

Analysis and Prospect of Key Technologies of Hydrogen Energy Storage and Transportation

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Abstract: Combined with various physical objects, this paper introduces in detail the development status of various key technologies of hydrogen energy storage and transportation in the field of hydrogen energy development in China and the application status of relevant equipment, mainly including key technologies of hydrogen energy storage and transportation such as gaseous hydrogen, liquid hydrogen, solid material hydrogen storage and organic liquid hydrogen storage, as well as pipeline transportation technology after natural gas hydrogen mixing. The related hydrogen storage materials and their main related equipment are introduced in detail, and the specific advantages and main disadvantages of various hydrogen storage and transportation technologies and equipment are described in detail. Finally, it is analyzed and pointed out in detail that liquid and solid hydrogen storage has the advantages of high density, safety and convenient transportation. With the popularization and application of hydrogen fuel cell technology, hydrogen energy is expected to be widely used in the field of transportation; Hydrogen doped natural gas pipeline transportation is the inevitable development trend of large-scale and large-area regional radiation application of hydrogen energy, and the relevant technologies and standards still need to be further improved; Finally, the development direction of hydrogen energy storage and transportation technology and key equipment in the future, as well as the key points and suggestions of feasibility technology research are clarified.

Keywords: Hydrogen Storage Equipment, Hydrogen Storage Technology, Hydrogen Blending of Natural Gas, Hydrogen Storage Materials, Hydrogen Storage in Solid Materials

1. Introduction

In recent years, with the rapid development of global economy and the sharp rise of energy consumption, the reserves of traditional fossil energy dominated by oil, natural gas and coal have decreased sharply, and the problems of greenhouse effect and environmental pollution have become increasingly serious. It is urgent for countries all over the world to develop and utilize new alternative energy with clean, low-carbon and sustainable development. Among them, hydrogen energy, as a high-quality renewable clean energy carrier, has the advantages of clean, zero carbon, no pollution, high energy storage density (142kj/g), wide sources and diverse application forms. It is rated as the "most ideal new energy in the 21st century" and has broad application prospects [1, 2].

However, in order to realize the large-scale and

commercial application of hydrogen energy, there are still a series of key technical problems to be solved. Among them, the development of safe, efficient, economical and convenient storage and transportation technology is an important premise for the wide application of hydrogen energy. Under normal temperature and pressure, the density of hydrogen is very low (only 1/14 of the air), the energy storage density per unit volume is low, flammable and explosive, etc., which makes it difficult to transport and store hydrogen energy safely and efficiently [3, 4].

At present, according to different existing forms, hydrogen energy storage and transportation technologies are mainly divided into: gas hydrogen (GH₂) storage and transportation, liquid hydrogen (LH₂) storage and transportation, solid hydrogen (SH₂) storage and transportation, organic liquid hydrogen (LOHC) storage and transportation and natural gas hydrogen mixing pipeline

transportation, which have different characteristics and adaptability. This paper systematically analyzes the characteristics and research status of various key technologies of hydrogen energy storage and transportation, summarizes the advantages and disadvantages of existing technologies and the bottleneck problems, and looks forward to the development direction of key technologies of hydrogen energy storage and transportation.

2. Key Technologies of Hydrogen Energy Storage and Transportation

2.1. High Pressure Gas Hydrogen Storage and Transportation

Under normal temperature and pressure, the density of hydrogen is low (about 0.0899g/L), and its unit volume energy density is also very low. Therefore, in order to improve the energy storage density of gas hydrogen, reduce the transportation cost and improve the transportation efficiency, the high-pressure gas hydrogen (GH₂) storage and transportation is usually carried out by pressurizing the hydrogen, compressing the volume and storing it in a special container [5-6]. According to different hydrogen storage pressure, it can be divided into low-pressure gas hydrogen storage and transportation (< 35MPa) and high-pressure gas hydrogen storage and transportation (≥ 35 MPa).

