DOE Hydrogen Program

Glass Microspheres for Hydrogen Storage

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STP27

Overview

Timeline

- April 16, 2005
- June 30, 2008 (Phase I)
- 90% completed

Budget

- Total project funding = $490,017
  - DOE share = $300,000 (FY05-FY08)
  - Contractor share = $190,017
- Funding received in FY 07 = $96,723
- Funding for FY08 = $78,277

Partners

- Alfred University (lead partner)
- Savannah River National Laboratory
- Mo-Sci Corp.

Barriers

- Barriers addressed

  (A) System Weight and Volume

  (B) System Costs

  (D) Durability/Operability

Characteristic	Units	2010 Target	Current Status
Gravimetric	kg H_2/kg	0.060	0.022
Volumetric	kg H_2/l	0.045	0.004
Fuel Purity	% H_2	99.99	Unknown, but at least 99%
Safety			Non-toxic Non-explosive

Objectives

- Demonstrate that hydrogen storage in hollow glass micro-spheres (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 for maximum crush strength (maximize fill pressure) and minimum reaction time for response to changes in light intensity

Milestones

1: Produce several grams of HGMS containing desired dopands (NiO, CoO, FeO) for testing of photo-induced hydrogen diffusion effect and capable of containing at least 10,000 psi (69MPa) of hydrogen: Phase 1 (in progress)

2: Fill HGMS with high pressure hydrogen: Phase 1 (done)

3: Measure kinetics of photo-induced hydrogen release from HGMS: phase 1 (done)

4: Demonstrate ability to store 0.1 kg of hydrogen per kg of HGMS (10 wt% on basis of materials only): Phase 2

5: Determine maximum fill pressure for HGMS: Phase 2

6: Produce a working demonstration unit within 4 years, with assessment of ability to meet goals of DOE program: Phase 2

7: Provide a viable scientific understanding of photo-enhanced diffusion in glasses. Publish results in reviewed journals. Phase 2

Go/No Go Decisions

- **Go/No Go at end of Phase 1** (1 year of funding pending delays in funding):
- Demonstrate ability or a probable path forward to hit the 2007 DOE Gravimetric and Volumetric targets of 4.5wt% H_2 and 0.036 kg H_2/L respectively. (Note: these 2007 DOE targets refer to system targets, but in this case, the Go/No-Go point is referring solely to the material)

- **Go/No Go at end of Phase 2** (2 years of funding pending delays in funding):
- Demonstrate the ability or a probably path forward to hit the 2010 DOE Gravimetric and Volumetric targets of 6wt% H_2 and 0.045 kg H_2/L respectively (for the material rather than the system).
- Determine the energy efficiency of the system compared to a 60% total round-trip energy efficiency per the goal of the DOE Multi-Year Research, Development and Demonstration Plan.
- Demonstrate that the energy content of the hydrogen delivered to the automotive power plant should be greater than 60% of the total energy input to the process, including the input energy of hydrogen and any other fuel streams for generating process heat and electrical energy.

Approach

- Primary goals of this study include determination of the storage capacity of hollow glass microspheres and the demonstration that the kinetics of filling and hydrogen release of hollow glass microspheres can meet the response time demands of automotive applications.

- Rates of filling and release are determined using residual gas analyzers (RGA) and "pressure-volume-temperature" (PVT) facilities designed and constructed at Alfred. These facilities allow determination of amounts of gas contained within a set of HGMS and the rates of gas entering and exiting the HGMS.

- Preliminary work with low pressure (up to one atmosphere) hydrogen will be used to determine glass compositions and the identities and concentrations of dopants which result the photo-induced hydrogen diffusion effect. This information will be used to optimize kinetics of filling and hydrogen release.

- Subsequent studies of samples filled with high pressure (up to 69 MPa) at Savannah River National Laboratory (SRNL) 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 supply rates.

- Achieve a sound scientific understanding of photo-induced hydrogen diffusion in glasses through studies 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.

Why use HGMS for hydrogen storage?

HGMS have a number of outstanding characteristics, as indicated in the figure.

