

Advancements and Challenges in Hydrogen Storage Technologies

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Abstract. The over-reliance on fossil fuels has led to severe pollution issues, prompting the development of renewable energy sources. Hydrogen energy, with its abundant reserves and environmentally friendly byproducts, is a promising alternative. Efficient and safe HS is crucial for its widespread application. This review analyzes several HS methods and materials, focusing on their principles, performance, advantages, and disadvantages. The storage of high-pressure gaseous hydrogen is mature and low-cost but has low density and safety risks. Low-temperature liquid HS offers higher density but involves significant energy consumption and costs. Solid-state hydrogen storage (SHS), including carbon materials, metal-organic frameworks (MOFs), and metal hydride material, shows potential for high density and purity but faces challenges in material costs and performance. The paper highlights advancements in activated carbon, graphene, carbon nanotubes, MOFs, and Mg-based and Ti-based metal hydrides. It discusses the progress and challenges in improving HS capacities, stability, and cost-effectiveness. Future research will focus on increasing HS density, reducing costs, and enhancing safety through interdisciplinary collaboration. This review provides insights into the current state and future directions of HS technologies, essential for advancing the hydrogen economy and achieving sustainable energy solutions.

1 Introduction

In recent years, the over-reliance on fossil fuels has led to increasing pollution during their extraction and use. Issues like air pollution and the greenhouse effect have become particularly severe, prompting countries worldwide to develop and promote renewable energy sources. China has set "dual carbon" goals to achieve carbon neutrality and peak carbon emissions. Hydrogen energy, with its abundant reserves, environmentally friendly byproducts, lightweight, and high energy density, is considered one of the most promising options among emerging energy sources. HS is crucial for utilizing hydrogen energy and plays a vital role in its widespread application. Therefore, developing efficient and safe hydrogen storage (HS) methods remains a key focus in hydrogen energy research. This review examines several commonly used HS methods and materials, analyzing their

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principles, performance characteristics, advantages, and disadvantages, and provides a summary and outlook on the future applications of HS materials [1].

2 Research progress and prospects of HS materials

Currently, extensively researched HS methods include high-pressure gas storage, cryogenic liquid storage, and solid-state storage. Apart from that, high-pressure gas storage is the most developed and widely utilized approach. It is characterized by low energy consumption and cost but has relatively low HS density and risks of leakage and explosion. Compressing and cooling hydrogen to $-253\text{ }^{\circ}\text{C}$ is necessary for cryogenic liquid HS, where it is then stored in insulated cryogenic tanks. This method offers much higher mass and volume HS densities than high-pressure gaseous storage and other methods like hydrides and physical adsorption. However, liquid hydrogen systems require a large initial investment and significant energy consumption for liquefaction, approximately 15.2 kWh/kg [2]. Solid HS is widely regarded as the most effective method, relying on various materials to store hydrogen through adsorption and chemical reactions. It boasts high volumetric HS density and high hydrogen release purity (Table 1) [3].

Table 1. Comparison of HS technologies

Type of Hydrogen Storage	Volumetric HS Density (g/L)	Technology Maturity	Advantages	Disadvantages
High Pressure Gaseous HS	≤ 40	Mature	Mature technology, relatively low cost, simple structure, fast hydrogen charging and discharging	Low volumetric HS density, poor safety, strictly regulated under hazardous materials regulations
Low Pressure Liquid HS	$70\sim 78$	Relatively Mature	High HS density	High energy consumption for liquefaction, stringent requirements for storage devices, high cost
Solid HS	≤ 80	Comparatively Mature	High volumetric HS density, high purity of released hydrogen	High material cost, low mass HS density, average recyclability

Some of the most notable SHS materials encompass carbon-based HS materials, MOFs, and metal hydrides. Carbon-based storage and MOFs primarily rely on the porous structure of the material's surface to adsorb hydrogen which achieves HS [4]. Metal hydride materials store hydrogen through chemical reactions between hydrogen and transition metals, alkali metals, or alkaline earth metals in their elemental form or as alloys, forming metal hydrides and enabling HS.