The development of high-pressure gas hydrogen storage and transportation technology is the most mature. It is the most common and direct hydrogen energy storage and transportation mode used in industry at present. The required hydrogen can be released conveniently and quickly by connecting the pressure reducing valve. High pressure gas hydrogen storage and transportation has the advantages of low operation cost, mature compressed hydrogen technology, simple pressure vessel structure, low energy consumption, fast hydrogen charging and discharging response, etc. At the same time, its disadvantages are also more prominent: first, although the unit volume energy density of high-pressure hydrogen is increased after compression, the hydrogen storage density is still very low. According to statistics, the hydrogen storage weight in high-pressure hydrogen storage bottle accounts for about 1% ~ 2%, and the hydrogen storage capacity is small; Secondly, the compression of high-pressure hydrogen needs to consume other energy, resulting in energy consumption; Finally, high-pressure hydrogen storage requires high performance of pressure vessel materials, which need to have strong safe pressure bearing and leakage prevention capacity. Hydrogen storage cylinders generally have wall thickness and self weight [7, 8]. Therefore, the technology has poor economy and is only suitable for occasions with scattered users and short transportation distance (transportation radius of 200 km).

At present, large-scale high-pressure gas hydrogen transportation usually adopts two methods: container bottle and long tube Trailer (as shown in Figure 1), and the hydrogen storage capacity is about 5 ~ 10kg/bottle and 250 ~

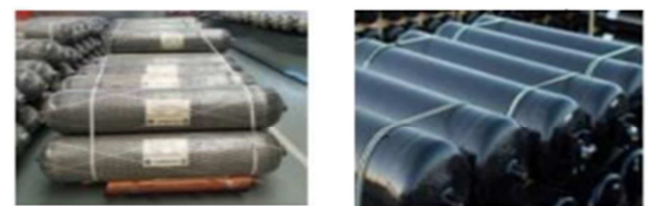
500kg/vehicle respectively. Container bottles are suitable for occasions with narrow site and small usage, such as laboratories and small factories. Long tube trailers are suitable for occasions with wide site and large usage, such as hydrogenation stations. Among them, the storage and transportation cost of container bottles is about twice that of long tube trailers. Long tube trailers are most commonly used in China, and the nominal working pressure of gas cylinders is 10 ~ 30MPa. The hydrogen storage container for fuel cell vehicle usually adopts metal lined filament wound hydrogen storage bottle (type III) and plastic liner fully wound cylinder (type IV), as shown in Figure 2. Type IV bottle is a fully wound bottle with plastic lining, which can reduce weight, but high-pressure gas is easy to penetrate outward from the non-metallic lining, and the connection strength between metal valve seat and non-metallic structure is difficult to ensure. There have been many type IV bottle explosion accidents in China. Therefore, type III bottle is mainly used in the domestic on-board system. Type III bottle is usually made of forged aluminum alloy as the inner liner and coated with carbon fiber, Hydrogen storage pressure is mainly 35MPa and 70MPa [9]. Actively developing light hydrogen storage pressure vessels with higher pressure bearing capacity and combined with hydrogen transportation of natural gas is one of the necessary means for large-scale hydrogen energy and large-area regional radiation.



(a) Container Bottle

(b) Tube Trailer

Figure 1. Container Bottle and Tube Trailer Physical Map.



(a) Type III Bottle

(b) Type IV Bottle

Figure 2. Type III Bottle and Type IV Bottle Physical Map.

2.2. Low Temperature Liquid Hydrogen Storage and Transportation

Due to the extremely low energy density per unit volume of hydrogen at normal temperature and pressure, although the energy storage density of high-pressure hydrogen has been improved after pressurizing and compressing the volume of hydrogen, it is far from meeting the large-scale actual demand. Therefore, in order to further improve the energy storage density, the hydrogen is cooled at low temperature below the liquefaction temperature for storage and transportation in

liquid state, That is, low temperature liquid hydrogen (LH₂) storage and transportation. Liquid hydrogen can be used not only as an intermediate carrier for hydrogen energy storage and transportation, but also as a high-quality low-temperature and high energy liquid fuel. Under standard atmospheric pressure (i.e. 0.1MPa), the boiling point of liquid hydrogen is -253°C and the density is 76.98g/l (856 times that of hydrogen).