Non-toxic

Mechanically strong

Low cost

Light weight

Reusable

Environmentally friendly

Chemically durable

Commercially available

High hydrogen mass density, 6 to 14 wt%

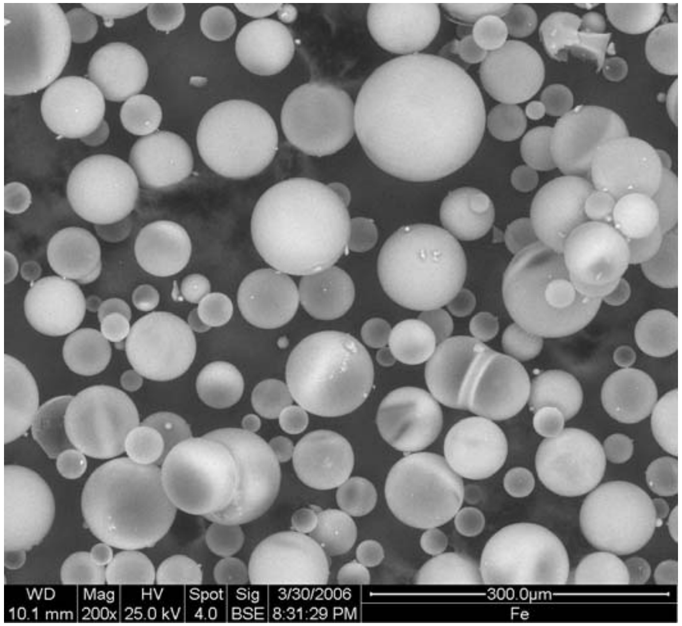
Ultra pure hydrogen

Fire safe—non-explosive

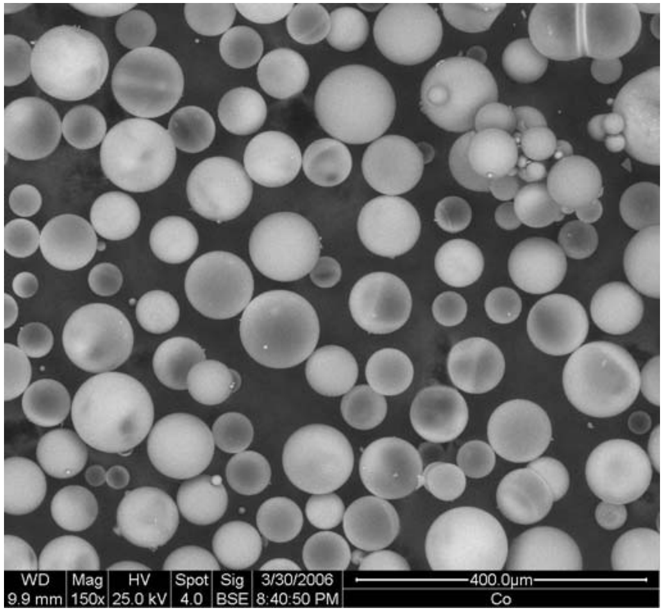
General Data for Hollow Glass Microspheres (HGMS)

Diameter	10 to 200 microns
Wall Thickness	1-10% of diameter (1-8 microns)
Density	0.2 to 0.6 $g \cdot cm^{-3}$
Compressive Strength	200 to 30,000 psi
Composition	Variable (soda lime silica, borosilicate, high silica, *etc.*)

HGMS are spherical. Size distribution is large.



