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ADVANCED HYDROGEN TRANSPORT AND STORAGE TECHNOLOGIES

The future use of hydrogen to generate electricity, heat homes and businesses, and fuel vehicles will require the creation of a distribution infrastructure of safe and cost-effective transport and storage. Present storage methods are too expensive and will not meet the performance requirements of future applications. Transport technologies will need to be developed based on the production and storage systems that come into use as the hydrogen energy economy evolves.

Different applications will require the development of different types of storage technologies. Utility electricity generation and home and office use will have storage fixed in one location—stationary storage—and size and weight will be less important than energy efficiency and costs of the system. Fueling a vehicle, however, will require hydrogen storage in an “on-board” system—mobile storage—with weight and size similar to the gasoline tank in today’s vehicle. Researchers are working to develop physical and solid-state storage systems that will meet these diverse future application demands.

PHYSICAL STORAGE SYSTEMS

Hydrogen is used today in industrial applications, generally in the form—or state—of compressed gas or cryogenic liquid, referred to as physical storage. Technologies for stationary storage and transport in these physical states are commercially available and currently in use. Mature-stage research is being conducted, primarily focusing on increasing the energy content per unit of volume or weight of hydrogen storage systems.

Hydrogen gas is currently stored at high pressures of 14 to 17 megapascals (MPa). Mobile storage of enough hydrogen gas to provide a range comparable to a gasoline-powered vehicle would require a tank too large and too heavy for practical use. New graphite composite material has the potential for storing hydrogen at pressures up to 41 MPa in much lighter weight tanks. Research on these materials may make it possible for hydrogen gas to be a cost-effective fuel for near-term zero emission vehicles.

MASTER

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One Possible Future Hydrogen Infrastructure

A recently completed study evaluated technologies and economics for alternative near-term systems to distribute hydrogen fuel—in the form of compressed gas—to a potential growth market for zero emission vehicles. In the study's most likely scenario, fleet refueling stations would be supplied by truck with liquid hydrogen from existing plants. As demand increased, small dedicated pipeline systems would be built to provide gaseous hydrogen from new centralized reforming plants. A pipeline serving 80,000 fuel-cell cars—the number of zero emission vehicles projected for Southern California by 2001—could deliver hydrogen gas at about \$13 per gigajoule, the energy equivalent of about \$0.45 per liter (\$1.70 per gallon) of gasoline.

SOLID-STATE STORAGE METHODS

For longer-term hydrogen energy applications, solid-state transport and storage technologies are inherently safer and have the potential to be more efficient than gas or liquid storage. Solid-state technology refers to the chemical or physical binding of hydrogen to a solid material. These technologies are in early stages of development and require research to improve the amount of hydrogen contained in a given volume of material—the volumetric density—or a given weight of material—the gravimetric density. Some of the most promising solid-state technologies are metal hydrides, gas-on-solids adsorption systems, and glass microspheres.

METAL HYDRIDES

Metal hydrides have excellent potential for hydrogen storage because of their high volumetric density, safety, and the ability to deliver pure hydrogen at a constant pressure. There are more than 80 metals in existence that form metal hydrides by absorbing and retaining hydrogen under certain temperature and pressure conditions. These metals release the hydrogen—dehydride—under different conditions.

The volumetric densities and safety of metal hydrides make them suitable for stationary storage, but they are limited for use in vehicles by their low gravimetric density, expressed as hydrogen as a percent of total hydride weight (wt%). Researchers are working to develop hydrides with higher gravimetric densities that can operate under

temperatures and pressures consistent with mobile storage. Some of the more promising hydride technologies are improved metal alloys, high-efficiency metal hydrides, and nonclassical metal hydride complexes.

Improved Metal Alloys—New metal alloys have been developed that offer better hydrogen storage characteristics than single metal hydrides. Hydrogen storage capacities of the alloys vary between 2.5 wt% and 6.2 wt% depending on the composition. Thin film alloys of magnesium-iron-aluminum-nickel-titanium have exhibited improved gravimetric and volumetric energy densities. Efforts are being made to scale up production of these alloys.

High-Efficiency Metal Hydrides—Metal hydrides that dehydride hydrogen at very high temperatures show promise for utility stationary storage because they offer greater storage efficiency at less cost than lower temperature hydrides under development. A stationary system provides alternatives for the high heat requirements of dehydriding that are not available in mobile systems. A phase change material—such as a mixture of salts—can be used to retain hydriding energy as heat of fusion and then return the heat for the dehydriding process. A nickel-coated magnesium hydride material and the salt mixture can be placed in a shell-and-tube heat exchanger to perform this process.