Compared with high-pressure gas hydrogen storage and transportation, the hydrogen storage energy density and transportation capacity of low-temperature liquid hydrogen storage and transportation have been greatly improved, which is a very ideal hydrogen energy storage and transportation technology and an important development direction [10-11]. Low temperature liquid hydrogen storage and transportation has the advantages of high hydrogen storage energy density, high transportation efficiency, suitable for long-distance large-scale transportation, small storage volume, direct application as high-quality and high-energy liquid fuel and so on. However, its disadvantages are also obvious: first, the cooling of gas hydrogen to liquid hydrogen consumes a lot of energy and costs a lot. The energy consumed by hydrogen liquefaction reaches more than 30% of its stored hydrogen energy, and the production cost of low-temperature liquefaction process is high; Secondly, the structure of liquid hydrogen storage container is complex and the processing cost is high. Because the boiling point of liquid hydrogen is very low and the temperature difference between liquid hydrogen temperature and external heat transfer is large, the liquid hydrogen storage tank must use vacuum insulation structure and include safety control, sealing and vibration damping devices. The overall system is complex and the processing cost is high; Finally, due to the sensitivity of liquid hydrogen to external high temperature, the gasification loss rate is high, about 1% per day. Therefore, liquid hydrogen is not suitable for intermittent applications such as automobiles, but its high energy density is especially suitable for use as fuel or low-temperature propellant of aviation launch vehicles [12].



(a) Low Temperature Insulated Hydrogen Storage Tank



(b) Liquid Hydrogen Transport Tank

Figure 3. Low Temperature Insulated Hydrogen Storage Tank and Liquid Hydrogen Transport Tank Physical Map.

At present, low-temperature liquid hydrogen storage and transportation usually places liquid hydrogen in highly low-temperature insulated hydrogen storage tank and liquid hydrogen transportation tank (as shown in Figure 3) and transports it by tank car, train and barge. The hydrogen storage capacity is about 40 ~ 65m³/bottle and 300 ~ 600m³/car respectively. In order to reduce the transmission of external heat into the insulated hydrogen storage tank, multiple insulation layers are usually installed on the tank wall. The fewer contact points between the insulation layers, the better, so as to reduce the loss caused by heat conduction. However, due to the heat exchange caused by the vibration and impact inside the tank during transportation, the heat is transferred from the outside to the inside of the insulated tank, resulting in the inevitable gasification loss. Some experts also envisage the use of insulated pipeline for liquid hydrogen transportation, but due to the cost and technical reliability, it is still in the research stage.

2.3. Hydrogen Energy Storage and Transportation with Solid Materials

"Solid hydrogen" (SH₂) storage and transportation technology is a method to complete the storage, release and transportation of hydrogen energy by physical adsorption or reversible chemical reaction with solid hydrogen storage materials. Among them, hydrogen storage materials are the key to realize the storage and transportation of solid hydrogen. It is necessary to make the hydrogen be adsorbed / released efficiently or react with fully and reversibly. According to different hydrogen storage principles of solid materials, solid hydrogen storage and transportation can be mainly divided into physical adsorption (carbon material adsorption) hydrogen storage, metal (or alloy) hydride hydrogen storage and other solid hydrogen storage, which is an important research direction of hydrogen energy storage and transportation in the future [13-14].

Physical adsorption (carbonaceous material adsorption) hydrogen storage is the use of material adsorption for hydrogen storage. The adsorption mechanisms used in industrial production usually include temperature swing adsorption, pressure swing adsorption, volumetric agent replacement and so on. Due to the excellent characteristics of

strong anti-toxic performance, high hydrogen absorption / desorption efficiency and large amount, safety, reliability and recyclability, carbonaceous materials, as a new hydrogen storage matrix, have attracted more and more attention, mainly including carbonaceous hydrogen storage materials such as activated carbon, carbon fiber and carbon nanotube [15-16]. Activated carbon materials can be divided into high specific surface area activated carbon and super activated carbon. They have the advantages of large adsorption capacity, acid resistance, alkali resistance, good chemical stability and long cycle life. However, the hydrogen storage density is low and the storage process needs to be kept in a low temperature environment, which increases the cost relatively. The surface of carbon fiber material is usually molecular fine pores, and its interior is a hollow tube with a diameter of about 10 nm. It has a large specific surface area and is integrated into carbon nanofibers with fish bone like special structure. A large amount of hydrogen can be condensed and released in carbon nanofibers, with high hydrogen storage capacity (up to 1.9wt%), but it needs to be stored in high-pressure environment, and the hydrogen storage density needs to be improved [17]. Carbon nanotube is the adsorption material with the largest hydrogen storage capacity, and its hydrogen storage capacity can reach 10.0wt%. However, the formation mechanism of carbon nanotube is complex, and the preparation technology is not mature. Further research is needed to improve the hydrogen storage capacity and large-scale production. Therefore, carbonaceous hydrogen storage materials need to strengthen the research on hydrogen absorption / desorption and corresponding catalytic mechanism, and look for carbonaceous materials with larger hydrogen storage capacity and lower price.