5 wt % FeO

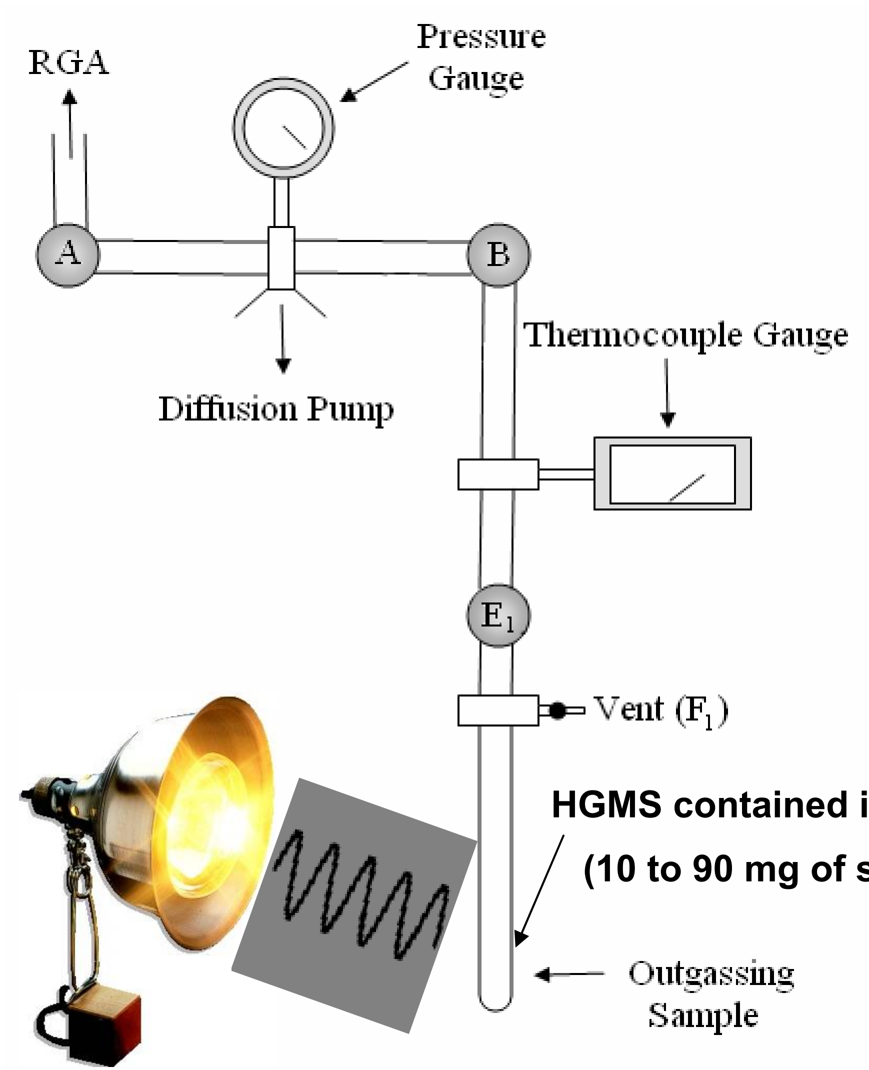


5 wt % CoO

Back scattered image (200X)

- Typical micrographs of microspheres used in this study.
- Note the excellent sphericity of the individual spheres and the range of diameters.

Apparatus used to measure photo-induced hydrogen release from filled HGMS



HGMS contained in 6 mm glass tube

(10 to 90 mg of sample)

Accomplishments

- Demonstrated proof-of-concept that it is possible to store large quantities of hydrogen in hollow glass microspheres and to release this hydrogen on demand by exposure to light in the near infrared spectral region. Specifically, we have achieved the following goals:

- Produced adequate amounts of HGMS containing desired dopants (NiO, CoO, FeO) and capable of containing at least 10,000 psi (69MPa) of hydrogen for testing of photo-induced hydrogen diffusion effect

