Final Report: A Radically New Method for Hydrogen Storage in Hollow Glass Microspheres

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1. Executive Summary

The primary goal of this project is to demonstrate that hydrogen gas can be rapidly extracted from hollow glass microspheres (HGMS) using a photo-induced heating effect. The results of the project demonstrate that diffusion of hydrogen is readily induced by exposure to light from an IR lamp in transition metal-doped HGMS filled to as much as 5,000 psi with hydrogen gas, which contain approximately 2.2 wt% hydrogen. Doped HGMS in conjunction with optically induced outgassing provide a solution to the traditional limitation of HGMS – *i.e.*, the slow release of hydrogen from HGMS that are heated using a furnace. This information will also be invaluable in designing process changes for future production of HGMS able to hold higher pressures of hydrogen.

2. Experimental Procedures

2.1. Hollow Glass Microspheres (HGMS)

MoSci Corporation supplied custom-made HGMS for this project. Commercially available amber glass frit was modified to produce HGMS of three varieties: 1) HGMS containing no dopant (Code 1402), 2) HGMS containing 1 mol% NiO (Code 1436), and 3) HGMS containing 5 mol% NiO (Code 1394). The amber glass frit used as a raw material also contains a trace amount of iron oxide (~0.2 wt%) so that all lots of HGMS contain trace amounts of iron.

2.2. Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was performed to find glass transformation temperatures (T_g) of glass frit (*i.e.*, the same frit used to produce the three types of HGMS) provided by MoSci Corp. Samples were placed in an uncovered aluminum pan and heated to ~630°C from room temperature at a heating rate of 20 K/min. The extrapolated onset T_g was obtained and recorded.

2.3. Density

Tap densities of the HGMS were measured using 4-mm-ID 6-mm-OD Pyrex glass tubes. The tubes were flame sealed at one end, while the other end had a flame-polished opening. The empty tubes were weighed, and then reweighed after filling to the desired depth with HGMS. The height of the column of spheres was measured, and the volume of the packed bed was calculated. The mass and packed bed volume of the HGMS was used to calculate tap density. In addition, a helium pycnometer was used to determine the true density of the HGMS; three measurements were performed to determine an average value.

2.4. Scanning Electron Microscopy

Environmental scanning electron microscopy (SEM) was used to examine the shape and size of the HGMS. The spheres were placed as a thin layer on a small round sample holder which was covered with conductive tape. The holder was loaded into the sample chamber, which was then evacuated. A working distance of between 9.6 mm and 10.8 mm was used with a spot size of 4.0 μm and an accelerating potential of 12.5 kV.

ImageJ software was used to obtain particle size measurements. Approximately 500 microsphere diameters were measured for unsieved spheres and 200 diameters for sieved spheres. The maximum, minimum, and mean values of the size distributions were determined.

2.5. Confocal Raman Microscopy

Confocal Raman microscopy was used to measure the diameter and wall thicknesses of the HGMS. A silicon standard was used to optimize the signal gain. HGMS were placed on a microscope slide and first observed under a 10x or 100x objective to measure the sphere diameter. The 100x objective was then focused on or just above the surface of a particular sphere and a Raman scan was done over a 20 μm line distance (used to find the apex of the sphere surface) and a 10 μm depth into the sphere.

2.6. Saturation/Outgassing Experiments

2.6.1. Mass Spectroscopy

The saturation/outgassing method developed by Jewell at Alfred University was used to investigate the storage of hydrogen in HGMS.¹ The initial method used a furnace for outgassing; Rapp and Kenyon extended this technique by using a lamp for photo-induced outgassing.^{2,3}

2.6.2. Sample Preparation

Outgassing samples were prepared by placing ~0.1 g of HGMS in Pyrex tubes (4 mm ID, 6 mm OD) that were flame sealed at one end. A plug of glass wool (~0.1 g) was then inserted into the tube to secure the light weight HGMS during evacuation of the saturation and outgassing systems. Control experiments were performed in which tubes containing only glass wool were exposed to hydrogen and then outgassed; minimal hydrogen was released from the glass wool under furnace heating and no outgassing was observed when the glass wool was illuminated with the lamp.

2.6.3. Saturation of HGMS with Hydrogen

Figure 1 shows a schematic of the system used to fill the HGMS. The filled Pyrex tubes are placed into a larger silica tube and attached to the system. A preheated tube furnace (400°C unless otherwise stated) is raised around the silica tube. Valves A – D are all in the closed position where the vacuum pump is turned on. When the pressure

reaches 100 mtorr, valves B and C are opened very slowly to ensure no damage to the pressure gauge. When the pressure reaches ~30 mtorr, valve D is opened to evacuate the sample chamber. Once the sample chamber reaches the desired temperature, the system is flushed with the gas which will be used to fill the HGMS by quickly opening and closing the valve to the gas bottle. Once the flushing gas is removed, valve B is closed, and the fill gas is slowly introduced to the system to the desired pressure.

Once the filling treatment has been conducted for the desired amount of time, the furnace is lowered, and valve B is opened to evacuate the system. At this point, valve A is opened to vent the system, and a fan is used to blow air onto the silica tube to cool the samples quickly to prevent loss of gas. The samples are now ready to be outgassed.

In addition to the outgassing samples prepared at Alfred University, a limited quantity of HGMS were filled to higher pressures (up to 5,000 psi) by Savannah River National Laboratory. Lower quantities (~10 mg) of the high pressure-filled HGMS were used for outgassing experiments due to the higher quantity of hydrogen that was released.