Metal (or alloy) hydride hydrogen storage technology is to store hydrogen by reacting metal or alloy with hydrogen at a certain reaction temperature and pressure, and release hydrogen when reverse reaction occurs. The positive reaction absorbs hydrogen and releases heat, and the reverse reaction releases hydrogen and absorbs heat. Metal alloy hydrogen storage materials are mainly divided into four series: rare earth system (AB₅ type), magnesium system (A₂B type), zirconium system (AB₂ type) and titanium system (AB type). Due to different hydrogen storage capacity, hydrogen absorption and desorption rate and hydride generation heat, four kinds of metal alloy hydrogen storage materials are suitable for different occasions [18-19]. Different from high-pressure gaseous hydrogen storage and low-temperature liquid hydrogen storage, metal hydride hydrogen storage has the advantages of low hydrogen storage pressure, light weight, easy to carry, good reversible circulation, no pollution and high safety. As a solid-state hydrogen storage technology, it has a good application prospect in vehicle and ship power systems. However, with the increase of the number of reversible cycle reactions, the metal alloy is easy to pulverize, and the thermal conductivity of the powder becomes poor. In addition, the high price limits the large-scale application of this technology. Therefore, the main research direction in this field is to modify the metal alloy and actively develop

materials with large hydrogen storage capacity, low cost and strong recyclability.

In addition, other solid-state hydrogen storage technologies also include coordination hydride and hydrogen hydrate hydrogen storage. However, due to its harsh reaction conditions, complex hydrogen absorption / desorption process and high cost, it is still in the experimental research stage, and there is still a certain gap from industrial application [20].

Solid material hydrogen storage technology has developed rapidly in recent years. It has the advantages of large hydrogen storage capacity (hydrogen storage density per unit volume can reach 40 ~ 50kg/m³), low hydrogen storage pressure, high safety, no pollution, high transportation efficiency, easy transportation, reusable and so on. However, the mass hydrogen storage density is only 1 ~ 3%, which requires high performance of hydrogen storage materials. In order to realize large-scale hydrogen storage and transportation, it is necessary to improve the performance of hydrogen storage materials and continue to carry out research and development of new materials, so as to improve the mass hydrogen storage density, reduce material cost and improve recyclability. Compared with gas hydrogen and liquid hydrogen, solid hydrogen storage and transportation modes are more abundant and diverse. Solid hydrogen storage tanks can be transported by various means of transportation (as shown in Figure 4), and the transportation process is safe and reliable.



(a) Solid Hydrogen Storage Tank



(b) Hydrogen Storage Alloy Powder

Figure 4. Solid Hydrogen Storage Tank and Hydrogen Storage Alloy Powder Physical Map.

2.4. Storage and Transportation of Organic Liquid Hydrogen

Organic liquid hydrogen (LOHC) storage and transportation technology is a method to realize hydrogen energy storage by reversible reaction (hydrogenation and dehydrogenation reaction) between unsaturated hydrocarbons (such as benzene, toluene, naphthalene, etc.) and corresponding saturated hydrocarbons (such as cyclohexane, methylcyclohexane, tetrahydrogen or decahydronaphthalene, etc.) with hydrogen [21-22]. In this technology, the liquid organic hydrogen energy carrier is firstly used for catalytic hydrogenation and energy storage, and then the hydrogenated liquid is transported to each station for distribution. Finally, it is input into the dehydrogenation reaction unit for catalytic dehydrogenation reaction (as shown in figures 5 and 6) to release hydrogen energy. As early as 1975, scholars such as Sultan and Shaw first proposed the idea of using organic liquid compounds as hydrogen storage carriers, and developed the research of organic liquid hydrogen storage technology. In general, the main development track of liquid organic dehydrogenation technology is from gas-phase dehydrogenation to liquid-phase dehydrogenation, and then to multiphase dehydrogenation reaction. At present, typical liquid organic hydrogen storage representative systems include cyclohexane benzene hydrogen storage (CBH) system, methylcyclohexane toluene hydrogen storage (mth) system and decahydronaphthalene naphthalene (DNH) hydrogen storage system [23-24]. Among them, the mass hydrogen storage density and volume hydrogen storage density of CBH are 7.19wt% and 56g/L respectively, and benzene and cyclohexane have similar properties with gasoline, which is convenient for storage and transportation, and can also be recycled. It is an ideal on-board hydrogen storage system.