3 Research and application of carbon-based HS materials

Activated carbon is a primary type of carbon-based HS material, graphene, carbon nanotubes, and carbon aerogels. These materials use the strong polar dangling bonds on the surface of carbon atoms to adsorb hydrogen molecules. From a microscopic structural perspective, the

core factor affecting the adsorption performance of carbon-based materials is pore distribution, particularly pore size, and pore volume. The molecular diameter of hydrogen is 0.29 nm, and the ideal pore size for hydrogen adsorption is approximately 2-3 times larger than this diameter, which is between 0.6-0.7 nm, within the micropore size range [5]. Carbon-based HS materials primarily rely on many microporous structures to adsorb hydrogen molecules for HS.

3.1 Activated carbon adsorption HS

The production of activated carbon is mainly from carbon-rich substances. For example, coal, petroleum coke, asphalt, and biomass through processes including pretreatment, carbonization, activation, and post-treatment. It possesses a high surface area, well-developed pore structure, excellent adsorption capacity, stable properties, easily controllable surface chemical structure, and relatively low cost, making it a highly potential and competitive carbon-based HS material. The diagram illustrates the principle of hydrogen adsorption by activated carbon, where H₂ is adsorbed onto the micropores of the carbon surface. By increasing the surface area and enriching the microporous structure, the HS capacity of activated carbon can be increased to some extent.

Setareh Elyasi and others summarized the latest progress in biomass-derived porous carbon materials for HS. They believe that these materials have great potential for application in HS equipment due to their wide availability, low cost, adjustable structure, simplified production process, excellent specific surface area, and porosity. In practical applications, researchers often modify activated carbon with different types of acids, bases, and salts. For example, modifying activated carbon with urea or K₂CO₃ can result in an effective H₂ adsorption capacity of up to 2.21% at 77K/1 bar. Using different ratios of KOH for modification, the hydrogen capacity at 20MPa can reach 6% at -196°C and 1.22% at 25°C. Some researchers used a confined space method to activate carbon precursors at high temperatures, achieving a specific surface area of ≥ 4090 m²/g for activated carbon, and an HS capacity of ≥ 7.40 wt% at 77K and 80 bar [6].

3.2 Graphene

Graphene is a carbon material with a two-dimensional hexagonal single-layer structure formed by the sp² hybridization of carbon atoms. Carbon-based materials derived from graphene are shown in the diagram. However, some studies suggest that pure graphene has chemical inertness, which is not conducive to gas adsorption. Therefore, researchers have endeavored to enhance the HS capabilities of graphene through atomic doping or group modification. Dai Xiaole and others enhanced the HS performance of DHQ graphene by modifying it with super alkali clusters. By constructing a supercell, they studied the HS performance of DHQ graphene. The results showed that the clusters could stably adsorb on DHQ graphene, with maximum adsorption of 4 hydrogen molecules and an average binding energy of 319 eV, effectively preventing the aggregation of Li atoms. Each cluster could adsorb up to 11 hydrogen molecules, with an average hydrogen adsorption energy of 0.20 eV, and a maximum HS capacity of up to 12.05 wt% [7].

Other researchers have used fluorinated graphene to coat magnesium borohydride composite HS materials, utilizing the excellent properties of fluorinated graphite through a solvent-antisolvent method to achieve controlled preparation of the composite HS materials in one step. This composite HS material can be used in solid propellants and has high safety.

