IV.D.4 Glass Microspheres for Hydrogen Storage

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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 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 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 I.

TABLE 1. Progress Toward Meeting Technical Targets for Hydrogen Storage in Hollow Glass Microspheres Coupled with the 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 hollow glass microspheres (HGMS).
- Demonstrated the photo-enhanced outgassing of hydrogen loaded HGMS, including on-off switching.
- Demonstrated that the photo-enhanced effect increases with increasing dopant content.
- Measured hydrogen loss from filled microspheres at room temperature.
- 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.

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 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 HGMS, along with the kinetics of hydrogen filling and outgassing of these spheres. Rates of filling and outgassing are determined using "pressure-volume-temperature" (PVT) and residual gas analyzers (RGAs) 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

Significant quantities of HGMS doped with 0, 1, or 5 wt% CoO have been produced at Mo-Sci Corp. The base glass (0 wt% dopant) 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. Limited study of samples of the same composition produced using clear, colorless container frit instead of amber glass support this hypothesis in that almost no detectable amount of hydrogen is released during exposure to near-infrared light from these spheres.

Measurements of photo and thermally driven curves have been made at a large number of temperatures and hydrogen pressures. As was shown in the previous report, results demonstrate that photo-induced outgassing results in a much faster response than that obtained by application of heat, even though the temperature used in the thermal outgassing process is approximately 150 to 250 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. The effect of dopant concentration for CoO on RGA outgassing response of HGMS is shown in Figure 1. Data are collected for 300 seconds before the lamp is turned on to establish the instrument background. The response is much faster for the samples containing 5 wt% CoO than for those containing only 1 wt% CoO, while the response for the undoped (amber) samples is not detectable on this scale.

Samples were filled to 10.35 MPa (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 10.35 MPa contains so much gas, it was necessary to reduce the sample size by a factor of nine as compared to the sample filled to the lower pressure in order to keep the RGA signal on scale. The high pressure sample contains approximately 118

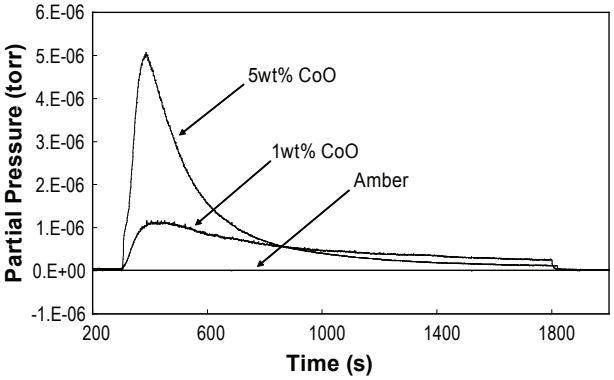

FIGURE 1. Comparison between Photo-Induced Outgassing Curves for Samples Containing Varying Concentrations of CoO as a Dopant

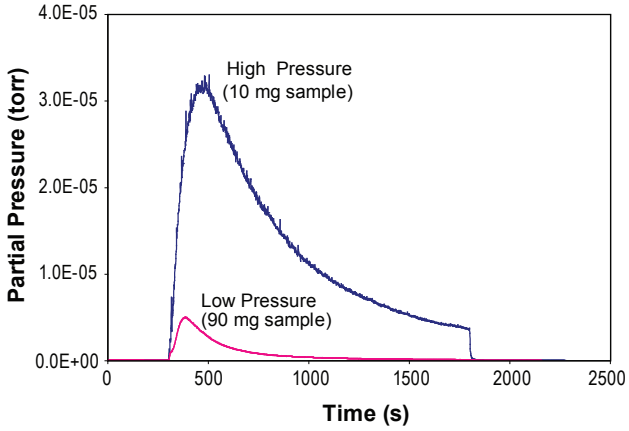

FIGURE 2. Comparison Between Photo-Driven Outgassing of Hydrogen from Doped HGMS Filled to 10.35 MPa and 700 torr of H_2

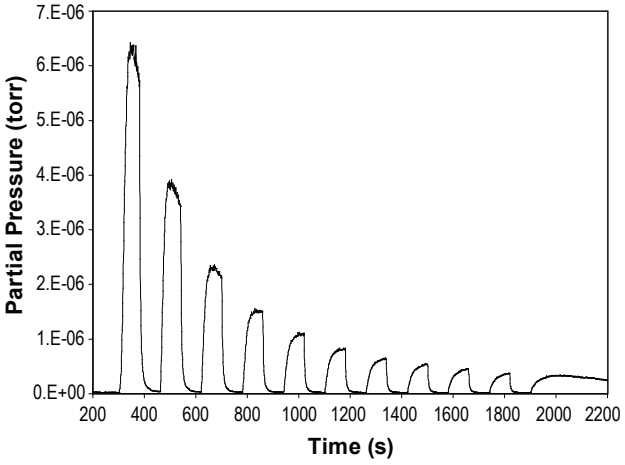

FIGURE 3. Demonstration of "On-Off" Switching Behavior of 5 wt% CoO Doped HGMS Filled to 700 torr of H_2 (The switching interval is 80 seconds.)

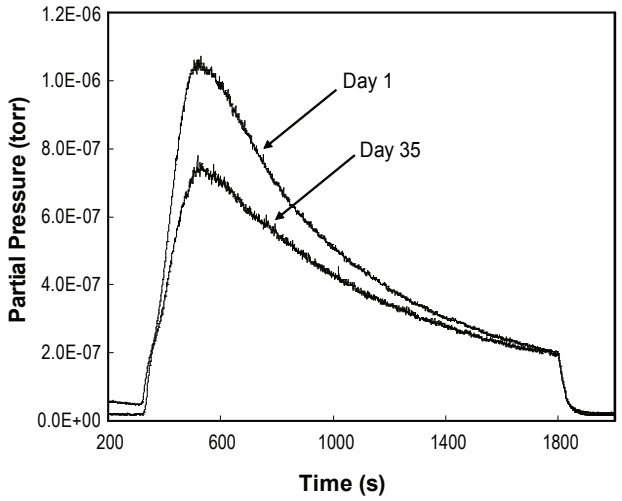

FIGURE 4. Comparison of Outgassing Curves for Identical Samples Measured on the Day of Filling with Hydrogen and After Refilling Under Identical Conditions and Holding for 35 Days at 50°C

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 to at least 69 MPa. 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.

The "on-off" response of the 5 wt% HGMS filled to 700 torr is shown in Figure 3. The overall decay in the signal is due to depletion of the hydrogen from the very small sample as the experiment progresses. The lamp was turned on and off in 80 second intervals. The rapid response to the cycling of the exposure to light on the release of hydrogen from the sample is evident in the sharp increases and decreases in RGA signal following changes in the light source. Similar results were obtained for samples filled to high pressure.

Preliminary study of the retention time for hydrogen in the HGMS at -20 to 50°C has been performed. Initial results for samples stored at 50°C in a water bath indicate that approximately 20% of the gas is lost in 35 days (Figure 4). Losses at lower temperatures are smaller than this value. 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 10.35 MPa 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 69 MPa 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 2007 Publications/Presentations

1. M. J. Snyder, "Hydrogen Storage in Hollow Glass Microspheres," M. S. Thesis, Alfred University, October, 2006.