Discussion on Hydrogen Storage Technology

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Abstract

With the increasing shortage of oil and gas resources and people's increasing energy demand and increasingly severe environmental problems, the development, use of efficient, clean, sustainable use of energy has become the primary problem facing human beings in the 21st century. As a clean, safe, efficient and renewable energy source, hydrogen is one of the most economical and effective alternative energy sources for mankind to get rid of the dependence on the "three major energy sources". Hydrogen storage technology, as a bridge from production to utilization of hydrogen, refers to the technology of storing hydrogen in a stable form of energy for convenient use. How to store hydrogen safely and easily is the key to whether hydrogen energy can be widely used in the future.

Keywords

Hydrogen storage technology, High-pressure gaseous, Low-temperature liquid, Metal hydride, physical adsorption, Coordination hydrides.

1. Introduction

In the face of the increasingly depleted earth's resources, a new type of alternative energy is on the horizon. Hydrogen energy is an efficient and clean energy source. With the development of hydrogen and the expansion of production plant scale, the amount of compressed gas transported in different places is increasing. But how to store and transport large quantities of hydrogen to meet industrial and commercial needs is a difficult problem in the world. Research has been carried out in many countries around the world. From metal hydrides to nano-carbon materials, countries are looking for ways to increase the amount of hydrogen stored per unit volume in order to achieve continuous use. This also involves the study of hydrogen storage materials. How to achieve safety and portability is also the key to whether hydrogen energy can be widely used in the future[1].

Hydrogen is a gas at room temperature and pressure, and its density is only 1/14 that of air. At the same time, hydrogen is flammable and explosive gas. When the hydrogen concentration is 4.1% ~ 74.2%, it will explode when exposed to fire. Therefore, safety must be considered when evaluating the advantages and disadvantages of hydrogen storage technology. The use of a technology must also take into account factors such as economy, energy consumption and life cycle. Generally, hydrogen storage can be divided into high-pressure gaseous hydrogen storage, low-temperature liquid hydrogen storage, hydrogen storage by metal hydride, physical adsorption hydrogen storage material and coordination hydrides store hydrogen[2].

2. High-pressure gaseous hydrogen storage technology

High-pressure gaseous hydrogen storage technology is to compress hydrogen under high pressure and store it in high-density gaseous form. It has the characteristics of low cost, low energy consumption, easy dehydrogenation and wide working conditions, and is the most mature and commonly used hydrogen storage technology. However, the hydrogen storage density of this technology is greatly affected by the pressure, which is also limited by the tank material. Therefore, the research focus is on the improvement of tank material. ZUTTEL et al. found that the mass density of hydrogen increased with the increase of pressure, which increased rapidly at 30 ~ 40 MPa, but changed little when the pressure was greater than 70 MPa. Therefore, the working pressure of the storage tank should be between 35 and 70 MPa. At present, high pressure hydrogen storage tank mainly includes metal storage tank, metal lined fiber wound storage tank and fully composite lightweight fiber wound storage tank.

The metal storage tank is made of metal materials with good performance (such as steel). Due to its pressure resistance, the storage pressure of early cylinders was 12 ~ 15 MPa and the mass density of hydrogen was lower than 1.6%. In recent years, by increasing the tank thickness, hydrogen storage pressure can be increased to a certain extent, but the tank capacity will be reduced. The maximum capacity at 70 MPa is only 300 L, and the hydrogen mass is low. For mobile hydrogen storage systems, transportation costs will increase. As the storage tank is made of high strength seamless steel pipe, the sensitivity to hydrogen embrittlement increases with the increase of material strength, and the risk of failure increases. At the same time, because the metal hydrogen storage cylinder is a single layer structure, the safety status of the container cannot be monitored online. Therefore, this kind of storage tank is only suitable for the fixed and small amount of hydrogen storage, far from meeting the requirements of vehicle system.

In 1940, americans discovered that some fibrous materials (such as phenolic resins) were light, strong, modular, fatigue resistant, and stable, and used them to make airplane metal parts. With the development of hydrogen energy and the increasing requirement of hydrogen storage technology on the carrying capacity of containers, zheng jinyang et al. creatively designed a kind of metal lined fiber wound storage tank. It is made of stainless steel or aluminum alloy with metal lining, which is used to seal hydrogen. The pressure of hydrogen storage can reach 40 MPa by using the fiber reinforced layer as the pressure layer. Because there is no pressure, the thickness of the metal lining is thinner, greatly reducing the tank quality. At present, the commonly used fiber reinforced layer materials are high-strength glass fiber, carbon fiber, kevlar fiber, etc. The winding scheme mainly includes laminate theory and grid theory. The use of multi-layer structure can not only prevent the internal metal layer from being eroded, but also form a closed space between the layers, so as to realize on-line monitoring of the safe state of storage tank.

In order to further reduce the quality of storage tank, people used plastic with certain stiffness instead of metal to make a full composite lightweight fiber wound storage tank. The cylinder body of this kind of storage tank generally includes 3 layers of plastic liner, fiber reinforced layer and protective layer. The plastic liner not only keeps the tank shape, but also doubles as a filament winding mold. At the same time, the impact toughness of the plastic liner is better than that of the metal liner. Because the quality of the fully composite lightweight filament wound storage tank is lower, about 50% of the same storage cylinder, it is more competitive in on-board hydrogen storage system. The new lightweight pressure resistant hydrogen storage container made of carbon fiber composite materials newly launched by Toyota is a fully composite lightweight fiber wound storage tank, with a storage pressure of up to 70 MPa, a mass density of hydrogen of 5.7%, a volume of 122.4 L and a total hydrogen storage capacity of 5 kg. At the same time, in order to further lighten the storage tank, three optimal winding methods are proposed: strengthening the loop winding of the cylinder, strengthening the high-angle spiral winding of the edge and strengthening the low-angle spiral winding of the bottom, which can reduce the number of winding cycles and reduce the amount of fiber by 40%.

