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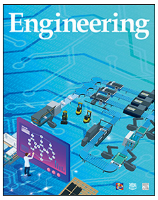

Views & Comments

Expediting the Innovation and Application of Solid Hydrogen Storage Technology

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1. Introduction

Hydrogen energy can be stored and transported, which is not only one of its advantages, but also the main bottleneck in its application. Solid hydrogen storage provides an important means of storing hydrogen energy with high density and safety. First, this method can greatly improve the hydrogen storage density. Among the three existing hydrogen storage methods, namely, high-pressure compression, liquefaction, and solidification, solid-state hydrogen storage has the highest volumetric hydrogen storage density. For example, the volumetric hydrogen storage density of MgH_2 can reach 106 kg H_2 per cubic meter, which is 1191 times higher than that of standard hydrogen density, 2.7 times higher than that of 70 MPa compression hydrogen, and 1.5 times higher than that of liquid hydrogen. Second, solid-state hydrogen storage can enhance the safety of hydrogen storage and transportation, because it makes it possible to store hydrogen under atmospheric temperature and pressure, with an easy-to-seal storage tank. Even in the emergency case of hydrogen leakage, a solid-state hydrogen storage tank can automatically reduce the flow rate and amount of hydrogen leakage, so as to gain valuable time for taking safety measures.

However, high-pressure compression technology still remains dominant in the storage and transportation of hydrogen energy, and solid-state hydrogen storage technology is limited to small-scale applications in certain specific scenarios. The main reasons are as follows: First, the overall performance of solid hydrogen storage cannot fully meet the requirements of onboard hydrogen storage systems. The gravimetric density of well-developed hydrogen storage materials, such as rare earth series, titanium (Ti) series, and titanium vanadium (TiV) solid solution materials, is relatively low. TiV solid solution materials, which have the greatest reversible hydrogen storage capacity among these materials, have a capacity of only 2.6 wt%. Lightweight and high-capacity hydrogen storage materials, such as complex hydrides, amides, and metallic aminoborane, are still under development. Although these materials have a high gravimetric density (e.g., the capacity of ammonia borane is as high as 19.6 wt%), they also have disadvantages, such as the high temperature, slow speed, and poor cycle life of hydrogen absorption and desorption. Second, the cost of solid hydrogen storage is relatively high, because the technology is mostly in the demonstration application stage. Hydrogen storage materials and systems are still in the laboratory or pilot-scale phase; thus, small manufacturing batches, a low yield of hydrogen storage materials and systems, high processing costs for materials and containers, and high prices for accessories such as valves and pipelines all result in the high cost of a solid hydrogen storage system.

In order to promote the application of solid hydrogen storage in the hydrogen energy market, fully make use of its advantages of high density and safety of hydrogen storage, increase the market shares, and continuously improve this technology in practical application, suggestions and ideas include:

(1) Expanding the market for hydrogen energy applications beyond transportation. More mature technologies should be adopted as soon as possible for specific market segments, and effective measures should be taken to control costs in order to meet specific market requirements, such as those of distributed energy supply systems.

(2) Combining solid hydrogen storage with compression and liquid hydrogen storage in order to develop composite hydrogen storage, such as static compression high-density hydrogen storage integration systems and composite hydrogen slurry using magnesium-based hydrogen storage materials.

(3) Speeding up the development of onboard hydrogen storage systems and related high-capacity materials. A green hydrogen supply chain should be established, the hydrogen supply process should be simplified, and the cost of hydrogen supply should be reduced through the application of low-pressure and high-density onboard hydrogen storage systems in fuel cell vehicles.

2. Expediting the application of mature technologies in stationary hydrogen storage

Mature metal hydrogen storage materials have a low gravimetric density for hydrogen storage, but are very suitable for stationary applications due to their high volumetric density for hydrogen storage, small occupied area, low storage pressure, and high safety. The key to developing the stationary hydrogen storage market lies in identifying market segments, effectively controlling

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costs, and boosting the technical and economic competitiveness of solid hydrogen storage.

