Research Progress of Hydrogen Storage Materials

Cheng Wang *

Science and Technology Faculty of Materials and Metallurgy, Wuhan University of Science and Technology, Wuhan, 430000, China

* Corresponding author: ChengWang0701@wust.edu.cn

Abstract. Hydrogen energy has become increasingly popular as a clean and renewable source of energy in recent years due to the high levels of carbon pollution worldwide. This essay examines the current research status on various hydrogen storage techniques and materials for hydrogen energy. There are currently three primary hydrogen storage methods: high-pressure gaseous hydrogen storage, low-temperature liquid hydrogen storage, and solid-state hydrogen storage. The most widely employed method in China is high-pressure gaseous hydrogen storage. It entails compressing hydrogen fuel into a container under high pressure. As a result, high-pressure gaseous hydrogen storage is commonly used for stationary hydrogen storage. Low temperature liquid hydrogen storage involves compressing the hydrogen at first and then cooling it down with liquefaction technology. However, due to the strict requirements for compression and container insulation, its actual performance is often limited. This paper focuses on the study of solid hydrogen storage materials. The physical adsorption materials that are successively introduced include carbon-based hydrogen storage materials, metal-organic frameworks (MOFs), and Covalent organic frameworks (COFs). In the current study, carbon-based hydrogen storage materials show better performance only in low-temperature and high-pressure environments, but MOFs and COFs have great prospects in hydrogen storage. The chemical absorption hydrogen storage materials introduced in this paper are metal alloy hydrogen storage and hydrogenation complexes hydrogen storage, mainly rare earth-based hydrogen storage materials and magnesium-based hydrogen storage materials. Among them, magnesium-based hydrogen storage materials have become one of the most promising hydrogen storage materials due to their low cost and good hydrogen storage performance.

Keywords: Hydrogen, hydrogen storage, physical adsorption, chemical absorption.

1. Introduction

Climate change caused by the surging global energy demand is a significant issue in today's society [1]. The predominant use of fossil fuels as an energy source contributes to environmental pollution, making them the primary culprits [1]. Fossil fuel combustion not only exhibits characteristics of being non-renewable, highly polluting, and low in calorific value but also hinders the progress towards clean and efficient renewable energy solutions. Among the alternatives, hydrogen is emerging as a promising option due to its potential to address carbon neutrality and achieve sustainable development. However, transitioning from fossil fuels to hydrogen energy poses a multitude of challenges, with production, transportation, storage, and application being the key areas of focus for hydrogen energy development [2]. Storage and transport are the most important and core technology in the hydrogen energy engineering system, and is the key to using hydrogen energy for practical production. Although China's domestic research progress in hydrogen storage materials may not be leading the way, the hydrogen storage materials industry has a promising future considering China's long-term goals of carbon neutrality and peak carbon emissions. In this paper, we hope to summarize the latest research on hydrogen storage materials in order to navigate the future development of hydrogen energy, and also to provide a reference for future research. Previous review articles introduced and summarized various hydrogen storage materials to a certain extent. However, research on hydrogen storage materials is rapidly evolving and new review articles need to summarize the latest research results.

The primary aim of this article is to provide a summary of the most recent research on future methods of storing hydrogen for energy purposes, with a particular focus on storage materials in the context of the worldwide endeavor towards carbon neutrality. To begin with, the paper provides an in-depth description of the principles and current uses of three distinct methods of hydrogen storage: high-pressure gaseous storage, low-temperature liquid storage, and solid material storage of hydrogen. Subsequently, the paper turns its attention to the hydrogen storage materials employed in solid material hydrogen storage, initially addressing physically adsorptive hydrogen storage materials before delving into hydrogen storage materials based on carbon (carbon nanotubes, carbon nanofibers, and activated carbon), MOFs, and COFs materials, and comparing their hydrogen storage properties and development prospects. Finally, the paper introduces chemical absorption hydrogen storage materials, categorized as metal-alloy and hydride-complex materials, both of which are magnesium-based hydrogen storage materials exhibiting low-cost, high-performance characteristics, and which represent the most promising hydrogen storage materials.

2. Storage Mode of Hydrogen

2.1. High-pressure Gaseous Hydrogen Storage

The high-pressure storage of gaseous hydrogen is a widely employed technique in China. It involves compressing hydrogen fuel into containers using high-pressure techniques. This method is primarily used for stationary hydrogen storage. Different types of containers, such as seamless bottle containers and austenitic stainless steel strip containers, are used [3]. There are four main structure types for high-pressure gas cylinders: I-type, N-type, M-type, and rv-type. Each type has some applications in the hydrogen fuel vehicle industry. At present, the composite lightweight fiber-wound storage tank with plastic instead of steel has been successfully developed and put into application by Toyota in Japan, company has successfully developed and put into application. The advantages include fast filling and discharging speed and high hydrogen storage capacity. However, the compression work required is substantial, and there are risks associated with high pressure during transportation and the potential for explosion or equipment rupture.

