IV.D.5 Glass Microspheres for Hydrogen Storage

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Objectives

- Demonstrate that hydrogen storage in hollow glass microspheres (HGMS) is a viable, safe method for meeting the goals of the DOE.
- Prove that photo-induced hydrogen diffusion results in rapid release of hydrogen on command.
- Optimize the composition of the glass used to produce hollow glass microspheres for hydrogen storage.

Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) System Weight and Volume

(B) System Costs

(D) Durability/Operability

Technical Targets

This project deals with fundamental studies of hydrogen storage in hollow glass microspheres, with enhanced delivery rates by use of photo-induced hydrogen storage. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the DOE 2010 hydrogen storage targets listed in Table 1.

TABLE 1. Progress Toward Meeting Technical Targets for Hydrogen Storage in Hollow Glass Microspheres Coupled with Photo-Induced Hydrogen Diffusion Process

Characteristic	Units	2010 Targets	Alfred Current Status
Gravimetric Capacity	kg H_2/kg system mass	0.060	0.022
Volumetric Capacity	kg H_2/L system	0.045	0.0037
Fuel Purity	% H_2	99.99	unknown
Environmental Health and Safety			Non-toxic Non-explosive

Accomplishments

- Completed construction of all apparatus required for this project.
- Produced doped HGMS.
- Demonstrated photo-enhanced outgassing of hydrogen-loaded HGMS, including on-off switching effect.
- Demonstrated that photo-enhanced effect increases with increasing dopant content.
- Determined hydrogen loss rates from filled microspheres at 0, 25, and 50°C for up to 16 weeks.
- Produced HGMS filled to 0.0037 kg/L (0.022 kg/kg) based on mass of material with hydrogen and outgassed these HGMS using the photo-enhanced process, with a response of ≤1 second for onset of hydrogen release.
- Demonstrated that storage capacity of NiO doped spheres increases with repeated use.

Introduction

Hydrogen is stored and transported as high pressure gas in heavy cylinders or as liquid hydrogen at cryogenic temperatures. These cylinders are dangerous and costly, while use of liquid hydrogen is very capital intensive. Storage of hydrogen in HGMS, which can contain hydrogen at pressures up to at least 69 MPa (10,000 psi) is much safer since the gas is distributed in tiny individual glass microspheres. Hydrogen is retained in the microspheres until needed, when it is released by

exposing the microspheres to intense light of the proper wavelength. Since HGMS are made of non-toxic, inexpensive, and completely recyclable materials, similar to those used in ordinary bottles, this method for storage of hydrogen offers major advantages over competing materials, which are expensive, often toxic, and difficult to produce. Technology for producing HGMS is well established, with a number of current commercial applications.

Results of this project will demonstrate that a working hydrogen storage and delivery device can be produced using the newly discovered phenomenon of photo-induced hydrogen diffusion in glasses. A basic scientific study will provide an understanding of the mechanism(s) underlying photo-enhanced hydrogen diffusion in glasses. This information will be used to optimize the application of photo-enhanced hydrogen diffusion in glasses to a working device. Accomplishment of these goals requires development of the technology necessary to produce HGMS of desired compositions and quality in sufficient quantities to provide proof-of-concept of this storage method and to determine the parameters for filling the HGMS with high pressure hydrogen and their behavior during cycling to high pressures.

Approach

The primary aim of this project is the determination of the storage capacity of HGMS, along with the kinetics of hydrogen filling and outgassing of these spheres. Rates of filling and outgassing are determined using "pressure-volume-temperature" and residual gas analyzers (RGA) designed and constructed at Alfred. This facility allows determination of amounts of gas contained within a set of HGMS and the rates of gas entering and exiting HGMS. Preliminary work involves low pressure hydrogen, with subsequent study of samples filled with high pressure (up to 69 MPa) at Savannah River National Laboratory (SRNL). These studies will provide the density of gas, expressed as kg/L or kg/kg, in the HGMS and will duplicate the operating conditions in automotive applications, allowing determination of the response time of the system for photo and thermally induced hydrogen outgassing.