In 2012, we developed a solid hydrogen storage system with a hydrogen storage capacity of 40 m^3, which was successfully coupled with a 5 kW fuel cell system to provide a continuous power supply for a communication base station for nearly 17 h. However, the system has not been well promoted after its demonstration, due to a lack of market demand. When the third generation (3G) of mobile telecommunications technology was replaced by 4G in that year, the power consumption of communication base stations decreased significantly, such that lithium-ion batteries could meet the application demand. Moreover, as the cost of lithium-ion batteries dropped rapidly, the price of fuel cells, which were priced as high as 10 000 $CNY{\cdot}kW^{-1}$ in that year, was obviously uncompetitive. In the past two years, with the promotion of 5G, the power consumption of communication base stations has increased, highlighting the advantages of the powerful and long-term power supply of fuel cells. At the same time, fuel cell technology in China has developed rapidly in the last two years, causing the price per kilowatt of fuel cells to drop to 1699 CNY, and rapidly improving the technical and economic competitiveness of fuel cells in the base station power-supply market. A supporting solid hydrogen storage device should be developed synchronously in order to fully meet the technical and economic requirements of a base station communication power supply. If the cost of solid-state hydrogen storage is controlled at about 8000 CNY per kilogram of H_2, the energy storage cost can compete well with that of lithium-ion batteries. Reducing the cost of solid hydrogen storage quickly has become an urgent task in order to accelerate the commercial application of fuel cell backup power-supply systems.

Onsite hydrogen storage that matches the scale of hydrogen production from renewable energy sources is another important arena for the current application of mature solid-state hydrogen storage technologies. The McStore magnesium-based solid-state hydrogen storage system developed by the McPhy Energy S.A. in France has been used in renewable-energy-scale energy storage. We have also developed a 1000 m^3 TiFe solid-state hydrogen storage system, which is expected to be used in the Hebei Guyuan wind power hydrogen production project as a safe and compact onsite hydrogen buffer, providing a 6N (99.9999%) high-purity hydrogen source for high-value utilization. The key point that this solid-state hydrogen storage system can be recognized by the market, is whether the comprehensive cost of the system is competitive in comparison with high-pressure hydrogen storage. Important ways to reduce the cost of a solid-state hydrogen storage system include reducing the cost of hydrogen storage materials and expanding their application scale appropriately.

3. New attempts at composite hydrogen storage

To broaden the application of metal hydrogen storage materials, solid hydrogen storage is combined with high-pressure and liquid hydrogen storage to develop composite hydrogen storage technologies, such as static compression high-density hydrogen storage integrated systems and composite hydrogen slurry using magnesium-based hydrogen storage materials. As these new technologies develop, it is expected that new application fields for solid hydrogen storage can be exploited.

In the process of hydrogen absorption and desorption, hydrogen storage materials exhibit a plateau. When the temperature rises, the plateau pressure increases exponentially. Given this characteristic, a heat-exchange medium can be used to realize the static pressurization of hydrogen—that is, hydrogen storage at a low pressure and low temperature, and hydrogen refueling at a high pressure and high temperature. Moreover, this type of hydrogen storage has a low hydrogen storage pressure, a high hydrogen storage density, and good safety when stored at atmospheric temperature, which can reduce the area occupied by storage tanks and decrease the necessary safety distance between stations. In order to improve the rapid response characteristics of hydrogen desorption in storage tanks, solid-state hydrogen storage and compression hydrogen storage can be appropriately combined, and the rapid response characteristics of a mixed hydrogen storage system can be improved by utilizing the rapid hydrogen desorption characteristics of compression hydrogen storage. Based on this principle, we have successively developed 45 and 90 MPa static compression and high-density hydrogen storage integrated systems.

Magnesium has a high hydrogen storage density but a high hydrogen desorption temperature. As long as the links of high-temperature hydrogenation and dehydrogenation are fixed at the application terminal and hydrogen transport is maintained at atmospheric temperature and pressure, magnesium-based hydrogen storage will be a very good method for high-density and high-safety hydrogen transportation. In order to increase the hydrogen transport capacity of a single vehicle, magnesium-based hydrogen storage materials should be packed in a large tank in order to significantly reduce the weight of the hydrogen transport tanks, and multi-tube bundle reactors should be fixed at the terminals of hydrogenation and application. This method requires magnesium-based hydrogen storage materials to flow. To realize such flow, we have combined magnesium-based hydrogen storage materials with organic hydrogen storage materials to form a hydrogen slurry. In this hydrogen slurry, magnesium-based hydrogen storage material powder and organic liquid are both high-density hydrogen storage media.