2.6.4. Outgassing of Hydrogen from HGMS

A residual-gas analyzer (RGA) was used to monitor changes in the partial pressure of gases in a high-vacuum system. The RGA is attached to the vacuum system shown schematically in Figure 2. The system contains a mechanical vacuum pump, a diffusion pump, high-quality steel vacuum plumbing, and an attachment for the sample tubes. Several valves allow for controlled evacuation of the system. Two pressure gauges monitor the system, a less-precise thermocouple pressure gauge for initial evacuation and a sensitive digital pressure gauge for high-precision high vacuum monitoring.

The two pumps, i.e., diffusion and mechanical, are connected to allow the mechanical pump to bypass the diffusion pump. This arrangement allows the initial evacuation or to be performed by the mechanical pump by switching a lever on a three-way valve to the “closed” position. After the roughing, the valve to the mechanical pump is switched to “backing,” and the valve connecting the diffusion pump to the system is put in the “open” position.

Once the sample tube is attached to the system, valves A and F₁ are closed, and valve E₁ is opened while the mechanical pump is in the roughing mode, and the system is pumped down to ~30 mtorr. Then the valve to the diffusion pump is opened, and the system is allowed to pump down to ~ 1 to 2 × 10⁻⁵ torr. Valve A is opened, and the system is pumped down to 4 to 5 × 10⁻⁶ torr. The filament is turned on and heated for 5 minutes. Once the filament is heated and the pressure reaches ~ 1 × 10⁻⁶ torr, the experiment is started. Background data are recorded for 5 minutes before the lamp is turned on, or a preheated furnace is raised around the tube. In photo-outgassing experiments, the lamp, equipped with a Sylvania 250 Watt incandescent infrared bulb, was positioned so that the HGMS were ~2.5 cm away from the center of the bulb. In some experiments, a reflector consisting of a half cylinder of cardboard covered with aluminum foil was placed around the sample tube with the sample tube placed in the center of the reflector tube. At the end of an outgassing experiment, the furnace was lowered, or the lamp was turned off, and the sample tube was allowed to cool to room

temperature. The RGA filament was then turned off, valves A and E were closed, and valve F was opened, allowing the sample tube to vent to air.

2.6.5. Pressure – Volume – Temperature (PVT)

A schematic of the pressure – volume – temperature (PVT) apparatus is shown in Figure 3. Apparatus of this type are thoroughly described by Shelby in “Handbook of Diffusion in Solids and Melts” and have been used by many researchers for related studies.⁴ This version of a PVT system was developed at Alfred for use with HGMS with the ability to both fill and outgas spheres without transporting samples from one system to another. A data logger was used to record the pressure data produced by the system. The system uses a “high pressure” gauge to record changes in pressure during the fill stage and a “low-pressure” gauge to record changes in pressure during the outgassing stage. It is important to note there is a switch between the two gauges which allows the data logger to only record the data created by one pressure gauge at a time. Once the data are collected, the data logger is downloaded to a computer for analysis.

The spheres are prepared similarly to the spheres used with the RGA, but, in this case, a larger, 12-mm-O.D. silica tube is used. Glass wool is placed on top of the HGMS to keep them in place throughout the experiments. The silica tube is then attached to the system, and a preheated furnace is raised around it and used to heat the sample to the desired temperature. All the valves are closed prior to the start of evacuation. Once the valves are closed, the system is evacuated to ~ 60 mtorr. Valves B and G are opened, and the system is pumped down to ~ 100 mtorr, where valve D is opened. Once the system is pumped down to ~ 30 mtorr, valve C is quickly opened and closed to flush the system with the filling gas. The system is now ready for a filling experiment once the vacuum returns to ~ 30 mtorr. Valve C is used to meter the gas into the system slowly to the desired pressure, which is monitored by the high-pressure gauge. Once the gas is in the system, the data logger begins to record data.

After a desired amount of time, the data logger switch is switched to the off position (center), and valves B and E are opened at the same time to evacuate the gas from the system. Once the high-pressure gauge reads ~ 0 torr, valve G is closed, and then valve B is closed when the vacuum gauge reads ~ 300 mtorr. Once valve B is closed, the data logger is switched to the low-pressure gauge. Once the sample has outgassed for the desired time, the data logger switch is turned off. Valves B and G are opened, evacuating the system. Valve E is then closed so that the low-pressure gauge is maintained under vacuum. Valve A is then opened to vent the system, and the furnace is lowered to cool the sample tube. Since all PVT experiments use the same saturation and outgassing temperatures, it is not necessary to remove or change the temperature of the furnace during an experiment.

Figure1. Schematic of fill system

Figure 2. Schematic of outgassing apparatus

Figure 3. Schematic of pressure – volume – temperature apparatus

3. Results and Discussion

3.1. Density

The density of the HGMS provided by MoSci Corp. as measured by helium pycnometry are shown in Table I. The density of the undoped HGMS is the highest of the three samples; the Ni1 HGMS are slightly more dense than the Ni5 HGMS.

Table I. Tap density and true density of HGMS.

HGMS Sample	Tap Density ± 0.01 (g/cm ³)	True Density ± 0.01 (g/cm ³)
Undoped (Code 1402)	0.36	0.43
Ni1 (Code 1436)	0.24	0.28
Ni5 (Code 1394)	0.22	0.23

3.2. Differential Scanning Calorimetry

The T_g 's of Code 1394 and 1402 glasses were measured to be 555°C and 560°C, respectively.

3.3. HGMS Size Distribution and Wall Thickness

3.3.1. Scanning Electron Microscopy

Microsphere particle size distributions were measured using SEM micrographs and ImageJ software; the data are provided in Table II and in Figures 4 and 5. Results for the 5 wt%-doped spheres (1394) measured at Alfred are compared to data provided by MoSci Corp. The undoped amber bottle glass (1402) particle size data are not available (NA) from MoSci. It is also important to note that the particle size of the glass frit used to produce the spheres is ~65µm for both the doped and undoped spheres. A representative SEM micrograph of the HGMS is shown in Figure 6.