Achieving a sound scientific understanding of photo-induced hydrogen diffusion in glasses will require study of the parameters affecting this process, including determination of the effects of glass composition on photo-induced hydrogen diffusion in glasses, role of the identity and concentration of dopant in the process, including coupling of their optical absorption with the light source and how that affects the efficiency of the process, and the specific wavelengths of radiation which induce this effect.

Results

We have demonstrated proof-of-concept that it is possible to store large quantities of hydrogen in HGMS and to release this hydrogen on demand by exposure to light in the near infrared spectral region. Specifically, we have produced adequate amounts of HGMS containing desired dopants (NiO, CoO, FeO) and capable of containing at least 10,000 psi (69 MPa) of hydrogen for testing of photo-induced hydrogen diffusion effect, filled these spheres to 5,000 psi (35 MPa), and measured the photo-induced outgassing behavior of these spheres. We have also determined the effect of storage temperature on hydrogen retention in samples for up to 16 weeks. Finally, we have demonstrated the ability to store 2.2 g of hydrogen per kg of HGMS (2.2 wt%) and shown that the storage density is directly proportional to the hydrogen fill pressure, indicating that this value can be at least doubled in near future by filling at 10,000 psi (69 MPa).

Outgassing curves for 5 wt% NiO samples filled to either 13.5 or 5,000 psi are shown in Figure 1. The sample filled at 5,000 psi is approximately one tenth of the size of the one filled to 13.5 psi. The areas under the curves, normalized by the mass of the sample, represent the relative amounts of hydrogen in the samples. By use of a calibration standard, the normalized areas can be converted to wt% of hydrogen. The sample filled to 5,000 psi contains approximately 2.2 wt% hydrogen. When combined with results of earlier studies of samples filled to other pressures, the results show that the storage capacity of these spheres is directly proportional to the fill pressure, indicating that the ultimate storage capacity is limited by the ability to attain higher fill pressures and by the strength of the spheres.

Samples were filled to 35 MPa (5,000 psi) of hydrogen at 400°C at SRNL. Most of the samples exhibit a low rate of failure by crushing during filling or due to the tensile stresses induced after filling due to their internal hydrogen pressure. In one case (sphere diameters exceeding 100 µm for the 1 wt% NiO

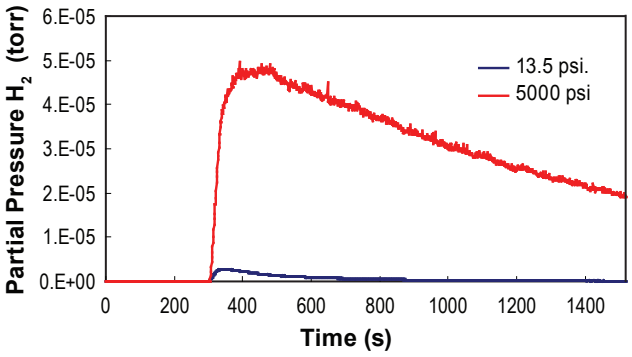

FIGURE 1. Comparison between photo-driven outgassing of hydrogen from doped HGMS filled to 13.5 and 5,000 psi of H_2.

sample), however, a large fraction of the spheres were found to be broken after filling. This sample exhibited "popping" behavior when heated or exposed to light to make the RGA outgassing measurements, as shown in Figure 2. It is believed that the very high ratio of the sphere diameter to wall thickness of the spheres in this sample result in a failure strength very near the internal pressure of the hydrogen. Heating the samples results in expansion of the gas and an increase in the internal pressure, causing the weakest of the unbroken spheres to break and release their gas in tiny bursts, indicated by the spikes on the outgassing curve shown in Figure 2. Once a significant amount of the hydrogen has exited the spheres during outgassing, the popping ceases, or, possibly all of the weaker spheres have already broken, so the popping phenomenon ceases after about 300 seconds of outgassing. The greater strengths of the smaller diameter spheres eliminates the popping behavior (Figure 2). Since the samples used here are the same mass, the relatively low area under the curve for the larger spheres is due to the fact that a large fraction of the spheres in the sample are already broken and have released their hydrogen before the measurement is made. The most gas is stored in the spheres with an intermediate diameter, indicating that there is a tradeoff between strength, which decreases with increasing diameter, and internal volume per gram, which increases with increasing diameter. These findings will be used to optimize the sphere manufacturing process to produce a high yield of the intermediate sized spheres.