In addition, magnesium-based hydrogen storage materials can be used as catalysts for organic liquid hydrogen storage, while organic liquid hydrogen storage materials can be used to improve the heat and mass-transfer characteristics of magnesium-based hydrogen storage materials; thus, these two types of material complement each other. Preliminary experiments have demonstrated that hydrides have a good catalytic effect on hydrogen storage and release in organic liquids, and can replace the original noble metal catalysts. Magnesium-based hydrogen storage materials still have good hydrogen absorption and desorption performance at the gas–solid–liquid three-phase interface. These results prove the feasibility of this idea.

4. High-density onboard hydrogen storage systems for a green hydrogen supply chain

The original intention of hydrogen energy application is to develop "green" hydrogen. We should make full use of the characteristics of green hydrogen, build a green hydrogen supply chain, simplify the hydrogen supply process, and reduce the hydrogen supply cost. The 4 MPa green hydrogen obtained by the electrolysis of water using electricity from renewable energy sources can be directly introduced into a 4 MPa pure hydrogen transmission pipeline and sent to a low-pressure hydrogen refueling station without pressurization. It can then be directly charged into the low-pressure and high-density onboard solid-state hydrogen storage systems of fuel cell vehicles. Low-pressure hydrogenation makes it unnecessary to use a high-pressure compressor or high-pressure storage tank in a high-pressure refueling station, thus significantly reducing the equipment costs of refueling stations, improving the safety and reliability of hydrogenation, and reducing the hydrogenation cost, all of which stem from the application of low-pressure onboard hydrogen storage systems.

We have undertaken a preliminary exploration using TiMn hydrogen storage materials. A low-pressure solid hydrogen storage system loaded on a 9 m fuel cell bus can be refilled fully with 17 kg of hydrogen in 15 min under 5 MPa low-pressure hydrogenation. The hydrogen consumption per 100 km under a full-load bus mode is 4.77 kg, so a hydrogen storage capacity of 17 kg can meet the requirements for driving continuously for more than 300 km with one charge. However, the hydrogen consumption of a fuel cell bus using solid hydrogen storage per 100 km is still 0.2–0.3 kg higher than an equivalent bus using compression hydrogen storage. Reducing the weight of the hydrogen storage system is an urgent task; furthermore, it is particularly urgent to develop hydrogen storage materials with higher capacity. The LiMgBNH material we have developed can absorb 5.3% of hydrogen in 10 min at 150 °C and 8 MPa, and can release 4.1% of hydrogen at 0.1 MPa. The gravimetric density of a hydrogen storage tank using this material is similar to that of a 35 MPa compression hydrogen storage system. An onboard hydrogen storage system using this material, developed by our partner Maximilian Team in Karlsruher Institut für Technologie (KIT) of Germany, was coupled with a high-temperature proton-exchange membrane fuel cell and met the application requirements for fuel cells [1]. Recently, an MXene incompletely etched with hydrofluoric acid, which was developed by Jianglan Shui et al. at Beijing University of Aeronautics and Astronautics, China, showed an unprecedented hydrogen uptake of 8.8 wt% at room temperature and 60 bar H_2 (1 bar = 10^5 Pa). The hydrogen release was controllable by pressure and temperature below 95 °C. The MXene also exhibited a good reversible cycle performance of hydrogenation and dehydrogenation [2]. These researches are exploring a new path for the application of high-capacity hydrogen storage materials.

There is still a long way to go to achieve high-density onboard hydrogen storage systems based on a green hydrogen supply chain. The reliability and economics of high-temperature proton-exchange membrane fuel cells still need to be verified, the performance of high-capacity hydrogen storage materials must be continuously enhanced, and the relevant standards of solid-state hydrogen storage systems require improvement. Once these problems are solved, the situation of the application of hydrogen energy will be changed.

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