At present, all countries are vigorously developing full composite lightweight fiber wound storage tank, however, the real commercial countries are only Japan and Norway. In general, the fully composite lightweight fiber wound storage tank is superior to the metal storage tank and the metal lined fiber wound storage tank in terms of economy and efficiency. However, in the process of research and development and commercialization, it still mainly faces the following technical problems: (2) connection and sealing of the plastic liner and the metal interface; How to further improve the hydrogen storage pressure and mass density of hydrogen storage tank; How to further reduce the tank quality[3].

3. Low-temperature liquid hydrogen storage technology

Low temperature liquid hydrogen storage is to cool pure hydrogen to -253℃, so that it is liquefied and stored. Liquid hydrogen storage has a high volume energy density. At room temperature and pressure, the density of liquid hydrogen is 845 times that of gaseous hydrogen, and its volume energy density is several times higher than that of compressed storage. The high-pressure hydrogen density of 70MPa is 39.062kg/m3, and the density of liquid hydrogen is 70kg/m3, so the hydrogen storage density of liquefied hydrogen is higher. However, the cost of hydrogen liquefaction is high, generally 1kg of hydrogen liquefaction requires 17kWh of power. In addition, liquid hydrogen storage containers must use special containers used for ultra-low temperature, which also leads to high cost of liquefied hydrogen storage.

This hydrogen storage method is light and compact, with mass and volume hydrogen storage rates of 5% (wt) and 37g/L, respectively. The liquid hydrogen storage process is particularly suitable for vehicles with limited storage space, such as rocket engines for space shuttles, automobile engines, and intercontinental flight vehicles. If only from the mass and volume, liquid hydrogen storage is an ideal way of hydrogen storage. However, as hydrogen liquefaction consumes a large amount of cooling energy, it takes 4 ~ 10kWh of electricity to liquefy 1kg of hydrogen, which increases the cost of hydrogen storage and hydrogen use. In addition, the storage container of liquid hydrogen must use special containers used at low temperature. The storage cost of liquid hydrogen is expensive and the safety technology is also complicated because of the high evaporation loss caused by the imperfect charge and insulation of liquid hydrogen storage. Highly adiabatic hydrogen storage vessels are the focus of current research.

4. Hydrogen storage by metal hydride

Such materials have the property that when exposed to hydrogen at a certain temperature and pressure, they can absorb large amounts of hydrogen to form metal hydrides. Under the condition of heating, the metal hydride releases hydrogen, which can be effectively stored by this characteristic. The hydrogen in metal hydride is stored in the alloy in atomic state, and when it is released again, it experiences diffusion, phase change and combination. These processes are restricted by the thermal effect and speed, so metal hydrides are safer to store hydrogen than liquid and high-pressure hydrogen, and have a high storage capacity. However, the defects of metal hydride lie in its low mass hydrogen storage rate, poor anti-impurity gas poisoning ability, and performance degradation after repeated absorption and release. There is still a long way to go to meet the hydrogen requirements of fuel cell vehicles (high reversible hydrogen capacity, high cost performance, long life).

5. Physical adsorption hydrogen storage material

Adsorption hydrogen storage is a new method of hydrogen storage. Because of its safety, reliability and high storage efficiency, it develops rapidly. The methods of hydrogen adsorption and storage can be divided into physical adsorption and chemical adsorption. The materials used mainly include molecular sieve, activated carbon with high specific surface area and new adsorbent. Due to its advantages of moderate pressure, light weight of storage container and wide choice of shape, it has attracted wide attention. However, at present, the hydrogen storage mechanism, structure control and chemical modification still need further research and breakthrough, and the synthesis cost is high.

6. Coordination hydrides store hydrogen

Coordination hydrides mainly refer to the hydrides formed by coordination of alkali metals or alkaline earth metals with the third main group elements and hydrogen, such as NaBH4, KBH4, LiBH4, etc. Compared with the hydrogen storage alloy, the main difference between the absorption and release reaction of coordination hydrides under non-hydrolytic conditions is that there is no reversible hydrogenation reaction of coordination hydrides under normal conditions, so the application of coordination hydrides in "reversible" hydrogen storage is limited. However, if the appropriate catalyst is used and the appropriate catalytic conditions are selected, it is possible to realize the reverse reaction of the reaction under relatively mild conditions. Although the reaction conditions are somewhat harsh, this chemical "reversible" hydrogen storage and drainage undoubtedly opens a new way for efficient hydrogen storage and drainage of coordination hydrides.

7. Conclusion

In order to realize the wide application of hydrogen energy, the key is to develop efficient, low-cost and low-energy hydrogen storage technology. At present, the commonly used hydrogen storage technology includes physical hydrogen storage, chemical hydrogen storage and other hydrogen storage. The physical hydrogen storage cost is lower, the hydrogen release is easier, the hydrogen concentration is higher, but the storage condition is more demanding, the security is poorer, and the storage tank material requirements are higher. Chemical hydrogen storage is achieved by generating stable compounds. Although it is safe, it is difficult to release hydrogen and obtain hydrogen with high purity. Although the problem of low safety of physical hydrogen storage can be avoided to some extent in other hydrogen storage, it also has the problems of difficult chemical hydrogen storage and displacing, low hydrogen storage density and relatively high cost. Hydrogen storage by hydrate method is characterized by easy dehydrogenation, low cost and low energy consumption, but its hydrogen storage density is low.

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