2.2. Low Temperature Liquid Hydrogen Storage

Low-temperature liquid hydrogen storage requires the cooling and liquefaction of hydrogen to very cold temperatures. The process includes pressurizing the hydrogen, cooling it to -253 °C to liquefy it, and then storing it in a vacuum adiabatic hydrogen storage tank through a throttle valve. Liquid hydrogen has an energy density nearly 850 times higher than gaseous hydrogen under standard conditions, making it a highly efficient storage option [4]. Liquid hydrogen Volatility is difficult to avoid, so it is less used as a large-scale hydrogen source, but it has advantages in aerospace and military applications, such as liquid propellants for rocket engines. However, this technology has specific requirements for insulated containers and is currently mainly used in the aerospace field. In order to further develop liquid hydrogen storage for a wider range of civil applications, research and development of insulation technology and insulated containers is essential.

2.3. Solid Materials Store Hydrogen

Solid-state hydrogen storage materials offer a promising solution for addressing safety concerns, particularly when compared to high-pressure gaseous hydrogen storage and low-temperature liquid hydrogen storage, which are viable options for hydrogen storage, this method stands out. Two types of hydrogen storage in solid materials are physical and chemical absorption hydrogen storage. Physical adsorption involves the adsorption of hydrogen to the surface of porous materials through van der Waals forces. In chemical absorption, hydrogen is locked within the lattice of metal hydrides through chemical reactions. Solid materials used for hydrogen storage demonstrate stability, high-speed adsorption, and reversibility at ambient temperatures [5]. Solid-state hydrogen storage is a widely used method, among the three mature hydrogen storage methods, and has received considerable attention for its safety and efficiency. Currently, research progress on solid-state hydrogen storage materials has not fully matured, and most of the effort is concentrated on developing novel materials. Research efforts predominantly concentrate on designing novel materials or implementing minor improvements to existing ones. Nevertheless, the theoretical investigation into solid-state materials for storing hydrogen and their underlying mechanisms requires further depth, which poses a challenge that needs to be addressed to achieve their engineering applications. The performance difference between the three hydrogen storage methods is demonstrated in Table 1 [6].

The report contrasts the pros and cons of physical and chemical adsorption hydrogen storage materials, and culminates in a synopsis of the future research and development of hydrogen energy industrial systems and solid-state hydrogen storage materials.

Table 1. The comparison of the characteristics of three different hydrogen storage methods [6].

Storage form	Operation pressure/MPa	Gravimetrie density/	Volumetric density/(kg•m^3)	Operation temperature/℃	Response speed
High-pressure gas	35 70	4.8 5.7	23 40.8	-30—120 -30—120	Fast Fast
Liquid hydrogen	0.4	5.11	70.8	-253	Fast
Metal hybride	(MgH_2) 0.01—0.1	7.6	132.4	200—400	Slow
	($TiFeH_{1.95}$) 1.5	1.86	83.7	20—100	Medium

3. Physical Adsorption Hydrogen Storage Materials

Such materials mainly include carbon substrates or other inorganic porous materials, and hydrogen is combined with the material in molecular form through the weaker van der Waals force. Improving the hydrogen adsorption effect of materials to make hydrogen molecules easier and more firmly adsorbed in the microporous materials, which becomes an important way to further increase the storage density of hydrogen in materials that physically absorb it.

3.1. Carbon-Based Storage Materials

Carbon-based materials mainly include carbon nanofibers, activated carbon, graphite fibers and carbon nanotubes, and their hydrogen storage performance characteristics are shown in Table 2 [7].

Table 2. Hydrogen storage properties of 4 carbon-based materials [7].

Category	Abbreviation	Temperature/K	Pressure/MPa	Mass hydrogen storage density/%
Activated carbon	AC	77 93 Room temperature	2-4 6 7.04	5.3-7.4 9.8 3.8
Graphite nanofibers	GNF	25 Room temperature	12 11	67 12
Carbon nanofibers	CNF	Room temperature	10-12	10
Carbon nanotubes	CNT	80 Room temperature	12 0.05	8.25 6.5

3.1.1. Carbon nanofibers

Hydrogen adsorption by carbon nanofibers under atmospheric pressure and low temperature conditions correlates with the total microporous volume, specifically with the porosity of the material, whereas hydrogen adsorption under room temperature and high pressure conditions depends on both the microporous volume and the microporous size distribution, through CO_2 oxidation, manganese dioxide oxidation, nitric acid oxidation, hydrochloric acid oxidation and water vapor oxidation can obtain different five samples, and finally through the test, the material adsorption effect obtained by water vapor oxidation is the best [5]. Carbon nanotubes activated by potassium hydroxide possess higher surface area, microporous volume, and these properties plays an important role in the improving hydrogen adsorption capacity. None of the above five materials showed good hydrogen storage performance in practical applications, but this material still provides a basis for future research on carbon nanofiber materials.