3.3.2. Confocal Raman Microscopy

Depth scans performed using confocal Raman microscopy were used to measure the wall thickness of HGMS of known diameter. Figure 7 shows the wall thickness of Ni5 HGMS between approximately 20 to 250 µm in diameter. It can be seen that the wall thickness tends to increase with increasing HGMS diameter; this trend is seen in all of the HGMS types.

Table II. Particle Size Distributions for 1394 and 1402 HGMS.

Particle Size (µm)	Percent of Microspheres in Range			
	1394 Alfred*	1394 MoSci	1402 Alfred*	1402 MoSci
0-40	13.3	4.0	42.3	NA
41-60	20.4	25.0	25.8	NA
61-80	42.5	27.0	18.8	NA
81-100	16.3	25.0	9.1	NA
100-120	5.9	13.0	3.6	NA
121-140	1.4	5.0	0.4	NA
140+	0.2	1.0	0.0	NA
Max	154.9	NA	123.7	NA
Min	2.5	NA	1.3	NA
Mean	61.2	76.9	39.9	NA
Median	64.5	NA	41.1	NA
StDev	27.1	26	25.4	NA

Spheres were sieved into three size fractions, i.e., greater than 100 µm, between 100 µm and 50 µm, and below 50 µm, using Precision Eforming LLC sieves with round openings. Several micrographs were taken of the sieved spheres and analyzed using the same procedures as for the unsieved spheres. Table III lists the particle size values.

Figure 4. Particle size distribution for 5 wt% Ni-doped HGMS (1394).

Figure 5. Particle size distribution for undoped HGMS (1402).

Figure 6. SEM micrograph of unsieved, undoped HGMS (Code 1402).

Figure 7. Wall thickness of Ni5 HGMS as a function of diameter. Solid lines are added as guides to the eye.

Table III. Particle Size Distributions for Sieved Spheres

		Sample ID	
Particle Size (μm)		1394	1402
< 50	Max	44.4	50.0
	Min	16.0	5.7
	Mean	36.8	34.6
	Median	40.0	36.1
	StDev	7.9	12.1
50 < x < 100	Max	94.6	96.5
	Min	50.3	36.0
	Mean	72.1	61.3
	Median	70.7	61.3
	StDev	13.2	13.6
> 100	Max	146.0	110.7
	Min	40.0	12.0
	Mean	113.5	64.3
	Median	113.1	64.4
	StDev	25.1	24.9

3.4. Outgassing – Saturation Measurements

3.4.1. PVT Measurements

Filling and outgassing experiments were conducted using the pressure – volume – temperature (PVT) apparatus at Alfred. All of the PVT data were collected using a furnace. Figure 8 shows a typical PVT curve obtained after helium filling and outgassing using MoSci 1394 HGMS. Figure 9 shows the filling part of several curves using different partial pressures of helium, i.e., 100, 300, 500, and 700 torr. Figures 10 and 11 show the helium outgassing curves for MoSci 1402 and 1394 HGMS, respectively, for several pressures. As expected, HGMS filled to a higher initial pressure outgas to produce a higher final pressure. Figure 12 is a linear extrapolation through zero of pressure dependence for the curve of outgassing pressure vs. fill pressure. Similarly behaving hydrogen-outgassing and pressure-dependence curves are shown in Figures 13 to 15.

3.4.2. Residual Gas Analysis

Data were collected using two different RGA systems during the course of this study. The change in RGA system during this work was due to a problem encountered after a significant amount of data was collected. RGA #1 and RGA #2 will be used to distinguish between data taken using the two different systems. Also two separate lamps were used with RGA #2; Lamp #1 is equipped with a 250-watt Sylvania and Lamp #2 is equipped with a 250-watt General electric bulb. RGA #1 was only run with

Lamp #1. Use of a reflector will be indicated for each data set collected for lamp outgassing of HGMS.

Table IV lists data obtained from mass spectroscopy (RGA #1) performed on undoped (1402) HGMS and 5 wt%-doped microspheres (1394). These data are for spheres of each composition saturated with 200, 300, 500, and 700 torr of hydrogen. The mass of the sample was measured during initial sample preparation. Integration of curves obtained during outgassing of HGMS was carried out using the computer program, which yields the area under the curve, pressure at maximum, and time at peak (time where maximum occurs). The extrapolated onset time was found by intersecting tangent lines from the baseline and initial slope of the curve. An example of an extrapolated onset time measurement is shown in Figure 16. Figures 17 and 18 show the low pressure dependence (200, 300, 500, 700 torr) of outgassing curves for hydrogen-filled HGMS for 1394 and 1402 samples, respectively (RGA #1). All times are measured after the start of the experiment after 300 seconds of measuring the background. The doped HGMS exhibit a substantially lower extrapolated onset time for outgassing relative to the undoped HGMS, presumably because the doped HGMS absorb the IR radiation more effectively. As before in the PVT system, the hydrogen partial pressure produced by outgassing increases with increasing fill pressure.

Figure 19 shows the difference between lamp and furnace outgassing for spheres filled to high pressure (1,500 psi). It is interesting to note that superior outgassing performance is achieved with Lamp #1 in comparison to Lamp #2, presumably due to a difference in spectral output. Figure 20 shows the difference between lamp and furnace outgassing for spheres filled to low pressures (700 torr). It is important to note that the "humps" in the initial portion of the curves in Figure 20 are artifacts of the measurement.

Table V lists outgassing data for high- and low-pressure spheres collected using either lamp (Lamp #1 or Lamp #2) outgassing or furnace outgassing (RGA #2). High-pressure spheres refers to spheres filled by Savannah River National Laboratory to 1500 psi (102.1 atm.) and low-pressure spheres refers to spheres filled at Alfred to 700 torr (0.92 atm), unless otherwise stated. It can readily be seen that HGMS filled at 1,500 psi release a substantially larger amount of hydrogen than HGMS filled at 700 torr.