3.3 Carbon nanotubes

Carbon nanotubes (CNTs) are formed by rolling single-layer graphene into a closed cylinder, with the structure consisting of carbon atoms arranged in a hexagonal pattern forming a circular tube. Single-walled carbon nanotubes (SWNTs) are composed of a single layer of graphene, while multi-walled carbon nanotubes (MWNTs) consist of several coaxial tubes. CNTs have a unique hollow tube structure and lattice arrangement, allowing them to adsorb large amounts of gas. They exhibit high chemical and thermal stability. Experiments have shown that CNTs can store a certain amount of hydrogen, but at room temperature and 12 MPa, the HS capacity of CNTs is less than 1.7%, which is insufficient for practical applications [8]. CNTs can be enhanced with other HS materials as effective additives to improve their kinetics. Researchers have attempted to improve the HS performance of CNTs by increasing their specific surface area, the number of tube walls, the size of gaps, and functional groups.

For example, Yu Zhenxing and others found that adding CNTs to magnesium-based HS materials improved the mass and heat transfer properties due to the strong adsorption capacity of CNTs for hydrogen molecules and their excellent thermal conductivity.

4 Techniques and uses of MOFs in HS

MOFs and Covalent Organic Frameworks (COFs) are common types of three-dimensional porous materials. They are constructed through connections made by metal ions or covalent bonds. MOFs possess permanent void structures, large specific surface areas, and various chemical bonds, offering significant advantages for HS. However, due to the low polarizability of hydrogen and the weak van der Waals forces between most MOFs and hydrogen, their HS performance at room temperature is inadequate. Thus, creating MOFs with enhanced HS efficiency at room temperature is a significant challenge and a major research direction in hydrogen energy storage [9].

4.1 Application of MOFs in magnesium-based HS materials

In recent years, the structural diversity of MOFs has provided multiple possibilities for designing MOFs-based catalysts with unique structures and functions. MOFs have unique advantages in structure and composition, including ultra-high porous structure with uniformly distributed metal nodes at the atomic level. These features not only provide abundant anchoring sites for MgH_2 but also enhance gas diffusion and electron transfer during hydrogen adsorption and desorption. Consequently, MOFs-based catalysts have garnered extensive attention in MgH_2 HS applications. Depending on different HS needs, MOFs can be regulated by selecting different metal nodes and organic ligands to form materials with specific catalytic activities and pore structures [10]. The high porosity of MOFs offers a large surface area, enabling more effective hydrogen adsorption and storage. These pores also provide convenient channels for hydrogen molecule diffusion, enhancing overall HS efficiency. The unique pore structure of MOFs promotes rapid hydrogen diffusion, while uniformly distributed metal nodes aid in electron transfer during the hydrogen adsorption and desorption process. These characteristics give MOFs-based catalysts significant advantages in improving the HS performance of MgH_2 .

Experimental studies have shown that reducing the size of Mg-based HS materials can effectively enhance their performance. This is primarily because it shortens the hydrogen diffusion distance while increasing the interface contact between H_2 and the material. Researchers synthesized three-dimensional flower-like Ni/Zn-MOF precursors by controlling different hydrothermal times. Comparative studies of different hydrogenation

times showed that the stability of the Ni₃ZnCo_{0.7}/Ni/ZnO multicomponent catalyst was relatively high. Kinetic performance tests indicated that the addition of 5 wt% Ni₃ZnCo_{0.7}/Ni/ZnO nanoparticles endowed the composite material with optimal kinetic performance, demonstrating good cyclic stability during hydrogen absorption and desorption [11].

4.2 Development prospects and applications of MOFs

With ongoing in-depth research on MOFs-based catalysts in MgH₂ HS applications, future work can focus on designing and synthesizing more MOFs with specific functions and structures to further enhance catalytic and HS performance. Exploring the optimal composite methods of MOFs and MgH₂ and optimizing their interface structure and interactions can achieve a more efficient HS process. During experimental procedures, it is also essential to reduce the synthesis cost of MOFs while enhancing their stability, promoting their application in practical HS devices, and achieving commercial breakthroughs.

