IV.D.4 Glass Microspheres for Hydrogen Storage

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Subcontractor:
Mo-Sci Corp., Rolla, MO

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Objectives

- Demonstrate that hydrogen storage in hollow glass microspheres is a viable, safe method for meeting the DOE storage goals.
- 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 Cost
(D) Durability/Operability

Technical Targets

This project is conducting fundamental studies of hydrogen storage in hollow glass microspheres, with enhanced delivery rates by use of photo-induced hydrogen diffusion. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the following DOE 2007 hydrogen storage targets:

- System gravimetric capacity 0.045 kg H_2/kg of system mass
- System volumetric capacity: 0.036 kg H_2/L of system volume
- Fuel purity: 99.99%
- Environmental health and safety: non-toxic, safe loss of useable H_2

Accomplishments

- Completed construction of all apparatus required for this project.
- Produced doped hollow glass microspheres (HGMS) for initial studies.
- Demonstrated photo-enhanced outgassing of hydrogen loaded HGMS.
- Produced HGMS filled to 0.007 kg/L (0.030 kg/kg) based on mass of material with hydrogen and outgassed these HGMS using the photo-enhanced process, with a response of $\leq$1 second for onset of hydrogen release.

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 hollow glass microspheres, which can contain hydrogen at pressures up to 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 hollow glass microspheres (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 hollow glass microspheres 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 will require 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 kinetics of filling and outgassing HGMS with hydrogen. Rates of filling and outgassing will be determined using "pressure-volume-temperature" (PVT) and residual gas analyzers (RGA) designed and constructed at Alfred. Use of this apparatus will allow determination of rates of gas entering and exiting HGMS. Preliminary work will involve low pressure hydrogen, followed by samples filled with high pressure (up to 10,000 psi) 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

Significant quantities of Co-doped and undoped control HGMS have been produced at Mo-Sci Corp. The base glass consists of 85 wt% recycled amber bottle glass, which contains ≈0.2 wt% iron oxide. Since iron is known to produce a photo-induced hydrogen diffusion effect, the small response found in our current work for the undoped glass has been attributed to the use of amber glass. Samples of the same composition produced using clear, colorless container frit instead of amber glass will be examined in the coming year.

The PVT and RGA systems have been completed. Measurements of photo and thermally driven curves have been made at a variety of temperatures and gas pressures for helium and hydrogen. Results demonstrate that photo-induced outgassing results in a faster response rate than that obtained by application of heat, even though the temperature used in the thermal outgassing process is hundreds of degrees (K) greater than that which results from the application of light. These results are a major step in proving the validity of the concept underlying this project. A typical RGA outgassing curve comparing the photo-induced outgassing curve with one obtained by heating to the same temperature obtained by exposure to light, but using a furnace as an energy source, is shown in Figure 1.

Samples were filled to 1,500 psi of hydrogen at 400°C at SRNL without measurable fracture of the HGMS. Results of photo-induced outgassing using the RGA system are compared with those of a sample filled with only 700 torr of gas in Figure 2. Since the sample filled to 1,500 psi contains so much gas, it was necessary to use only 10% as much of the HGMS as used in the sample filled to the lower pressure in order to keep the RGA signal on scale. Our measurements indicate that the sample filled to 1,500 psi contains approximately 118 times as much hydrogen as that filled to 700 torr, which compares favorably with the theoretical value of 111.

Work at SRNL will continue toward increasing fill pressure. Future work will include filling microspheres with different size distributions, obtained by use of precision sieves to separate the microspheres into known size increments, to determine the pressure limitations as a function of sphere diameter. This information will be used by Mo-Sci Corp to optimize the HGMS production process to yield the desired size for the HGMS.

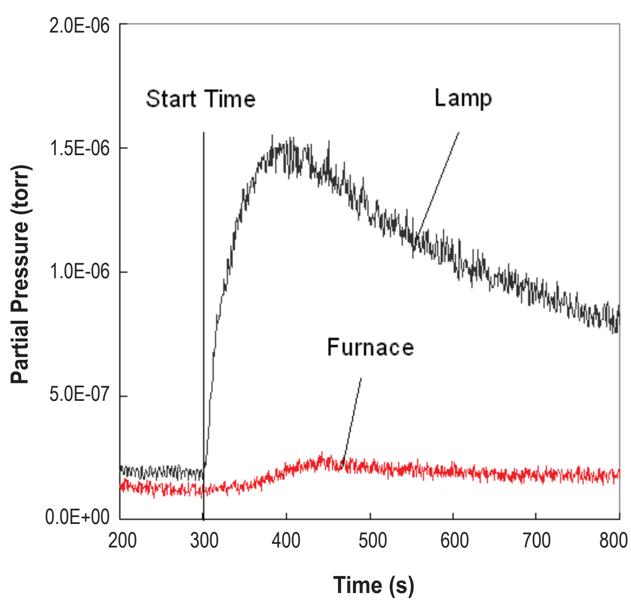

FIGURE 1. Comparison between Photo and Thermally Driven Outgassing of Hydrogen from Cobalt Doped HGMS