Table IV. Effect of Pressure on Lamp Outgassing Behavior for Low Pressures (RGA#1 No Reflector)

Sample	Mass (g)	Fill Pressure (torr)	Pressure at Max (torr)	Time at Peak (s)	Area Under Curve	Extrapolated Onset Time (s)
1394	0.10	200	5.0E-06	69	1.3E-03	1
1394	0.10	300	5.7E-06	80	1.6E-03	1
1394	0.10	500	9.5E-06	69	2.9E-03	1
1394	0.10	700	1.6E-05	47	4.8E-03	1
1402	0.11	200	1.9E-07	216	1.4E-04	14
1402	0.11	300	1.6E-07	271	1.6E-04	14
1402	0.11	500	2.7E-07	190	3.3E-04	14
1402	0.11	700	4.7E-07	780	5.2E-04	14

Table V. Comparison of Effects of High and Low Pressure on Outgassing Results (RGA#2 Lamp Data with Reflector)

Sample	Outgassing Method	Mass (g)	Fill Pressure	Pressure at Max (torr)	Time at Peak (s)	Area Under Curve	Extrapolated Onset Time (s)
1394	Lamp #2	0.010	1500 psi	6.2E-06	209	4.6E-03	2
1394	Lamp #1	0.012	1500 psi	3.3E-05	204	2.0E-02	1
1394	Furnace	0.010	1500 psi	4.6E-05	269	1.9E-02	10
1394	Lamp #2	0.090	700 torr	7.5E-07	199	6.3E-04	3
1394	Lamp #1	0.090	700 torr	5.0E-06	87	1.3E-03	2
1394	Furnace	0.099	700 torr	2.4E-06	145	1.2E-03	12
1402	Lamp #2	0.110	700 torr	NA*	NA*	NA*	NA*
1402	Furnace	0.130	700 torr	1.0E-06	230	6.7E-04	23

* No increase occurs

3.4.3. Effect of Outgassing Temperature/Method

3.4.3.1. PVT

Using several different temperatures, HGMS were filled with 700 torr of helium and outgassed. Undoped (1402) and 5 wt%-doped (1394) HGMS were analyzed using the PVT system (refer to Figure 7 for a typical filling and outgassing PVT curve). Temperature dependence of filling and outgassing at different temperatures, where the same temperature was used for both filling and outgassing, is shown in Figures 21 and 22. A consistent partial pressure, 700 torr, of helium was used for each measurement. Figure 21 shows the outgassing curves for 1394 HGMS, and Figure 22 shows the outgassing curves for 1402 HGMS.

Table VI lists the results obtained from the temperature-dependence data obtained from a log - Y vs. time plots (shown in Figure 23) in which Y is calculated using the equation

$$Y = (1 - P_2/P_2^*) = \exp [-(a + 1/a) L/T]$$

where P_2 is the pressure outside the microspheres, P_2^* is the pressure outside the microspheres at an infinitely long time, a is the ratio of the measuring-vessel volume to the internal microsphere volume (no dimensions), and τ is the time constant. The time constant t is determined from the curves shown in Figure 23 by finding the time where Y is equal to $1/e$ (0.367). The gas permeability, K , was calculated using the equation

$$\tau = (r_1 - L)L / 3RTK \quad (8)$$

where r_1 is the mean outer radius of the microspheres (30.6 μm for 1394 spheres and 19.95 μm for 1402 spheres), L is the microsphere mean wall thickness (1.8 μm for 1394 spheres and 3.9 μm for 1402 spheres), R is the gas constant (8.314 J / mol K), and T is temperature. Plots of $\ln 1/\tau$ vs. $1/\text{Temperature}$ are shown in Figures 24 and 25 for both 1394 and 1402 HGMS. Figure 25 gives a more accurate depiction of the results by eliminating the data at 150°C, where the spheres were not completely filled with hydrogen.

Table VI. PVT Data for 1394 and 1402 HGMS Filled (700 torr of Helium) and Outgassed at Different Temperatures

Sample	Temperature (K)	Inverse Temperature (1/K)	Tau (s)	Ln 1/Tau	Permiability (mol-m/m ² -s-Pa)
1394	573	0.00174	101	-4.62	3.6E-17
1394	548	0.00182	136	-4.91	2.8E-17
1394	523	0.00191	179	-5.19	2.2E-17
1394	423	0.00236	411	-6.02	1.2E-17
1402	573	0.00174	237	-5.47	1.8E-17
1402	548	0.00182	277	-5.62	1.7E-17
1402	523	0.00191	355	-5.87	1.4E-17
1402	423	0.00236	1135	-7.03	5.2E-18

3.4.3.2. RGA

Comparison of lamp and furnace outgassing was conducted using several experimental variations. A furnace preheated to 300°C was used unless otherwise stated, and two different lamps were used. Lamp #1 was equipped with a Sylvania 250 watt bulb, while Lamp #2 was equipped with a General Electric 250 watt bulb (if no lamp number is given, Lamp #1 was used). MoSci HGMS 1436, which contain 1 wt% dopant, were used in addition to the MoSci 1394 and 1402 HGMS.