Nonclassical Metal Hydride Complexes—

A new class of materials, known as nonclassical polyhydride metal complexes (PMCs), has recently been developed that may overcome the weight density problem of hydride storage systems. Classical PMCs are known to have relatively high gravimetric densities, but they generally undergo irreversible dihydrogen elimination. In the nonclassical PMCs, hydrogen bonds to the metal while still retaining significant hydrogen-to-hydrogen bonding, allowing a complete release of hydrogen under mild conditions and without high vacuum. This unique activity illustrates the high potential of this type of PMC as a hydrogen storage material.

Carbon nanotubes hold hydrogen on their surface by adsorption and also within the tube structures. This has the potential to significantly increase the amount of hydrogen contained over traditional activated carbon materials. Researchers are currently working with nanotubes ranging from 1 to 100 microns in diameter.

GAS-ON-SOLIDS ADSORPTION

The ability of high-surface-area carbons, when chemically activated, to retain hydrogen on their surfaces is well known. This process is called adsorption and takes place with these materials at relatively high pressures and extremely cold temperatures.

Hydrogen is released from the carbon surfaces at atmospheric pressure and ambient temperature. Currently, microcrystalline activated carbon can store about 4.8 wt% hydrogen at 87°K and 6 MPa of pressure.

The storage capacity of these materials, however, is limited by relatively low volumetric and gravimetric densities, and practical application is restricted by the cryogenic temperatures required and the high cost of the process. Carbon nanotubes and carbon aerogels are two technologies that may increase the potential for this storage medium to become practical and cost-effective in the long-term.

Carbon Nanotubes—A new form of high-surface carbon material—carbon nanotubes, or microscopic carbon tubes—has been synthesized in the laboratory. It has the potential for substantially increasing the volumetric and gravimetric densities of hydrogen-adsorption systems. The nanotubes contain microscopic pores of uniform size that encourage micro-capillary filling by hydrogen condensation. Hydrogen attaches to the carbon surface and also fills the micropores, allowing hydrogen gas to condense into a liquid state at relatively high temperatures. Preliminary results on nanotube-containing samples show storage of 8.4 wt% hydrogen at 82°K and 0.07 MPa hydrogen. Researchers are working to improve the quantity of hydrogen stored at near-ambient temperatures.

0.5–1.5 μm

Glass microspheres become permeable and can be filled with hydrogen gas under pressure at temperatures of 200°C to 400°C. When the temperature is lowered, the gas is confined within the spheres. This form of storage has potential for being a very cost-effective and safe method for bulk transportation and storage of hydrogen.

Carbon Aerogels—Carbon aerogels are a special class of open-cell foams with an ultra-fine cell/pore size, high surface area, and a solid matrix. These materials are usually synthesized from the aqueous polycondensation of resorcinol with formaldehyde, followed by supercritical extraction and pyrolysis—at about 1050°C—in an inert atmosphere.

Synthesized aerogels have a nanocrystalline structure with micropores less than 2 nanometers in diameter located within the interconnected carbon particles. Research on the aerogels has resulted in a hydrogen adsorption of 3.7 wt% at a pressure of 8.3 MPa. Research is directed at optimizing the aerogel structure for maximum hydrogen adsorption over a wide range of temperatures and pressures.

GLASS MICROSPHERES

These glass spherical structures have diameters of 25 to 500 microns and wall thicknesses of approximately 1 micron. At temperatures of 200°C to 400°C, the increased permeability of the glass permits the spheres to be filled by hydrogen under pressure by immersion in high-pressure hydrogen gas. When cooled to ambient temperature, the glass is no longer permeable and the hydrogen is locked into the spheres; subsequent raising of the temperature will release the hydrogen.

Spheres synthesized in the research laboratory are defect-free and have a membrane tensile stress at failure of about 1000 MPa, yielding a burst pressure three times as great as commercially-produced spheres. Research has determined that a small bed of such microspheres can contain hydrogen at about 62 MPa with a hydrogen mass fraction of 10%. In tests, 95% of a microsphere has been filled or released in about 15 minutes at a temperature of 370°C. These microspheres have the potential to be less costly to produce and safer than conventional pressurized gas or cryogenic liquid containers.

CONCLUSION

There are many additional technologies and research projects concerning hydrogen storage. Researchers continue to identify and develop transport and storage technologies for the future hydrogen energy infrastructure. To learn more about hydrogen transport and storage technologies or to inquire about opportunities for your company to be involved in the U.S. Department of Energy's cooperative research programs, please contact:

U.S. DEPARTMENT OF ENERGY

Neil Rossmeyssl,
Hydrogen Program Manager
Telephone: (202) 586-8668
Fax: (202) 586-0784

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