3.1.2. Activated carbon

Activated carbon is an active material with porous, high specific surface area, large porous volume and high surface activity formed by the activation of carbon materials, and microporous activated carbon has such characteristics. In subsequent studies, it was found that increasing the specific surface area and various functional group properties of the material enhanced the performance of activated carbon in adsorbing hydrogen. However, at present, on the surface of research, activated carbon materials can only show good hydrogen storage performance at low temperature and high pressure, which makes activated carbon hydrogen storage need breakthroughs in practical applications.

3.1.3. Carbon nanotubes

Carbon nanotubes are an extremely special material, in which there are extremely narrow channels can be stored by carbon nanotubes to reach 4.2 wt% [2], and the adsorption hydrogen adsorption in carbon nanotubes is a single-molecule-layer adsorption, and it has been found that there are differences in the hydrogen storage capacity of different types of carbon nanotubes; the storage capacity of the same type of carbon nanotubes is also different for different temperatures and pressure conditions, and at room temperature, most of the hydrogen can be released normally, compared to the other two carbon-based hydrogen storage materials, this material is the one with fewer actual application. Since the hydrogen storage mechanism of CNTs is still unclear, its hydrogen storage density has been controversial, and its hydrogen storage performance is relatively good at low temperature and high pressure, but greatly reduced at medium temperature and pressure.

3.2. MOFs and COFs

MOFs are coordination polymers composed of multi-toothed organic ligands containing oxygen, nitrogen, etc., and transition metal ions. Because this material can control the large specific surface area of pores, MOFs are more promising than other adsorbent materials and can actually be used for adsorptive separations and various different materials. MOFs are therefore a material with great potential for storing combustible gases, for example, to provide energy support for next-generation vehicles [8].

COFs are two-dimensional or three-dimensional porous crystalline polymers, and covalent organic frameworks can control open pores and skeletons more accurately than other organic framework materials [9]. One now incorporates alkali metal ions into COFs materials to improve their hydrogen storage properties at room temperature.

4. Chemical Adsorption Hydrogen Storage Materials

This type of storage is the production of hydrogen-containing compounds through chemical reactions, which has good safety compared with gaseous and liquid hydrogen storage methods. At present, common chemical methods include metal alloy, coordinated hydride, organic liquid, etc. [10]. This paper mainly discusses the hydrogen storage methods of metal alloys and coordinated hydrides.

4.1. Metal Alloy Hydrogen Storage

At a certain temperature, when the hydrogen concentration increases, Hydrogen is absorbed by the metal is used to form a solid solution containing hydrogen, known as the alpha phase, and as hydrogen is added, the alpha phase continues to react to form a metal hydride (β-phase). In reality, the absorption and release of hydrogen can be achieved by regulating the temperature and pressure of the system [10].

Metal alloy hydrogen storage materials can be divided into AB5, AB2 and AB3.0-3, 5 types according to different constituent molecules, The amount of hydrogen stored is controlled by A, while the reversibility of hydrogen uptake and release is controlled by B. In this case, A refers to an element that either absorbs hydrogen or has a strong affinity for it, while B refers to an element that repels hydrogen [10].

4.2. Coordination Hydride Hydrogen Storage

Coordination hydrides are formed by the combination of various different matching anions with metal light ions such as Li, Na and Mg. The difference between this material and metal alloys is that there is a transformation of this substance to ionic or covalent compounds during hydrogen absorption. Due to the presence of many light metal ions in this material, the hydrogen storage capacity is high.

4.2.1. Rare earth hydrogen storage materials

The hydrogen storage material is a rare-earth AB5 alloy, represented by LaNi5. It has a stable hydrogen storage capacity of 1.38 wt%, and the corresponding hydrogen storage compound is LaNi5H6. LaNi5 has several this material offers advantages as a hydrogen storage material, including fast absorption and release of hydrogen, small equilibrium pressure difference, easy activation in the early stages and good anti-poisoning performance [2]. At present, the development of rare-earth alloys mainly involves the use of mixed rare-earth Mm in LaNi5. Recent research is concentrated on replacing a portion of La in LaNi5 with a combination of rare-earth Mm (La, Ce, Nd, and Pr). The optimization of the performance of rare earth hydrogen storage materials greatly relies on achieving the best adjustment ratio of La and Ce elements. Developing rare earth hydrogen storage materials is of great importance for social and economic advancement. The promotion of development and use of China's abundant rare earth resources is emphasized.