Table VII lists results for 1394 and 1402 HGMS which were filled with 700 torr of hydrogen and outgassed with a furnace at either 150°C or 300°C, or a lamp with or without a reflector (RGA #1). The corresponding outgassing curves are shown in Figures 26 and 27. Figure 26 shows curves for 1394 HGMS, and Figure 27 shows curves for 1402 HGMS. Table VIII lists results for 1394 and 1436 HGMS which were filled with 700 torr of hydrogen and outgassed with a furnace at 300°C, or with Lamp #1 with and without a reflector. The curves corresponding to the data in Table VIII are

shown in Figures 28 and 29. It is seen that increasing the temperature of the furnace reduces the extrapolated onset time, although optically-induced outgassing is always more rapid. In addition, while the inclusion of a reflector has a minimal effect on the onset time, it does significantly increase the amount of gas that is released from the HGMS.

Table VII. Effect of Outgassing Method on Outgassing Behavior for 700 torr of Hydrogen in 1394 and 1402 HGMS (RGA #1)

Sample	Outgassing Method	Mass (g)	Pressure at Max (torr)	Time at Peak (s)	Area Under Curve	Extrapolated Onset Time (s)
1394	Lamp without reflector	0.12	1.4E-06	83	8.2E-04	2
1394	300°C	0.12	2.2E-06	138	1.1E-03	29
1394	150°C	0.12	1.3E-07	142	4.6E-05	59
1394	Lamp with reflector	0.12	1.7E-05	41	3.5E-03	6
1402	Lamp with reflector	0.10	2.0E-07	76	1.4E-04	35
1402	300°C	0.10	6.7E-07	61	6.4E-04	29
1402	150°C	0.10	NA	NA	NA	60

Table VIII. Effect of Outgassing Method on Outgassing Behavior for 700 torr of Hydrogen in 1394 and 1436 HGMS (RGA #2)

Sample	Outgassing Method	Mass (g)	Pressure at Max (torr)	Time at Peak (s)	Area Under Curve	Extrapolated Onset Time (s)
1394	Lamp #1 without reflector	0.120	1.3E-06	98	4.54E-04	3
1394	Lamp #1 with reflector	0.120	5.0E-06	87	1.3E-03	3
1394	Furnace	0.120	2.4E-06	145	1.2E-03	20
1436	Lamp #1 without reflector	0.092	1.1E-06	89	7.7E-04	7
1436	Lamp #1 with reflector	0.092	2.6E-06	166	1.4E-03	7
1436	Furnace	0.096	5.2E-06	172	2.3E-03	30

3.4.4. Dopant Comparison

The effect of dopant identity was analyzed using MoSci 1394, 1402, 1436, and 1386 HGMS. The 1386 HGMS are doped with 5 wt% iron oxide. Table IX lists results

obtained from 1394, 1402, and 1386 HGMS taken using Lamp #1 and a furnace at 300°C (RGA #1). Figures 30 and 31 show a comparison of outgassing curves for 1394, 1386, and 1402 HGMS outgassing using a lamp or furnace, respectively (RGA #1). While the onset times for the 1394 and 1386 HGMS are comparable, the 1394 HGMS reach a higher peak in optically-induced outgassing behavior in a shorter period of time. This supports the earlier optically-induced outgassing results of Rapp and Shelby on hydrogen-loaded monolithic pieces of doped borosilicate glass.⁵

Table IX. Effect of Outgassing Method and Dopant on Outgassing Behavior for 700 torr of Hydrogen Filled HGMS (RGA #1)

Sample	Outgassing Method	Mass (g)	Pressure at Max (torr)	Time at Peak (s)	Area Under Curve	Extrapolated Onset Time (s)
1394	Lamp	0.12	1.4E-06	83	8.2E-04	3
1386	Lamp	0.10	1.1E-06	127	6.1E-04	3
1402	Lamp	0.10	2.0E-07	176	1.4E-04	30
1394	300°C	0.12	2.2E-06	138	1.1E-03	36
1386	300°C	0.10	5.6E-07	160	3.0E-04	38
1402	300°C	0.10	6.7E-07	161	6.4E-04	56

Table X lists the outgassing results obtained from RGA #2 for 1394 and 1436 HGMS filled with 700 torr of hydrogen and outgassed with a lamp or a furnace. The data listed in Table X were obtained from the outgassing curves shown in Figure 32.

Table X. Effect of Outgassing Method and Dopant Level on Outgassing Behavior for 700 torr of Hydrogen Filled HGMS (RGA #2)

Sample	Outgassing Method	Mass (g)	Pressure at Max (torr)	Time at Peak (s)	Area Under Curve	Extrapolated Onset Time (s)
1394	Lamp	0.120	5.0E-06	87	1.3E-03	3
1394	Furnace	0.120	2.4E-06	145	1.2E-03	20
1436	Lamp	0.092	1.1E-06	89	7.7E-04	7
1436	Furnace	0.096	5.2E-06	172	2.3E-03	30

3.4.5. Response to Changes in Exposure to Lamp

A study of the effect of turning the lamp on and off on the outgassing of 1394 HGMS, with 80-second intervals was conducted using RGA #2 and Lamp #1. Figure 33 shows the comparison between outgassing of 1394 HGMS filled with hydrogen at high and low pressure as the lamp was turned on and off. Figure 34 shows the comparison of outgassing of 1394 and 1436 HGMS filled with 700 torr of hydrogen as the lamp is turned on and off. In both cases, it can be seen that the optically-induced outgassing response is immediately halted when the lamp is switched off.

3.4.6. Hydrogen Loss During Storage

The 1394 and 1402 HGMS were filled with 700 torr of hydrogen and stored at 50°C for 1 and 35 days. The samples were filled at the same time, and the sample tubes to be stored for 35 days were placed in a 50°C water bath. Table XI lists the results obtained from the curves for 1394 and 1402 HGMS measured the day after filling and 35 days after filling. The outgassing curves are shown in Figure 35 for 1394 HGMS and Figure 36 for 1402 HGMS. A measurable loss of hydrogen occurs after 35 days due to the short diffusion distance presented by the thin-walled HGMS. While the storage temperature of 50°C used in this experiment is higher than the typically expected ambient temperature, this loss of gas must still be considered if HGMS are to be used as a medium for long-term storage of hydrogen. This issue may potentially be addressed by engineering the glass composition to be less permeable to hydrogen, although such changes would also reduce the ability of the HGMS to release hydrogen on demand.