When samples of the NiO doped spheres are repeatedly filled at 400°C to 13.5 psi and outgassed, the spheres become much darker in color. A similar effect was noted after only a single fill at 5,000 psi at SRNL of spheres of these compositions. Measurements indicate that these spheres have become magnetic during these treatments, with the magnetic strength of the spheres filled at the lower pressure increasing with repeated filling treatments. Examination of the spheres using a scanning electron microscope reveals that the surface of the spheres is covered with small bumps Figure 3). Additional analysis using X-ray diffraction demonstrates that these effects are the result of the formation of nanocrystals of nickel within the walls of the spheres. Survival of these spheres for the 5,000 psi filling shows that the spheres retain their strength. Photo-induced outgassing measurements show that the response of these spheres to light is accelerated after repeated cycling and that they will contain more hydrogen than untreated spheres (Figure 4). These effects are believed to be due to (a) increased absorption of light, thus improving the response to exposure to the lamp and (b) possibly to additional storage of hydrogen

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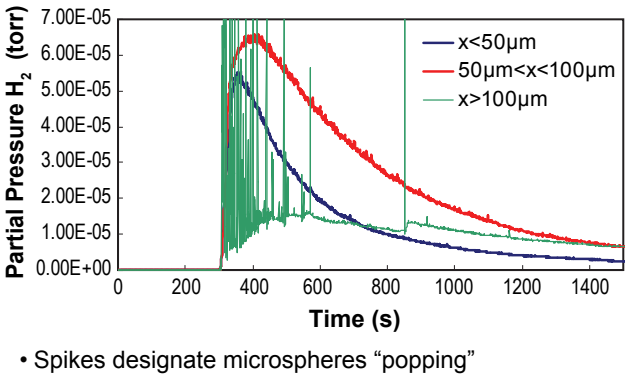

FIGURE 2. Comparison of the effect of sphere diameter on the storage capacity of HGMS. This figure also shows the "popping" of weak spheres during outgassing as a result of the initial increase in internal pressure within the spheres.

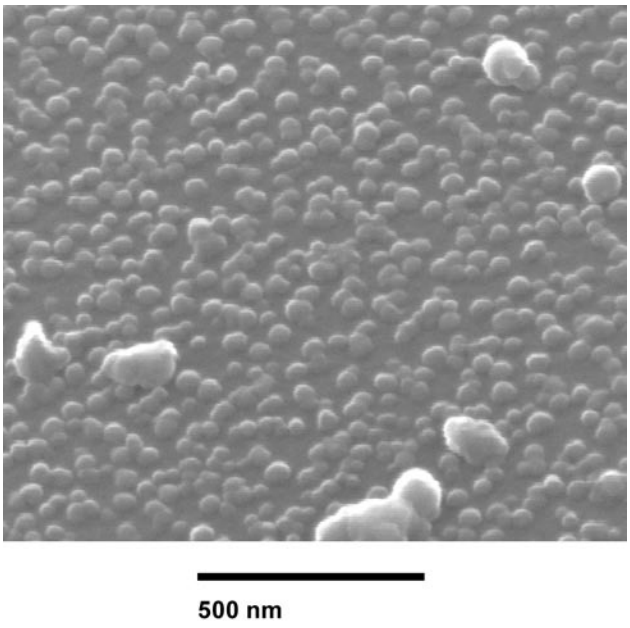

FIGURE 3. Scanning electron micrographs of 5 wt% NiO spheres after repeated filing to 13.5 psi at 400°C. Bumps on surface are due to nickel nanocrystals within the wall of the sphere.

