both hydrogen molecules and atoms are small-scale, when they are absorbed in the surface of metal materials, The concentration difference drives them into metal (mostly steel) containers,and cause the problem of stress dropping.Facing this environment for a long period, it is prior to consider the effect of hydrogen embrittlement. Hydrogen embrittlement is a phenomenon that for hydrogen absorption, material plasticity dramatically reduces, and material properties deteriorate. For the long-term safe operation,materials are required to be greatly anti-hydrogen-embrittlement.

According to research, when hydrogen partial pressure is $\leq 20MPa$, low alloy steel Q345R can meet the standard. When > 20 MPa, only excellent hydrogen resistance material can be chosen, such as austenitic stainless steel like S304, S316 and S316L which gains low sensitivity to hydrogen embrittlement [4]. Here are comparisons for different metal hydrogen storage containers as Table 1.

Tables 1. Different types of Hydrogen Storage Cylinders [5]

Type	I	II	III
Material	Pure steel cylinder	Steel liner fiber wound cylinder	Aluminium liner fiber wound cylinder
Operating Pressure/MPa	17.5~20	26.3~30	30~70
Volume Density for hydrogen storage ($g \cdot L^{-1}$)	14.28~17.23	14.28~17.23	35~40

2.2. Hydrogen Liquefaction

Hydrogen is a kind of gas which is not easy to liquefy. Actually, hydrogen liquefaction is to cool down the compressed hydrogen to 20.3 K using cryogenic technology and to store it in specific containers. Because liquid hydrogen exists in a small temperature and pressure interval,the condition for hydrogen liquefaction is restricted. There are several methods to realize liquefaction, and they can be classified from the expansion and heat transfer process during the whole compression.

2.2.1. Linde-Hampson Cycle Method

In Linde-Hampson Method, the air first comes into compressor. Then it is cooled down to environmental temperature by a cooler. After recooling in the latter heat exchanger, it passes by a throttle valve,works done through throttling effect and finally gets liquefied. Liquefied parts go into the storage cylinders and tanks. Meanwhile,gaseous part which is not successfully liquefied just flows back to be get into the cycle again. Through the reflux way, gas also provides heat for heat exchangers to promote heat transfer efficiency. Actually, Linde-Hampson method is the first in industrial history to produce hydrogen liquefaction. It gains advantages over others in simple and reliable devices,but low efficiency.

2.2.2. Claude Cycle Method

In 1902, French scientist Claude improved the Linde-Hampson cycle by adding an expansion machine. Actually, Claude made some of high pressure be the refrigerating medium. They are expanded to do work on the surrounding. And the cooling capacity is gotten, from heat exchanger passing to other hydrogen. Other gas finally gets liquefied.

Compared to Linde-Hampson method, Claude cycle can get more cooling capacity by isentropic expansion in expansion machine. But during the operating period, medium should hold gas so that turbine machine would not be broken by cavitation from liquid hydrogen drops. From aspect of exergic efficiency, Claude cycle is much higher than Linde-Hampson. So, production is also one times higher.

2.2.3. Reverse Brayton Cycle Method

The main difference between Reverse Brayton Cycle and Claude Cycle is refrigerating medium,which is changed into Helium gas. Helium gas is precooled by nitrogen, coming to the expansion machine to release cooling capacity in the surrounding temperature of 20K or so. And hydrogen gets liquefied below boiling point.

In the process of production, Reverse Brayton Cycle Method gains higher unit energy consumption in comparison with Claude Cycle, so it is not broadly large-scale applied. Some comparisons between Reverse Brayton Cycle Method and Claude Cycle Method are as Table 2.

Table 2. Comparison between Claude Cycle and Reverse Brayton Cycle [6]

Cycle Type	Energy Comsumptiom of Producing 1 kg Liquid Hydrogen ($KW \cdot h$)	Exergic Efficieny (%)
claude	13.58	21
Reverse brayton	29.2~49.4	4.4~7.4

Comparing all above, it is obvious to find that Claude Cycle Method is the most economic to produce liquid hydrogen, and the most suitable for large-scale liquefaction.

2.3. Low Temperature Gaseous Hydrogen Storage

The method is first proposed by Aceves. Low temperature compressed hydrogen is a kind of cooled supercritical gas. In $-233℃$,gaseous hydrogen can only be compressed but not liquefied. It gains great potential in both safety and reliability. Considering the presence of vacuum chamber, low temperature gaseous hydrogen storage has a high hydrogen massive storage density as 80 g/L, compared to Liquefaction Storage of 70 g/L. Ahluwalia evaluated the method and argued that it might meet standard of U.S. Department of Energy from hydrogen storage density, volume energy density and operating temperature. But this technique still needs basic available proof and cost reducing [7].

3. Chemical Hydrogen Storage

Chemical hydrogen storage uses kinds of reactions which hydrogen may take with other medium to produce hydride. Its hydrogen storage density is much higher than high pressure gaseous hydrogen storage and low temperature liquid hydrogen storage and gains good safety. So currently,it will be the focus of future hydrogen storage development. There are severel methods for chemical hydrogen storage as alloy hydrogen storage, organic liquid hydrogen storage and hydrate hydrogen storage.