Table XI. Effect of Time on 1394 and 1402 HGMS Filled with 700 torr of Hydrogen.

Sample	Outgassing Method	Mass (g)	Pressure at Max (torr)	Time at Peak (s)	Area Under Curve	Extrapolated Onset Time (s)
1394 Day 1	300°C	0.12	2.4E-06	145	1.2E-03	25
1394 Day 35	300°C	0.12	1.4E-06	168	9.1E-04	25
1402 Day 1	300°C	0.10	1.0E-06	230	6.7E-04	25
1402 Day 35	300°C	0.10	7.6E-07	218	5.7E-04	30

3.4.7. Effect of HGMS Size

Sieved HGMS were filled with 700 torr of hydrogen and outgassed (RGA #2). Table XII lists the results obtained from the curves. Furnace outgassing curves for 1394 and 1402 HGMS are shown in Figures 37 to 41. Lamp outgassing curves for sieved spheres are shown in Figures 42 to 46. Figures 42 and 43 compared the effects of sphere size for 1394 and 1402 HGMS, respectively. Figures 44 to 46 compare the effects for 1394 and 1402 HGMS for a given size range of spheres.

The effect of HGMS size was particularly pronounced in the limited number of samples that were filled at the highest pressure of ~5,000 psi. Figure 47 shows the optically-induced outgassing of Ni1 HGMS that are less than 50 µm, between 50 to 100 µm, and larger than 100 µm in diameter and were filled at ~5,000 psi of hydrogen by Savannah River National Laboratory. The erratic, noisy appearance of the outgassing curve for HGMS >100 µm in diameter is due to the fracture of spheres; the fracture of HGMS also manifested as an audible “popping” noise. This effect is likely related to the influence of HGMS aspect ratio (defined as the ratio of HGMS diameter to wall thickness) on mechanical properties. It is anticipated that the strength of HGMS should increase with *decreasing* aspect ratio – *i.e.*, the strongest HGMS would tend to be smaller in diameter and have thicker walls. While the confocal Raman microscopy data demonstrated that

larger HGMS tend to have thicker walls, this increase in wall thickness is not sufficient to reduce the aspect ratio.

3.4.5. Metallic Colloid Formation

Nickel-containing HGMS exposed to hydrogen gas at elevated temperatures for an extended period of time underwent a visible darkening in color. The source of this behavior is the reduction of the ionic Ni^{2+} dopant to form nanoscale metallic nickel colloids, as shown in Figure 48. The formation of the nickel metal colloids has an observable effect on ability of HGMS to release hydrogen when exposed to the IR lamp. Figure 49 shows the outgassing curves for a sample of Ni5 HGMS saturated with hydrogen for the first time and those same HGMS after being exposed to hydrogen for an extended period of time. The release of hydrogen is more rapid from the treated HGMS, presumably because the nickel metal colloids darkens the HGMS and increases their ability to absorb the IR radiation.

Table XII. Effect of Size on Outgassing of 1394 and 1402 HGMS Filled with 700 torr of Hydrogen.

		Sample ID			
Particle Size (μm)		1394 Lamp	1402 Lamp	1394 300°C	1402 300°C
< 50	Mass (g)	0.092	0.092	0.092	0.092
	Pressure at Max (torr)	8.9E-07	2.1E-07	7.9E-07	1.2E-06
	Time at Peak (s)	112	179	187	171
	Area Under Curve	2.7E-04	1.3E-04	4.4E-04	5.4E-04
	Extrapolated Onset Time (s)	2	36	36	34
50 < x < 100	Mass (g)	0.091	0.093	0.091	0.093
	Pressure at Max (torr)	1.3E-06	2.2E-07	1.5E-06	7.5E-07
	Time at Peak (s)	109	244	174	205
	Area Under Curve	5.1E-04	1.7E-04	8.2E-04	5.1E-04
	Extrapolated Onset Time (s)	3	36	22	30
> 100	Mass (g)	0.092	0.102	0.092	0.102
	Pressure at Max (torr)	1.9E-06	4.9E-07	2.1E-06	6.9E-07
	Time at Peak (s)	175	147	135	232
	Area Under Curve	7.6E-04	2.9E-04	1.1E-03	5.1E-04
	Extrapolated Onset Time (s)	2	22	23	22

Figure 8. Typical PVT curve.

Figure 9. Helium filling curve for 1394 HGMS.

Figure 10. PVT helium outgassing curve for the 1402 HGMS.

Figure 11. PVT helium outgassing curve for the 1394 HGMS.

Figure 12. Outgassed pressures vs. fill pressure for helium.

Figure 13. PVT hydrogen outgassing curve for the 1402 HGMS.

Figure 14. PVT hydrogen outgassing curve for the 1394 HGMS.

Figure 15. Outgassed pressures vs. fill pressure for hydrogen.

Figure 16. Example of extrapolated onset time using 1394 HGMS filled to 1500 psi.

Figure 17. Lamp outgassing (no reflector) curve for 1394 HGMS loaded with hydrogen with increasing fill pressures.

Figure 18. Lamp outgassing (no reflector) curve for 1402 HGMS loaded with hydrogen with increasing fill pressures.

Figure 19. Outgassing curves for 1394 HGMS loaded with 1,500 psi hydrogen outgassed by the lamp or the furnace (lamps used with reflector RGA #2).

Figure 20. Outgassing curves for 1394 HGMS loaded with 700 torr hydrogen outgassed by the lamp or the furnace (lamps used with reflector RGA #2).