Compared with other hydrogen storage technologies, liquid organic hydrogen storage has the advantages of low cost of organic liquid, high hydrogen storage density, large hydrogen storage capacity, convenient transportation, high safety, convenient operation and high recyclability. It has good application prospects in many aspects: (1) as a hydrogen source for hydrogen fuel cell vehicles, it only needs to fill cycloalkanes in existing gas stations, Through the hydrogen production by the vehicle mounted dehydrogenation reaction device, the aromatics produced by the reaction can be recycled, which can theoretically achieve the purpose of green environmental protection and efficient utilization; (2) Realize cross seasonal and cross regional energy storage. In case of excess hydrogen energy, hydrogen is stored by aromatics hydrogenation. In case of lack of hydrogen energy, hydrogen is produced by dehydrogenation process. With the current situation of uneven energy distribution and demand in the East and west of China, safe long-distance transportation can be carried out after hydrogenation of organic liquid to solve the problem of uneven energy distribution.

At the same time, there are also problems that restrict the

hydrogen storage of liquid organic hydride: (1) the dehydrogenation reaction efficiency is low, the side reaction leads to the low purity of hydrogen, and the catalyst is easy to coke and inactivate at high temperature and has a short service life; (2) The dehydrogenation reaction temperature is too high to meet the ideal working temperature of fuel cell vehicles, and the requirements of hydrogenation and dehydrogenation devices are high and expensive.

In general, organic liquid hydrogen storage is a promising technology with high hydrogen storage capacity and convenient and safe transportation. It can be transported and filled by using traditional petroleum infrastructure such as hydrogen storage tank cars, tank cars and pipelines, and the transportation process is safe and reliable [25]. At present, the theoretical mass hydrogen storage density of organic liquid hydrogen storage technology is closest to the goal of DOE. Improving the dehydrogenation rate and efficiency of organic liquid hydrogen storage medium at low temperature, catalyst reaction performance, improving reaction conditions and reducing dehydrogenation cost are the key to the development of this technology in the future.

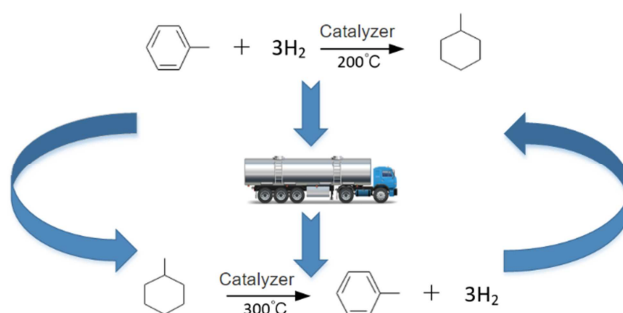


Figure 5. Schematic Diagram of Hydrogen Storage and Discharge System Using Organic Liquid.



Figure 6. Hydrogen Storage Organic Liquid.

3. Natural Gas Hydrogen Mixing Pipeline Transportation

From the perspective of large-scale and long-term development of hydrogen energy, the transportation mode of high-pressure gas hydrogen and low-temperature liquid hydrogen is far from realizing the large-scale and large-area regional radiation of hydrogen energy. Pipeline transportation is an inevitable trend in the future. At present, pure hydrogen pipeline transportation has been applied in some foreign

areas, but this kind of pipeline system is expensive and difficult to meet the needs of the rapid development of hydrogen energy; On the other hand, the constructed natural gas transmission and distribution pipeline network and infrastructure can be used for mixed transmission of natural gas and hydrogen, or pure hydrogen can be transmitted after transformation, which can realize low-cost, large-scale and continuous hydrogen energy supply. Therefore, using the existing mature natural gas pipeline network and supporting equipment to realize the hydrogen mixing transportation of natural gas is the most ideal feasible scheme in the future.