3.1. Alloy Hydrogen Storage

The principle of hydrogen absorption in alloys can be expressed as: When temperature is stable,pressure keeps rising. Then metal starts to absorb the hydrogen,produce metal solid solution and gets into alloy hydride.

By comparison, the main characteristic of alloy storage is high hydrogen storage capacity. Furthermore, when atomic hydrogen stored in the alloys are released again, they will experience a period of expansion, phase transition and combination. The period is restricted by rate and thermal effect of chemical reaction, which means more controllability for transfer. However, considering the stability of these hydride compound,high temperature is demanded.

Hydrogen storage alloys are generally composed of two elements. One is metal element which has high affinity to hydrogen. They are added to control the amount of hydrogen storage. Among them the representative part is metal from $\mathrm{I}A-VB$ families. The other is metal element gaining low affinity to hydrogen. Their effects are to form unstable hydride and to control the reversibility, enthalpy of reaction and velocity through the whole hydrogen storage.

3.1.1. Aluminum Hydride

Among all metals,aluminum hydride is a special hydride. It gains at least seven kinds of crystal types. Aluminum has a comparative high hydrogen capacity as hydrogen mass fraction is 10 % and comparative low hydrogen releasing temperature as 100~200 $°C$ [8]. In 1997, Bogdanovic added Ti into $NaAlH_4$, finding good reverse hydrogen absorption behavior in medium conditions [9]. G. Sandrock compared if adding mechanical ball mill affected the performance of $NaAlH_4$. As the result shows, adding small amount of $TiCl_3$ can lower the activation energy of reaction. When keeping adding, the activation energy of reaction remains stable. When reaction rate promotes a lot along with the amount of $TiCl_3$ addition, however, the storage capacity Monotonically reduces. Recently, Liu et al. used organic synthesis to compare hydrogen storage performance of $\alpha-AlH_3$ and in single phase, showing $\gamma-AlH_3$ is more active for the advanced transform to $\alpha-AlH_3$.

Although Aluminum alloy shows great performance in hydrogen storage, putting it into industrial application is still a tough challenge.

3.1.2. Magnesium Hydride

Magnesium hydride has the characteristics of high hydrogen storage capacity and low cost. Therefore, it is one of the research hotspots in hydrogen storage. Pure Magnesium gains theoretical hydrogen storage capacity of 7.6% [10]. However considering magnesium is easy to get oxidized,other elements are added to ameliorate and catalyze. Ghosh P et al. found that alloying modification can improve the performance of magnesium - based hydrogen storage system from thermodynamic properties of materials [11]. Zhang et al. came into a conclusion that when doped with Mo_2TiC_2,the premier temperature of magnesium hydride releasing hydrogen was dramatically lowered by the method of Isothermal dehydrogenation analysis [12].

However, Magnesium hydride needs high temperature to absorb and release hydrogen,restricting its scaled application in future.

3.1.3. Lanthanide Hydride

In all Lanthanide hydrides, intermetallic compound $LaNi_5$ is the most popular material for its excellent hydrogen storing performance in dynamics, pressure and temperature. $LaNi_5$ often reacts with hydrogen in normal temperature. It has great chemical stability, but low hydrogen storage ability about only 1.4% [13]. AB_3 alloy has theoretically higher capacity comparatively. $LaNi_3$ absorbs 1.25 atoms per mole. But part of hydrogen stored in $LaNi_3$ are rarely released.That is the main challenge for hydrogen desorption [14].

To promote the hydrogen storage capacity, scientists discovered that adding other alloys also helps. Recently Liu.F.C and Han.Z.G found that La alternated Ti in Ti-Fe alloy to exhibit higher hydrogen storage ability. In alternative alloy, main phase was Ti(Fe,Ni) phase. Adding La did not change the structure of phases. La distributed between main phase and second phase to enhance activation and hydrogen diffusion capacity [15]. Feng.T.C and Zhai.Z.Y found that adding graphene particles to compound La1.7Smd0.3Mg16Ni dramatically changed its chemical characteristics. Particles would be attached to the surface of the material and obstruct amouphous process of alloy grains. According to the experimental conclusion, when the graphene content reached 5wt.%, the diffusion coefficient D of the composite hydrogen storage alloy was 7.52×10-10 cm2/s, and the diffusion ability of the hydrogen atom was the strongest. These results indicate that the proper amount of graphene can improve the diffusion ability of the hydrogen atom in the La1.7Sm0.3Mg16Ni hydrogen storage alloy and enhance the kinetics of the alloy electrode [16].

La is a potential hydrogen storage metal material. However, on account of crystal structure restricting, it has low hydrogen storage capacity,and high cost.