Figure 21. Temperature dependence of helium outgassing from 1394 HGMS.

Figure 22. Temperature dependence of helium outgassing from 1402 HGMS.

Figure 23. Example of log-Y-vs.-time plot for different temperatures for 1394 HGMS filled with 700 torr of helium.

Figure 24. Plot of $\ln 1/\tau$ vs. $1/T$ for 1394 and 1402 HGMS filled with 700 torr of helium.

Figure 25. Plot of $\ln 1/\tau$ vs. $1/T$ for 1394 and 1402 HGMS filled with 700 torr of helium after removal of 150°C data.

Figure 26. Outgassing curves for 1394 HGMS filled with 700 torr hydrogen for samples outgassed by the lamp or the furnace as indicated (RGA #1).

Figure 27. Outgassing curves for 1402 HGMS filled with 700 torr hydrogen for samples outgassed by the lamp or the furnace as indicated (RGA #1).

Figure 28. Outgassing curves for 1394 HGMS filled with 700 torr hydrogen for samples outgassed by the lamp or the furnace as indicated (RGA #2).

Figure 29. Outgassing curves for 1402 HGMS filled with 700 torr hydrogen for samples outgassed by the lamp or the furnace as indicated (RGA #2).

Figure 30. Outgassing curves for 1402, 1394, and 1386 HGMS filled with 700 torr hydrogen outgassed using Lamp #1 with no reflector (RGA #1).

Figure 31. Outgassing curves for 1402, 1394, and 1386 HGMS filled with 700 torr hydrogen outgassed using a furnace at 300°C (RGA #1).

Figure 32. Outgassing curves for 1394 and 1436 HGMS filled with 700 torr hydrogen outgassed using a furnace at 300°C and Lamp #1 (RGA #2).

Figure 33. Outgassing curves for 1394 HGMS loaded at high and low pressure outgassed with 80 second interval shining of Lamp #1.

Figure 34. Outgassing curves for 1394 and 1436 HGMS loaded with 700 torr of hydrogen outgassed with 80-second-interval shining of Lamp #1.

Figure 35. Outgassing curves for 1394 HGMS filled with 700 torr of hydrogen and either outgassed directly after filling or after five weeks of storage in a water bath at 50°C.

Figure 36. Outgassing curves for 1402 HGMS filled with 700 torr of hydrogen and either outgassed directly after filling or after five weeks of storage in a water bath at 50°C.

Figure 37. Outgassing curves for different-size-range 1394 HGMS filled with 700 torr of hydrogen and outgassed with a furnace.

Figure 38. Outgassing curves for different-size-range 1402 HGMS saturated with 700 torr of hydrogen and outgassed with a furnace.

Figure 39. Outgassing curves for 1394 and 1402 HGMS greater than 100 μm filled with 700 torr of hydrogen and outgassed using a furnace.

Figure 40. Outgassing curves for 1394 and 1402 HGMS between 100 μm and 50 μm filled with 700 torr of hydrogen and outgassed using a furnace.

Figure 41. Outgassing curves for 1394 and 1402 HGMS less than 50 μm filled with 700 torr of hydrogen and outgassed using a furnace.

Figure 42. Outgassing curves for 1394 HGMS of different sizes filled with 700 torr of hydrogen and outgassed using Lamp #1.

Figure 43. Outgassing curves for 1402 HGMS of different sizes filled with 700 torr of hydrogen and outgassed using Lamp #1.

Figure 44. Outgassing curves for 1394 and 1402 HGMS greater than 100 μm filled with 700 torr of hydrogen and outgassed using Lamp #1.

Figure 45. Outgassing curves for 1394 and 1402 HGMS between 100 μm and 50 μm filled with 700 torr of hydrogen and outgassed using Lamp #1.

Figure 46. Outgassing curves for 1394 and 1402 HGMS less than 50 μm filled with 700 torr of hydrogen and outgassed using Lamp #1.

Figure 47. Optically-induced outgassing of sieved Ni1 HGMS filled at ~5,000 psi. The noise in the $>100 \mu\text{m}$ outgassing curve is due to fracture of HGMS.

Figure 48. SEM image of nickel metal colloids the surface of Ni5 HGMS.

Figure 49. Outgassing curves of new Ni5 HGMS and those same HGMS subjected to hydrogen treatment for an extended period of time.

Helium permeabilities were determined for 1394 and 1402 HGMS using the formula derived by Tsugawa *et al.*⁶ Figure 50 was constructed using data from Shelby.⁴ This figure shows the temperature dependence of the permeability of the two sets of HGMS and of glasses with similar compositions. CGW 0080 is an alkali, alkaline-earth silicate glass with a small amount of Al_2O_3 , while PPG Float glass is a traditional soda-lime-silicate float glass. The two comparison glasses are not available in the form of HGMS, but are similar in composition to the amber glass used by MoSci to make these HGMS. This figure shows that the permeability of the HGMS is in the range expected. Since neither of the glasses used for comparison contains boron or phosphorus, the values will be similar, but are not expected to be identical to that for the HGMS. Using the formula derived by Altemose⁷ and further developed by Tsugawa *et al.*⁶ the theoretical helium permeability at 300°C of HGMS was calculated to be 2.8×10^9 atom/s-cm-atm for 1394 HGMS and 4.4×10^9 atom/s-cm-atm for 1402 HGMS. The experimental helium permeability at 300°C of the 1394 HGMS is 2.2×10^{10} atom/s-cm-atm and for the 1402 HGMS was 1.1×10^{10} atom/s-cm-atm. The permeabilities are in the range expected using the formula. The calculated helium activation energies are 49,618 J/mol-K for 1394 HGMS and 47,523 J/mol-K for the 1402 HGMS. The experimental values of helium activation energy are 34,273 J/mol-K for the 1394 HGMS and 24,298 J/mol-K for the 1402 HGMS. The helium activation energies obtained using the Tsugawa *et al.*⁶ approach are low when compared to the other glasses. While the cause of this unexpected difference is not known, it should be noted that Tsugawa *et al.*⁶ found similar results for the HGMS in their study. The theoretical hydrogen permeabilities at 300°C found using an equation derived by Tsugawa *et al.*⁶ are 3.4×10^7 atom/s-cm-atm