5 HS Materials based on metal hydrides

Metal hydride HS materials, under certain temperature and pressure conditions, undergo the following chemical mechanism for hydrogen absorption and desorption:



This reaction is exothermic in the forward direction and endothermic in the reverse direction. The absorption and desorption kinetics of hydrogen are influenced by temperature and hydrogen pressure, affecting both thermodynamics and reaction rates. Common HS alloys include Mg-based, Li-based, and Ti-based alloys. The combination of different metals with different catalysts can improve their hydrogen absorption performance to some extent. Metal hydrides offer approximately 1000 times higher HS density compared to gaseous HS within the same volume, with a storage range of 1% to 8% (mass fraction) [12]. They offer high safety and ease of transportation. However, in their initial state, the hydrogen absorption and desorption functions are generally poor, and the preparation and use costs are relatively high.

5.1 Development prospects and applications of MOFs

The current research hotspot with industrialization prospects is MgH₂. However, owing to the high energy required of dehydrogenation and low diffusion coefficient, MgH₂ has a dehydrogenation temperature of up to 290 °C, a slow hydrogen release rate, and the tendency for high-temperature agglomeration, limiting its application in the hydrogen energy field. The principle of Mg as an HS material is a reversible reaction, with one unit mass of metal Mg able to store 7.6 wt% hydrogen and one unit volume of Mg able to store 110 g of hydrogen. Catalysts are necessary for the rapid dissociation of H₂. The adsorption principle is shown in the figure, where H₂ molecules are first adsorbed and dissociated into H atoms on the catalyst surface, then diffused into Mg, a process known as heterogeneous catalysis.

Transition metals and rare earth metals are widely recognized for their catalytic activity in dissociating H₂ molecules and making them the most commonly used catalysts in MgH₂ storage material. After decades of research and development, metals such as Ni, Ti, Nb, V, and Fe have proven particularly effective in enhancing the HS capabilities of Mg/MgH₂. Earlier studies, such as those by Zaluska et al. over 20 years ago, investigated catalyst combinations like Pd, Fe, V, Zr, Ti, and Mn, which were found to mitigate surface oxidation effects and improve activation in nanocrystalline Mg for better hydrogen absorption

performance. Recent work by Shang et al. involved ball-milling MgH_2 with metals such as Al, Ti, Fe, Ni, Cu, or Nb, demonstrating that $MgH+Ni$ mixtures exhibited superior hydrogen desorption kinetics and performance [13]. Biao Zou et al. studied the progress of catalysts in the MgH_2 HS system, finding that adding different catalysts could significantly improve the HS performance of MgH_2 . Studies show that these catalysts can effectively reduce the dehydrogenation temperature of MgH_2 , increase HS capacity, and improve hydrogen absorption and desorption rates. By providing more H diffusion channels and catalytic effects, the cyclic performance of the materials is enhanced. In practical applications, Mg-based metal hydrides can be used in Ni-MgH batteries. Compared with other alloy materials, Mg-based alloys have the highest HS capacity. Using Mg_2Ni as the electrode, the highest theoretical capacity is 999 mAh/g [14].

To enhance the capabilities of this HS alloy electrode, methods such as mechanical alloying and alloy component adjustment can be used to enhance the structure and performance of Mg-based HS alloys. In summary, using efficient catalysts such as monometallic and their compounds is crucial for improving the HS performance of MgH_2 , significantly enhancing the HS capacity of Mg materials.

5.2 Ti-Based HS materials

Titanium metal has a high mass HS capacity (3.78 wt %) and a fast hydrogen absorption rate. However, the dehydrogenation temperature of Ti hydrides is relatively high. Therefore, Ti-based HS materials need to be combined with other metal elements to form alloys, such as Ti-Fe, Ti-Zr, Ti-Mn, Ti-Cr-Mn, and others. Ti-based HS alloys mainly include AB-type (Ti-Fe) and AB_2 -type (Ti-Mn, Ti-Ni, etc.) alloys. Taking the well-studied intermetallic compound Ti-Fe as an example, its theoretical HS density reaches 1.86% (mass fraction), and the equilibrium hydrogen pressure at room temperature is 0.3 MPa. Wang Liming et al. added rare earth elements to Ti-V-based alloys, significantly improving the thermodynamics, cyclic stability, and anti-poisoning properties of hydrogen absorption and desorption while reducing the oxygen content in the material and enhancing its activation characteristics.