3.2. Organic Liquid Hydrogen Storage

The most common principle for organic liquid hydrogen storage is that unsaturated hydrocarbons such as alkanes, alkanes and aromatics react with hydrogen. Then using dehydrogenation reactions can realize hydrogen releasing process. In the whole system,hydrogen storage carrier is formed by hydrogen storage agent through process of catalytic hydrogenation. Generally speaking, carriers with excellent performance need high boiling point, high hydrogen storing temperature, low dehydrogenation temperature and commercial advantages like low cost and low poisonousness. More studied organic liquid is cyclohexane, Methylcyclohexane, toluene and naphthalene.MCH, toluene and naphthalene are the earliest carrier to use in industry.

3.2.1. MCH

MCH gains higher hydrogen storage density in normal temperature and lower cost for application. In addtion, it is even less toxic than others. So MCH gets widely applied. The main problem for MCH hydrogen storage is dehydrogenation. So, it depends more on the catalyst of process in dehydrogenation. In research studying domestically and overseas, scientists focus on precious metals Pt and Pd. Jing et al. produced Mg-Al mixed metal oxide by calcining dihydroxide. They used it as the support of Pt-Sn supported catalyst and studied the effects of Pt-Sn molar ratio, reduction temperature and reaction temperature on the activity and hydrogen evolution rate of MCH dehydrogenation catalyst in detail [17]. The performance of Pt-based catalysts with different support was compared and evaluated, and the performance was in the order from high to low: La_2O_3 >>TiO_2 > Al_2O_3 > MnO_2 > Fe_2O_3 > ZrO_2 > CeO_2 [18].

3.2.2. Naphthalene

The massive hydrogen storage rate of naphthalene is 7.3%, and its unit volume hydrogen storage capacity is 65.4 Kg/m^3. Considering its characteristics of high boiling point and low evaporation loss,naphthalene is also popular among research.

Qi S.T. et al. used initial wet infiltration method to produce activated carbon supported Pt-Ni bimetallic catalyst and corresponding Pt monometallic catalyst, finding Pt-Ni bimetallic catalyst had higher hydrogen evolution ability [19]. Wang et al. researched dehydrogenation of two organic liquids as tetrahydronaphthalene and decahydronaphthalene. Results show that Using 0.25%~1.0% Pt as catalyst, tetrahydronaphthalene and decahydronaphthalene could both produce pure hydrogen effectively. However,tetrahydronaphthalene showed more selectivity than decahydronaphthalene [20].

3.3. Hydrate Hydrogen Storage

Different from hydrogen storage materials above, the hydrate hydrogen storage of hydrate "traps" hydrogen molecules through a three-dimensional cage structure formed by hydrogen bonding between water molecules. From that point of view, the raw material for hydrate hydrogen storage is water. Its reversible aeration and venting process is environmentally friendly and of low cost. So, researchers regard it as an important hydrogen storage direction with great application potential. Current hydrate hydrogen storage research shows that, thermal conditions is vital for producing hydrate. Davoodabadi compared hydrogen hydrate to a hydrogen battery with a fixed structure. That is to say the hydrogen absorption and formation are like charging and discharging. And the state of three phases coexistence is the phase equilibrium of the system [21]. For pure water system,this phase is difficult to reach. However, the phase equilibrium conditions of hydrogen hydrate formation changed significantly after the addition of hydrate formation accelerators to the system. According to the reasearch, it is found that compared with other accelerators as Tetrabutylammonium bromide (TBAB), tert-butylamine and gas compound of H_2 and C_3H_8, THF has a better effect on the formation of hydrogen hydrate [22-24]. The main factor influencing the theoretical hydrogen storage density of hydrate is the crystal structure. The earliest discovery is that sH hydrate can be produced by hydrogen in pure water surrounding. Then it is determined that in specific conditions hydrogen also produces sI, sH and sC hydrates.

4. Conclusion

All popular hydrogen storage methods above have their own characteristics.For realizing large-scale utilization of hydrogen energy, it is necessary to develop safe and efficient hydrogen storage methods. Physical hydrogen storage has low cost is convenient for hydrogen discharge and does not need for hydrogen storage medium and carrier. However,it requires very strict storage conditions,and has a poor security. Meanwhile, chemical hydrogen storage, as an opposite view, having a higher controllable accuracy and being more secure, is difficult to realize the process of dehydrogenation.

Based on the analysis, focus should be taken on the following aspects: First, to develop lightweight and pressure-resistant hydrogen storage vessels is essential for hydrogen storage. Second, the hydrogen liquefaction cycle in physical hydrogen storage should be studied and perfected to improve the efficiency of cooling hydrogen.What is more, Further study on the thermodynamic and kinetic properties of hydrogen molecules should be taken to prepare for the improvement of unit hydrogen storage density. In addition, Optimization method of liquid hydrogen carrier should be taken to transform hydrogen economically and efficiently. Notably, Materials with low development cost, large reserves and good hydrogen desorption ability should be developed. Lastly, it is vital to improve hydrogen reaction theory and microscopic mechanism.

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