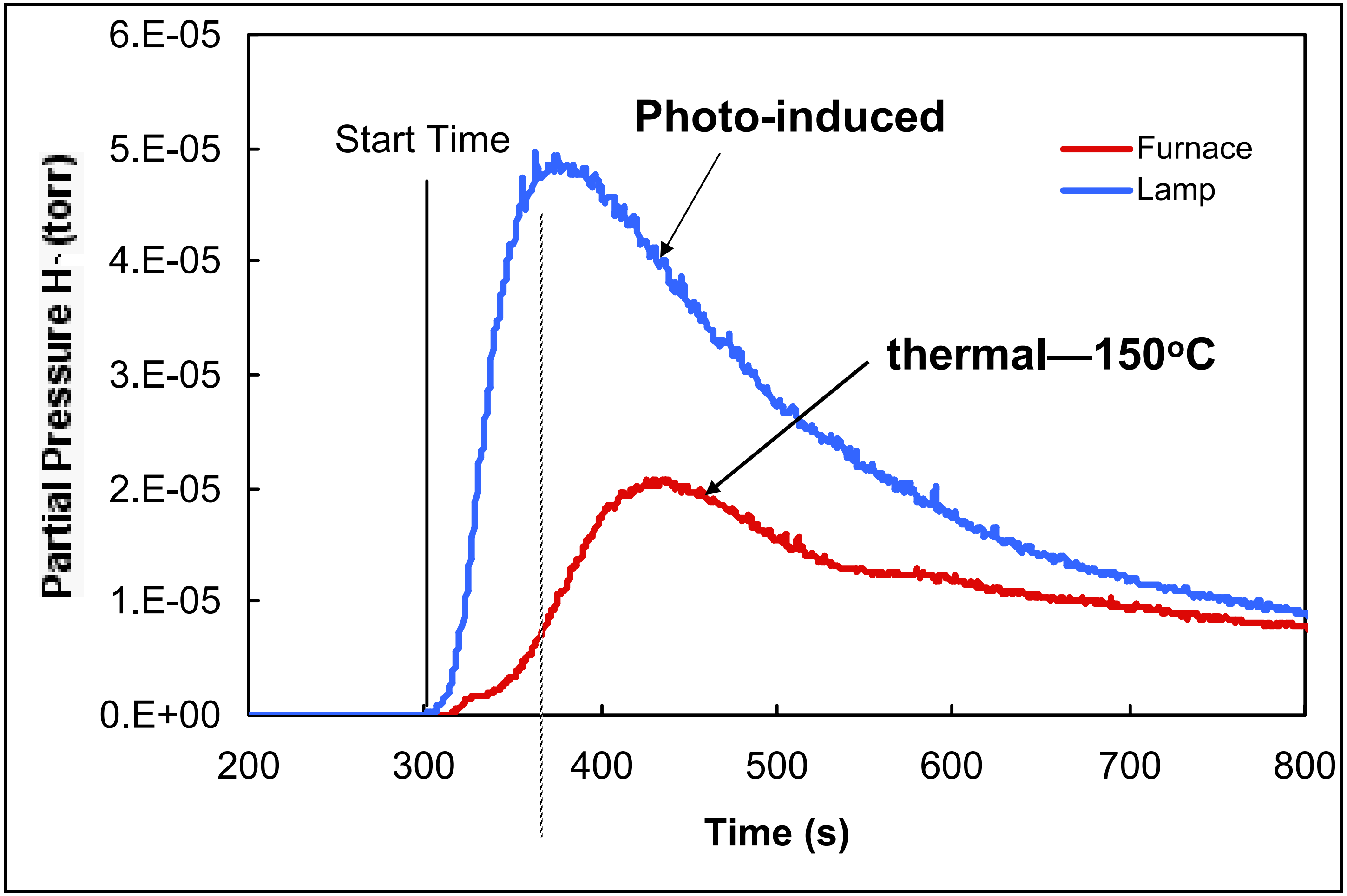
- Filled HGMS with 5,000 psi (35MPa) of hydrogen; fill to 10,000 psi (69MPa) in progress

- Measured kinetics of photo-induced hydrogen release from HGMS. Demonstrated fast response to changes in light intensity which allows control of the hydrogen supply rate by controlling the voltage applied to the lamp.

- Determined that wavelength of applied light must be between 1500 and 2300 nm to cause photo-induced hydrogen diffusion.