The size distribution of the HGMS was determined using an environmental scanning electron microscope (ESEM). Analysis of a large number of micrographs yielded a distribution of sizes of the HGMS for both the Co-doped (Figure 3) and the undoped HGMS.

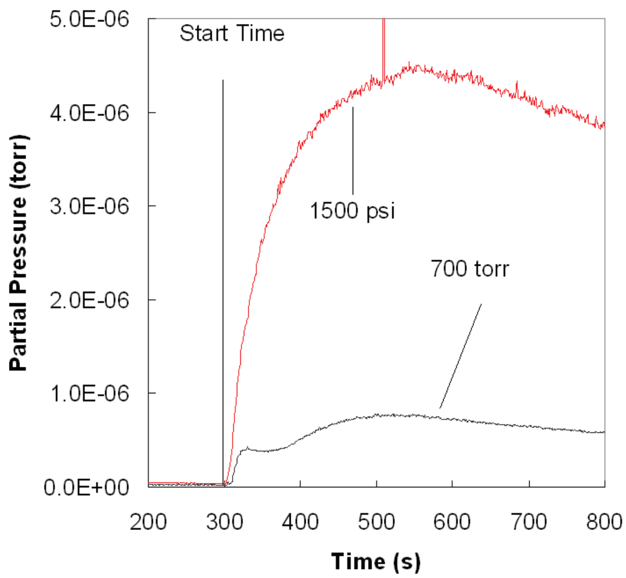

FIGURE 2. Comparison between Photo-Driven Outgassing of Hydrogen from Doped HGMS filled to 1500 psi and 700 torr of H_2, Respectively

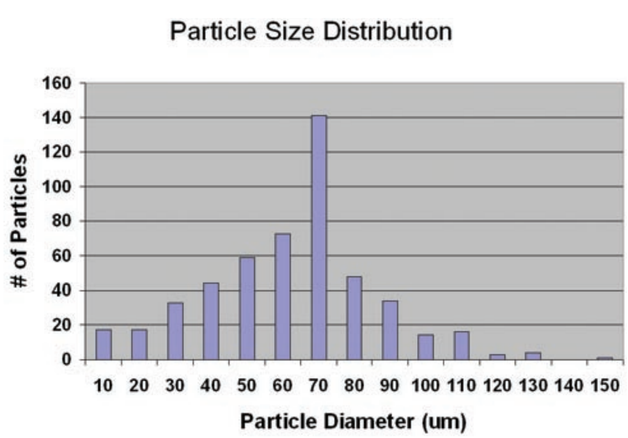

FIGURE 3. Size Distribution of Co-Doped HGMS

Measurements on the bulk glass used to produce the HGMS indicate that the HGMS are capable of withstanding thermal cycling to at least 500°C without degradation. Future work will include study of the chemical durability of these glasses under a variety of environmental conditions.

Study of the retention time for hydrogen in the HGMS at -20 to 50°C has begun. Preliminary results for samples stored in ambient conditions in the laboratory indicate that less than 10% of the gas is lost in 30 days. This study will be continued over the next year to define the needed storage conditions for filled spheres.

Conclusions and Future Directions

- Photo-induced hydrogen diffusion from Co-doped HGMS has been demonstrated.
- HGMS have been filled to 1,500 psi (7 gm/L) without significant loss of spheres by fracture.
- Preliminary tests indicate that hydrogen can be stored in HGMS for at least a month with little loss of pressure at ambient temperatures.
- Fill pressures will be extended to as much as 10,000 psi over the next year.
- Study of new doped compositions of HGMS will continue.
- A detailed study of retention times as a function of temperature will be carried out.

FY 2006 Publications/Presentations

1. J. E. Shelby and M. M. Hall, "Separation, Purification, and Storage of Hydrogen in Hollow Glass Microspheres, GOMD meeting of Am. Ceramic Soc., Greenville, SC, May, 2006.