According to the research results, when the content is low, hydrogen can be mixed into natural gas without major technical adjustment. Of course, the infrastructure needs to be evaluated before use. For most parts, it can withstand the proportion of 10% ~ 20% without major transformation [26]. Hydrogen mixed natural gas transportation will mainly cause hydrogen induced corrosion to pipelines and steel equipment, thus reducing the toughness and plasticity of metal materials and inducing cracks, delayed fracture and brittle fracture of metals. Relevant research shows that the key to vigorously develop natural gas hydrogen mixing pipeline transportation technology in the future is to solve the hydrogen mixing compatibility and adaptability of supporting equipment such as pipes, pressure regulating stations, flow meters and detectors, and improve the safety operation guarantee technology of pipe network. At present, natural gas hydrogen mixing pipeline transportation technology is one of the most effective means for large-scale and long-distance hydrogen transportation.

4. Comparative Analysis of Hydrogen Energy Storage and Transportation Technology

At present, hydrogen energy storage and transportation technology can be divided into high-pressure gas hydrogen storage and transportation, low-temperature liquid hydrogen storage and transportation, solid material hydrogen storage and transportation, organic liquid hydrogen storage and transportation and natural gas hydrogen mixing pipeline transportation. By comparing and analyzing the above key technologies of hydrogen energy storage and transportation, high-pressure gas hydrogen storage and transportation has low operation cost, relatively small energy consumption and fast response speed of hydrogen charging and discharging. It is suitable for short-distance and scattered users. It is the most commonly used storage and transportation mode at present, but it has high pressure requirements for equipment, low hydrogen storage density per unit volume and low safety. Low temperature liquid hydrogen storage and transportation has high energy density (the density is about 845 times that of gaseous hydrogen) and high transportation efficiency. It is suitable for medium and long-distance transportation. It is mainly used as propellant fuel of aviation launch vehicle. It has high requirements for vacuum insulation, vibration damping, impact

resistance and leakage prevention of hydrogen storage device, and there is a lot of consumption and high cost in cryogenic liquefaction. Solid hydrogen and organic liquid hydrogen storage and transportation are generally safe, efficient, high hydrogen storage density and good recyclability, but they have high requirements for the performance of hydrogen storage materials, which is an important research direction of hydrogen energy storage and transportation in the future. Natural gas mixed with hydrogen pipeline transportation has low cost and low energy consumption, and can realize continuous, large-scale and long-distance transportation of hydrogen energy. It is an inevitable development trend of large-scale utilization of hydrogen energy in the future.

5. Conclusion

Hydrogen is the gas with the lowest density in nature, which is easy to leak. The energy storage density per unit volume is four orders of magnitude lower than that of gasoline. The conventional way of hydrogen energy storage and transportation has low efficiency and high transportation cost, which restricts the development and utilization of hydrogen energy. Therefore, the development of safe, economic and efficient hydrogen energy storage and transportation technology is the premise to realize the large-scale industrial development of hydrogen energy. It is also the key to realize the low-carbon transformation of the global energy structure.

At present, the main bottleneck of hydrogen energy storage and transportation is the problem of low cost, high energy efficiency, safety and large-scale. In the short term, high-pressure gas hydrogen storage and transportation is still the mainstream, but the hydrogen storage density is low and the compression energy consumption is high. With the large-scale utilization of hydrogen energy, the pipeline transportation of natural gas mixed with hydrogen is an inevitable trend; Low temperature liquid hydrogen storage has high density but high cost, which is mainly used in the field of aviation; Solid hydrogen and organic liquid hydrogen storage and transportation have large hydrogen storage capacity, safety and economy, and great development potential. In the future, with the acceleration of the construction of hydrogenation station, it is suggested to strengthen the technical research on safety detection and certification of hydrogen energy supporting storage and transportation equipment.

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