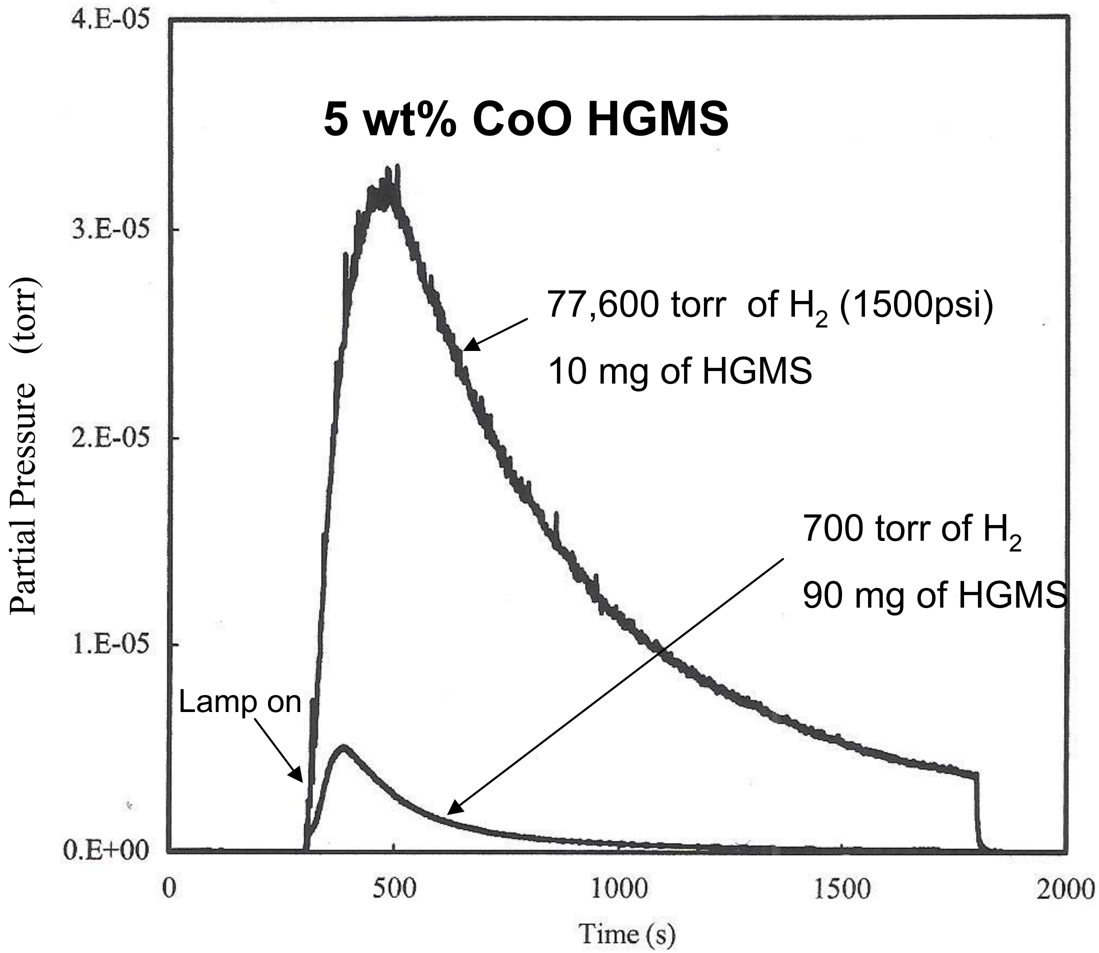
- Demonstrated ability to store 2.2 kg of hydrogen per kg of HGMS (2.2 wt%). Shown that the storage density is directly proportional to the hydrogen fill pressure, indicating that this value can be at least doubled in near future.

Comparison of photo-induced H_2 release curve vs. curve thermally induced by heating at 150°C. The sample is the same for both curves.



- Measurements indicate that samples heat to ≈150°C due to exposure to light.
- Response of photo-induced hydrogen release is much faster than thermally induced hydrogen release at approximately the same temperature.

Dependence of photo-induced hydrogen release curves on hydrogen fill pressure



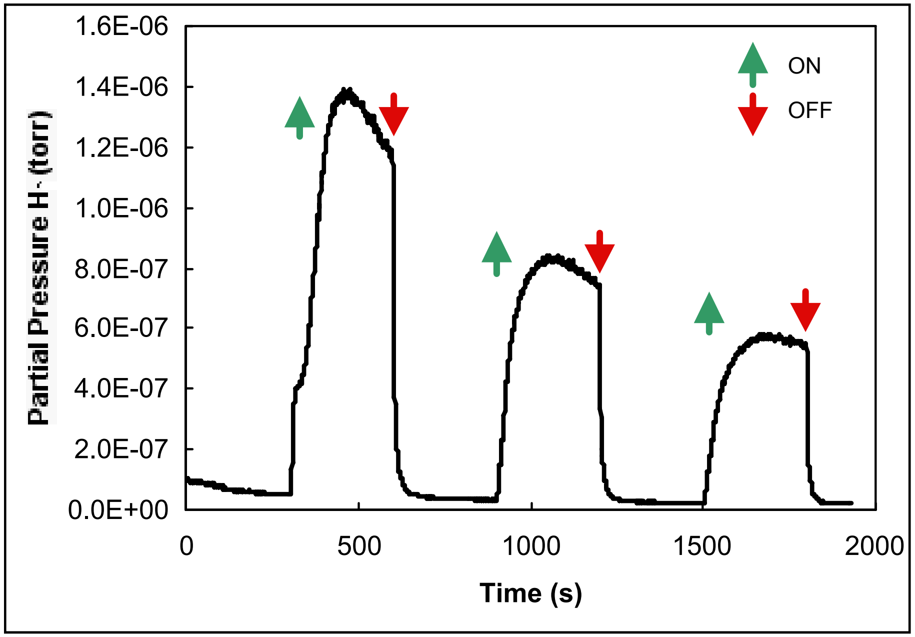
- These are typical hydrogen release curves obtained from hydrogen-loaded HGMS.
- Area under these curves are used to determine the total amount of hydrogen in the sample.
- Normalization by dividing by the sample mass yields the wt% of hydrogen in the sample.