4.2.2. Magnesium-based hydrogen storage materials

Magnesium-based hydrogen storage materials are currently among the most promising candidates for hydrogen storage due to their high hydrogen storage density and affordability. Although magnesium-based hydrogen storage materials offer potential benefits, their high hydrogen release temperatures and slow kinetics currently restrict their practical applications. Various methods have been developed to improve the hydrogen absorption and kinetic properties of magnesium-based materials, such as alloying, doping catalysts, nanotechnology, and light gold coordinated hydride complexation. Research has shown that these methods have produced promising results [11]. Transition metal (TM) is added to MgH2 to address the slow rate of hydrogen absorption and release in pure magnesium and the high hydrogen release temperature. This process creates Mg-TM-H system hydrides or modifies the Mg-Re-H and Mg-TM-Re-H system hydrides with rare-earth materials, resulting in what are known as magnesium-based hydrogen storage alloys.

5. Outlook

The original purpose of using hydrogen energy is to encourage the utilization of green hydrogen. Utilizing the characteristics of green hydrogen to establish an efficient green hydrogen supply chain is essential. Simplifying the hydrogen supply process and reducing its formation are necessary for safe and effective use of hydrogen energy. Metal hydrides are regarded as promising substances for hydrogen storage because of their high storage capacity and affordability. Nevertheless, it is expected that further research and development efforts will bring forth novel materials possessing even greater hydrogen storage capabilities and efficiency, which in turn facilitates global zero carbon emissions sooner. It is important to recognize that hydrogen fuel cells have significant potential as a leading player in the new generation of energy batteries over the next two decades. As a result, it is necessary to continuously develop new technologies.

6. Conclusion

Solid hydrogen storage materials have relatively good hydrogen storage and discharge temperatures among the current hydrogen storage systems. These materials have good development prospects concerning lifetime and reversibility. They are among the most valuable for research among the three hydrogen storage methods. The potential of solid hydrogen storage materials is restricted by kinetics and thermodynamics., and the practical applications suffer from insufficient hydrogen absorption and discharge capacity. Developing a stable solid hydrogen storage system requires the stabilization of a large amount of metallic raw materials, and overcoming the high manufacturing cost of high-capacity containers is also necessary. Thus, building an industrial system for the production and use of solid hydrogen storage materials is still a considerable challenge.

References

[1] Singla M. K., Nijhawan P., Oberoi A.S., Hydrogen fuel and fuel cell technology for 61a cleaner future: 61a review. Environmental Science and Pollution Research, 2021. 28 (13): 15607 - 15626.

[2] Jing C. S. P. E. F., Research Progress of Solid-State Hydrogen storage materials. Marine Electric & Electronic Engineering, 2019. 39 (09): 31 - 35+39.

[3] Hongxia Y.H.Y.Y.W., Overview of Research on Hydrogen Storage Vessels. Plant Engineering Consultants, 2021. 60 (02): 1 - 4.

[4] Han L., Li Q., Leng G., et al., Latest research progress of hydrogen energy storage technology. Chemical Industry and Engineering Progress, 2022. (In Chinese).

[5] Liu M. S. K., Zhao Q., Li J., et al., Research progress of solid hydrogen storage materials. Chemical Industry and Engineering Progress, 1 - 27.

[6] Zhou C., Wang H., Ouyang L., Zhu M., The State of the Art of Hydrogen storage materials for High-pressure Hybrid Hydrogen Vessel. Materials Reports, 2019. 33 (01): 117 - 126.

[7] Hua L., Technological Progress on the Research and Development of Solid Hydrogen storage materials. Petroleum and new energy, 2022. 34 (05): 14 - 20.

[8] Shi X., Shan Y., Du M., et al., Synthesis and Applications for Materials of Metallorganic Frameworks. Progress In Chemistry, 2005 (06): 164 - 169.

[9] Amna A., Nadeem B., Manzar S., Advances in Covalent Organic Frameworks. Acta Physico-Chimica Sinica, 2017. 33 (10): 1960 - 1977.

[10] Zhou P., Liu Q., Sui J, Jin H., Research progress in chemical hydrogen storage. Chemical Industry and Engineering Progress, 2014. 33 (08) 2004 - 2011.

[11] Gonzini O., Plaza A., Di Palma L., Lobo M.C., Electrokinetic remediation of gasoil contaminated soil enhanced by rhamnolipid. J. Appl. Electrochem, 2010, 40: 1239 – 1248.