for 1394 HGMS and 5.3×10^7 atom/s-cm-atm for the 1402 HGMS. The experimental hydrogen permeabilities at 300°C found here are 1.4×10^9 atom/s-cm-atm for 1394 HGMS and 9.1×10^8 atom/s-cm-atm for the 1402 HGMS. These values are in the general range expected, again suggesting the equations used will give a reasonable estimate of the permeability of HGMS.

Figure 50. Temperature dependence of helium permeability of 1402 HGMS, 1394 HGMS, CGW 0080, and PPG Float glasses.

4. Conclusions

Outgassing doped HGMS with a lamp results in faster response than the release of hydrogen from HGMS using heat applied by a furnace. The lag time for doped HGMS outgassed with Lamp #1 is between two and five seconds, while it is between 12 and 30 seconds when outgassed with a furnace preheated to 300°C. The presence of a dopant causes a significant change in the outgassing rate and amount of gas released when using the lamp. Little gas is outgassed with the lamp when undoped samples are used. The lamp outgassing from the undoped spheres may be due to heating of the sample by the lamp or an interaction with the small amount of iron contained in the amber bottle glass used to make the base glass 1402 HGMS. Almost instantaneous cessation of outgassing occurs when the light is turned off, followed by instantaneous outgassing again when the lamp is turned back on, suggesting a lamp can be a good way to regulate hydrogen release as is necessary in many applications. Formulas derived by Tsugawa et al. can be used to estimate gas permeabilities for HGMS and to analyze PVT data.

5. References

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6. Publications / Presentations generated as a result of this project:

Michael J. Snyder, Peter B. Wachtel, Matthew M. Hall, and James E. Shelby, "Photo-Induced Hydrogen Diffusion in Cobalt-doped Hollow Glass Microspheres" accepted by Physics and Chemistry of Glasses: European Journal of Glass Science and Technology Part B. Scheduled for publication in their February, 2009 issue.

J. E. Shelby, F. C. Raszewski, M. M. Hall, "Fuels – Hydrogen Storage: Hydrogen Storage in Glass Microspheres," Ency. Electrochemical Power Sources, Elsevier, (Invited) Accepted for publication. Publication date unknown.

P. F. Wachtel & J. E. Shelby, "High Pressure Storage of Hydrogen in Hollow Glass Microspheres," presented at Glass and Optical Materials Divisions of the American Ceramic Society Meeting, Tucson, AZ, May 19, 2008.

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

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

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

J. E. Shelby M. M. Hall, "Novel Applications of Hydrogen-Filled Hollow Glass Microspheres," University Conf. on Glass, Penn. State U., June, 2005. (Invited)

7. Comparison of actual accomplishments with project goals.

Task 1: Proof of concept for HGMS

Most of the targets of this task have been met. Proof that photo-induced diffusion occurs in both low and high pressure filled microspheres has been obtained. Storage capacities in excess of 2 wt% are routinely obtained.

Task 2: Extend work to high-pressure hydrogen

Analysis of samples filled to 5,000 psi at SRNL confirm earlier storage values of >2 wt% at this pressure. Samples to be filled to 10,000 psi could not be secured due to funding limitations. This issue represents a serious obstacle to the success of this project.

Indications of a relation between sphere diameter, wall thickness, and the survival rate for samples pressurized to 5,000 psi using samples sieved into 3 size ranges (0 - 50, 50 - 99, and >100 micrometers diameter) before sending the samples to SRNL for hydrogen filling to high pressure are confirmed. The crush failure of the HGMS is determined by the diameter to wall thickness ratio.

Task 3: Construct a bench-top demonstration facility and optimize engineering parameters.

This task was not slated for initiation until much later in this project. No work has been done on this task due to funding limitations.

Task 4: Supporting scientific study of photo-induced hydrogen diffusion mechanism

Detailed studies of the temperature response of samples of various hollow glass microspheres during exposure to either a preheated furnace or to radiation from an infrared lamp indicates that the rapid response previously designated as photo-induced diffusion is due to an extremely efficient transfer of energy from the light to the microspheres, which causes a rapid change in their temperature. It appears that the spectrum of the radiation from the lamp is such that the coupling with the absorption spectrum of the microspheres results in heating to temperatures in excess of 400 to 500°C, depending on dopant identity and concentration. Since the absorption spectrum of the undoped glass is such that light from the infrared source is not efficiently absorbed, those microspheres do not heat efficiently. The spectrum of the furnace has a maximum further into the infrared, where the doped HGMS do not absorb efficiently, thus reducing the efficiency of that heating process as well.

The confocal Raman microscope has been successfully used to measure the wall thickness of intact spheres. This work reveals that part of the variation

between batches of HGMS is caused by variations in wall thickness, as anticipated.

Scanning electron microscope examination of samples of Co and Ni doped HGMS previously filled to high pressure at SRNL reveals that they contain nanocrystals of those metals. Formation of those nanocrystals occurs due to reduction of the divalent ions by the hydrogen during the high temperature fill process. The SEM micrographs reveal that the formation of the nanocrystals caused the glass to elastic expand around the nanocrystal, producing small “hillocks” on the surface of the glass. This phenomenon has not been reported in previous studies of nanocrystal formation in glasses.