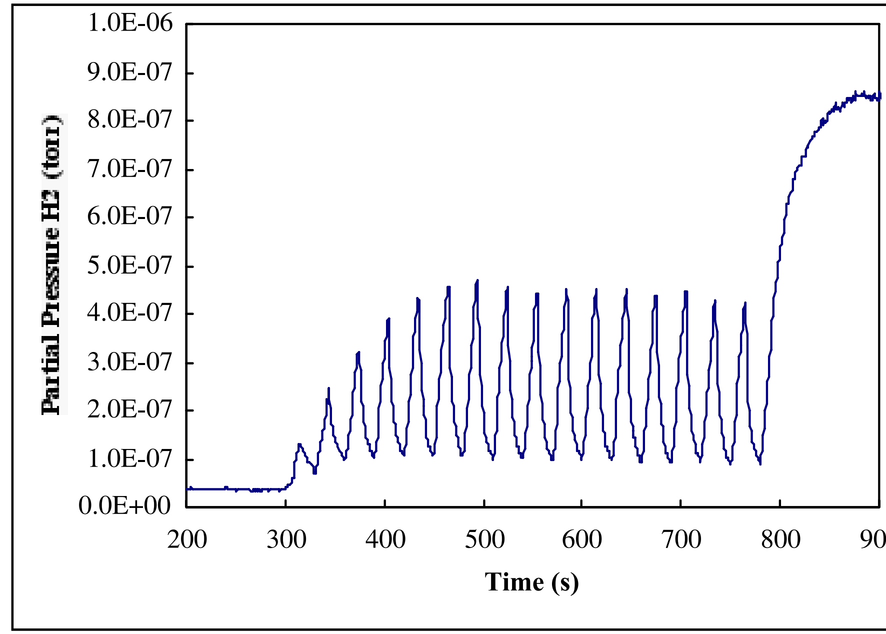
Hydrogen retention during storage

Storage conditions	Dopant	% Retention after 16 weeks
Freezer	5 wt% NiO	95
Room Temperature	5 wt% NiO	68
Room Temperature	5 wt% CoO	92
Water Bath at 50°C	5 wt% NiO	47
Water Bath at 50°C	5 wt% CoO	67

- Hydrogen diffuses out of HGMS over time
- Hydrogen is not lost, but will increase pressure in storage container
- % retention decreases with increasing temperature
- % retention is better for CoO doped HGMS than for NiO doped samples

Switch – like photo-induced H_2 release.