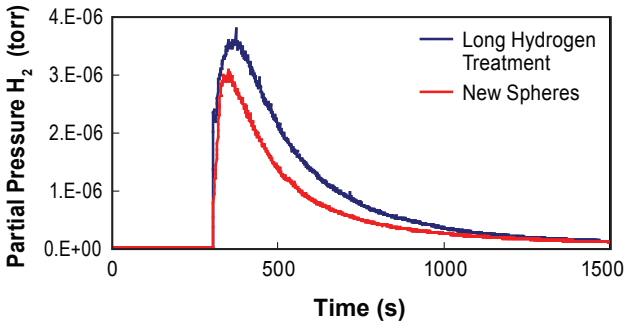

FIGURE 4. Outgassing curves for new spheres which have only been filled at 400°C once with the same sample after a number of filling cycles. The storage capacity of the spheres increases with increasing use.

in the walls of the spheres in the form of NiH. In any case, unlike many other hydrogen storage media, our materials become better with repeated cycling, i.e. their behavior is improved with use.

Studies of the retention time for hydrogen in the HGMS at –20 to 50°C has been performed for times up to 16 weeks. Results are summarized in Table 2. The Co-doped samples have superior retention characteristics. This effect is attributed to the differences in wall thickness and average sphere diameters between NiO and CoO doped HGMS. The greater average wall thickness and smaller average diameters of the Co-doped spheres results in a smaller area to wall thickness ratio, which decreases the permeability of the wall at any given temperature. Loss rates of as little as 0.5% per week have been obtained at room temperature for HGMS doped with 5 wt% CoO.

TABLE 2. Effect of Storage Temperature and Glass Composition on Hydrogen Retention for Samples Stored for 16 Weeks

Storage Conditions	Dopant	% of Original Amount of Hydrogen Retained after 16 Weeks
Freezer	5 wt% NiO	95
Room Temperature	5 wt% NiO	68
Water Bath at 50°C	5 wt% NiO	47
Room Temperature	5 wt% CoO	92
Water Bath at 50°C	5 wt% CoO	67

Conclusions and Future Directions

- Photo-induced hydrogen diffusion from Ni and Co-doped HGMS has been demonstrated; hydrogen release rates have been shown to increase with increasing concentration of these dopants.
- HGMS have been filled to 35 MPa; in some cases, significant fracture occurs, while very little fracture occurs in other samples.
- Repeated cycling of these spheres improves their outgassing response and increases their storage capacity.
- Hydrogen can be stored in HGMS for 16 weeks with loss rates as low as 0.5% of the original amount of hydrogen per week.
- Extend fill pressures to 69 MPa over the next year to double current storage capacity.
- Study changes in processing of HGMS to yield more optimum size distributions.
- Continue study of retention times as a function of temperature to include samples filled to high pressures.

FY 2008 Publications/Presentations

1. M.J. Snyder, P.B. Wachtel, M.M. Hall, & J.E. Shelby, Photo-Induced Hydrogen Diffusion in Cobalt-doped Hollow Glass Microspheres, submitted to Phys. Chem. Glasses: Eur. J. Glass Sci. Technol. B, Nov. 2007.

2. D.E. Day & J.E. Shelby, The Manufacturing and Characterization of Hollow Glass Spheres Designed for Storing Hydrogen, Materials Innovations in an Emerging Hydrogen Economy, Coco Beach, FL, Feb. 26, 2008.

3. P.F. Wachtel, J.E. Shelby, M.M. Hall & M.J. Snyder, High Pressure Hydrogen Storage in Hollow Glass Microspheres, Materials Innovations in an Emerging Hydrogen Economy, Coco Beach, FL, Feb. 26, 2008.

4. P.F. Wachtel & J.E. Shelby, High Pressure Storage of Hydrogen in Hollow Glass Microspheres, GOMD Spring Meeting, Tucson, AZ, May, 2008.