5.3 Other metal hydride HS materials

In addition to the commonly used Mg-based and Ti-based HS materials, there are other types of metal hydrides, including rare earth metal hydrides and metal-nonmetal coordination hydrides. A typical representative of rare earth HS materials is A-type HS materials, which absorb 1.4% hydrogen (hydrogen-to-metal ratio $H/M=1$) to form hydrides. Current research on A-type HS materials mainly focuses on optimizing components and adjusting stoichiometric ratios. Studies have shown that Pr, Nd, and Co significantly improve alloy capacity. However, due to their high cost, recent research has focused on finding efficient and cheap alternative elements for Pr, Nd, and Co alloys. In coordination hydrides, hydrogen combines with metals/non-metals through covalent bonds to form complex anions, which then combine with metal ions through ionic bonds to form hydrides. Generally, coordination hydrides can be represented by the formula, where A is usually an element from the first or second main group of the periodic table, and Me is usually B, Al, or N. Currently studied coordination hydrides mainly include aluminum hydrides, borohydrides, and amides, with theoretical HS capacities ranging from 5.5% to 21% (mass fraction). Typical products include $NaAlH_4$, $LiBH_4$, and $Mg(NH_2)_2$. Unlike metal hydrides, coordination hydrides undergo a transition to ionic and covalent compounds during hydrogen absorption and can release hydrogen through hydrolysis and thermal decomposition. They have high theoretical HS densities but face significant issues such as poor thermodynamic performance, complex

reactions, and poor reversibility. The actual HS capacity differs significantly from the theoretical value, and related technologies are mostly still in the experimental stage.

6 Conclusion

Hydrogen energy, as a new and popular energy source, holds great development potential in the future. Countries worldwide are continuously increasing their research and development efforts in hydrogen energy. HS technology, as a crucial aspect of hydrogen energy application, is of great significance for achieving a low-carbon economy and utilizing renewable energy. This review provides an overview of existing HS technologies and materials. It is evident that different types of HS methods have their advantages and disadvantages and differ significantly in terms of technical maturity, energy density, and application prospects.

High-pressure gaseous HS technology is widely used due to its maturity and cost-effectiveness, though it suffers from low storage density and poses leakage and safety risks. In contrast, cryogenic liquid hydrogen storage offers significantly higher volumetric storage density but is hindered by high costs and technical complexity, limiting its scalability. SHS materials, including carbon-based materials, MOFs, and metal hydrides, show considerable potential for enhancing storage density and safety. However, further research is necessary to improve their hydrogen absorption and desorption efficiency, stability, and cost control.

For carbon-based HS materials such as activated carbon, graphene, and carbon nanotubes, optimizing pore structure and surface chemistry could lead to significant improvements in hydrogen adsorption performance. However, in practical applications, these materials have yet to achieve ideal HS capacity levels. Enhancements through material modification and composite technologies are necessary to boost performance further.

Metal hydride HS materials, especially those based on magnesium and titanium, are prominent in research due to their high HS density and safety features. Magnesium-based materials can significantly enhance HS performance with the aid of catalysts, but the challenge of high-temperature dehydrogenation remains unresolved. Titanium-based materials, improved through alloying and the addition of rare earth elements, show enhanced hydrogen absorption, desorption characteristics, and cyclic stability. Future advancements can be achieved by optimizing components and structural design to further improve HS efficiency.

The future of HS technology development will focus on increasing HS density, reducing costs, and enhancing safety. Widespread adoption of hydrogen energy will require collaborative innovation in materials science, chemistry, and energy storage technologies. Despite existing challenges, ongoing research and development in HS technologies promise substantial contributions to the hydrogen economy and the broader goal of sustainable energy solutions.

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