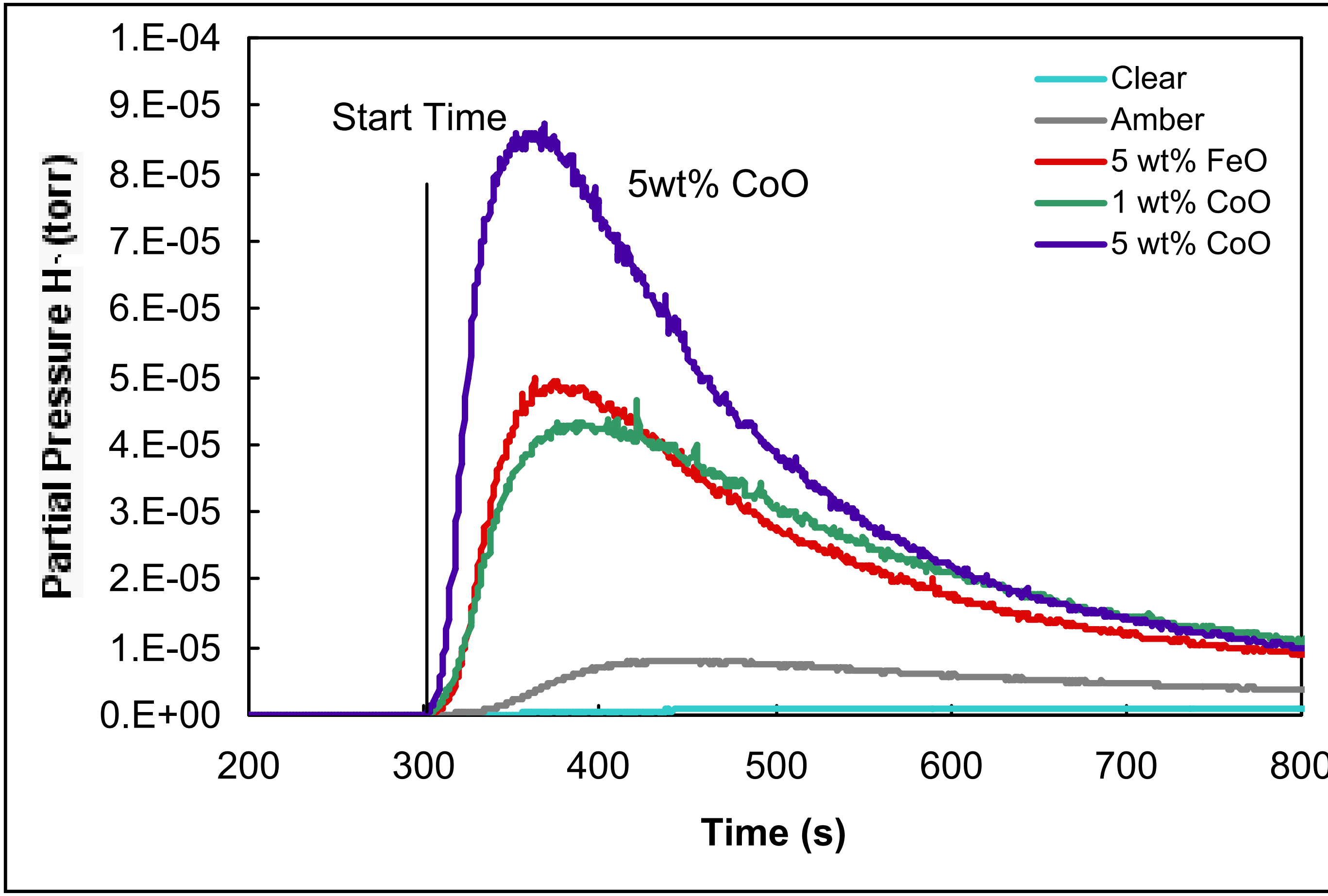




- 5 minutes ON/OFF cycle
- Max release decreases with each cycle due to lower pressure in HGMS as hydrogen is depleted. This is an artifact of the small sample size and does not occur for large samples.

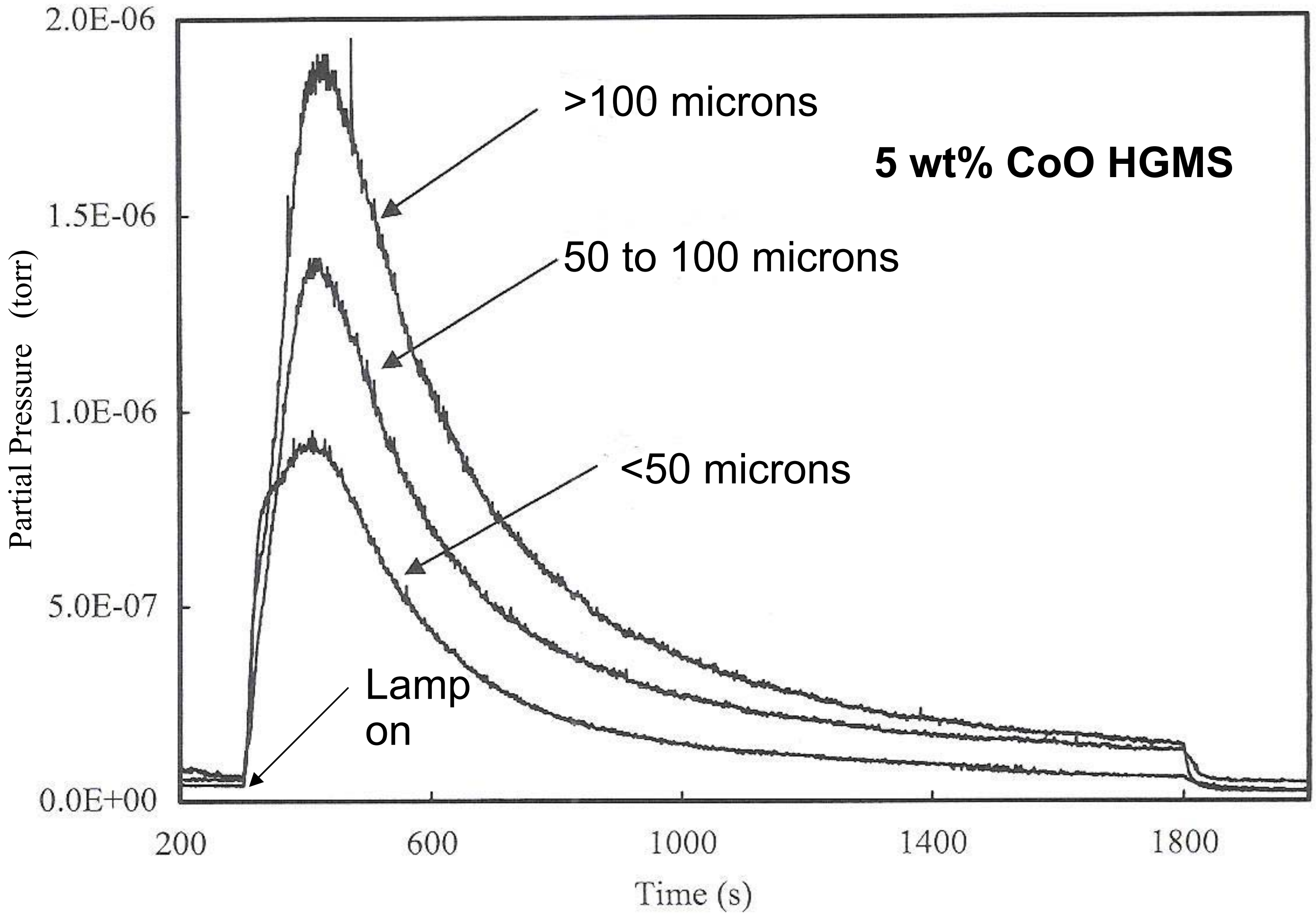
- 15 seconds ON/OFF cycle
- Lamp on full time after 780 seconds
- Response to cycling indicates that excellent control of hydrogen supply rate can be controlled by controlling exposure to light

Effect of Dopant Identity and Concentration on Photo-induced H_2 Release



- Photo-induced effect does not occur for clear (undoped) HGMS. A very small effect occurs for HGMS made from amber glass, which contains about 0.2 wt% FeO.
- CoO is more effective than FeO in photo-induced release.
- Rate of H_2 release increases with increasing concentration of CoO.

Effect of HGMS diameter on photo-induced hydrogen release curves.



- Larger diameter HGMS contain more hydrogen for same fill conditions for same weight of sample.
- Initial response to exposure to light is not affected by sphere diameter.
- Crush strength may decrease as sphere diameter increases, indicating tradeoff between effects.

Future Work

- **FY 08 (Complete Phase 1 of study)**
  - Extend fill pressures to 10,000 psi, which should double the current storage capacity
  - Complete study of effect of time and temperature on shelf-life of filled HGMS
  - Begin study of relation between fill pressure and survival rate of spheres during hydrogen loading
  - Begin study of application of Raman confocal microscopy to study of individual microspheres, e.g. total hydrogen content, wall thickness

- **FY 09 (Begin Phase 2 of study)**
  - Determine maximum fill pressure attainable without excessive crushing losses
  - Improve hydrogen release kinetics by optimizing compositions for base glass
  - Explore possibility of other dopants which would will yield superior hydrogen release kinetics
  - Explore methods for lowering hydrogen fill temperatures to increase storage capacity
  - Determine relation between storage capacity and crush losses

Summary

Relevance: This project will determine if HGMS can actually be used as storage vessels for hydrogen.

Approach: Determine if the discovery of photo-induced hydrogen diffusion in glass with allow the application of HGMS to vehicular applications as hydrogen storage materials. Determine the potential hydrogen storage capacity of HGMS.

Technical Accomplishments: Have shown that the kinetics of hydrogen release on demand from HGMS are extremely fast and readily controlled. Have achieved a storage capacity in excess of 2 wt%, with a near-term goal of extending this value to near 5 wt%.

Technology Transfer/Collaborations: Work closely with SRNL and Mo-Sci Corp. on high pressure studies and development of microsphere production technology, respectively. Increase publications, presentations, and patents.

Proposed Future Work: Continue to increase hydrogen fill pressure through efforts in conjunction with SRNL and Mo-Sci Corp. to lower fill temperature and to produce stronger HGMS.