Photo-Induced Hydrogen Outgassing of Glass

Douglas B. Rapp and James E. Shelby
New York State College of Ceramics at Alfred University

New Microsphere Concept

The recent discovery of photo-enhanced hydrogen diffusion in glass has allowed pressurized hollow glass microspheres to become a viable hydrogen storage technology.

FILL MICROSPHERES UNDER HIGH PRESSURE H_2 AT ELEVATED TEMPERATURE
↓
STORED H_2 AT AMBIENT TEMPERATURE
↓
PHOTO-INDUCED GAS RELEASE
↓
H_2 FOR FUEL CELL APPLICATION

Approach

A saturation/outgassing technique has been used to monitor the hydrogen release rates from glasses of varied composition, thereby providing data necessary for developing a glass optimized for the microsphere hydrogen storage application.

Materials

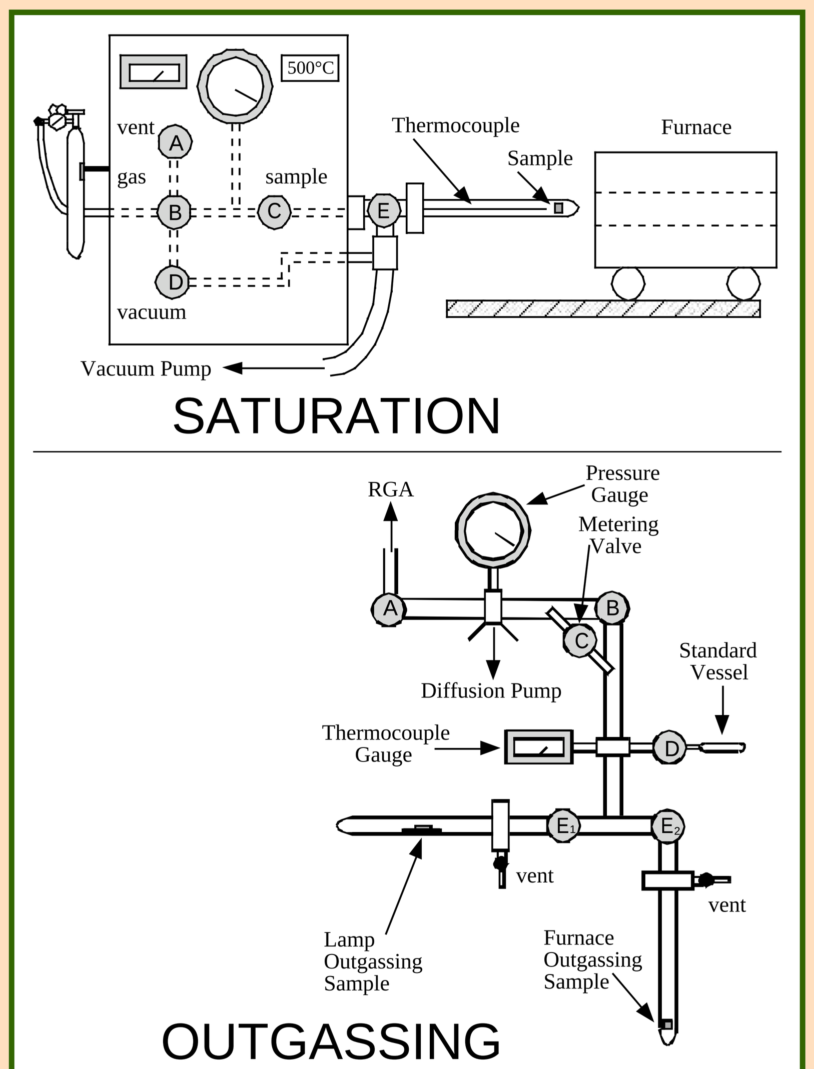
BASE GLASS	Fe_3O_4 (wt%)
CGW 7070	2.0, 1.0, 0.5, 0.25, 0.1
CGW 7740	2.67
CGW 7251	2.0
CGW 7059	2.0
$16Na_2O$-$10CaO$-$74SiO_2$	2.0

	7070	7740	7251	7059	SLS
SiO_2	72	81	77	49	74
B_2O_3	25	13	15	15	-
Al_2O_3	1	2	2	10	-
Li_2O	0.5	-	-	-	-
Na_2O	0.5	4	5	-	16
K_2O	1	-	-	-	-
CaO	-	-	-	-	10
BaO	-	-	-	25	-
As_2O_3	-	-	1	1	-

DOPED 7070
0.5 wt% Fe_3O_4
0.5 wt% CoO
0.5 wt% NiO
0.5 wt% V_2O_5
0.5 wt% Cr_2O_3
0.5 wt% TiO_2
0.5 wt% MnO_2

Experimental Procedure

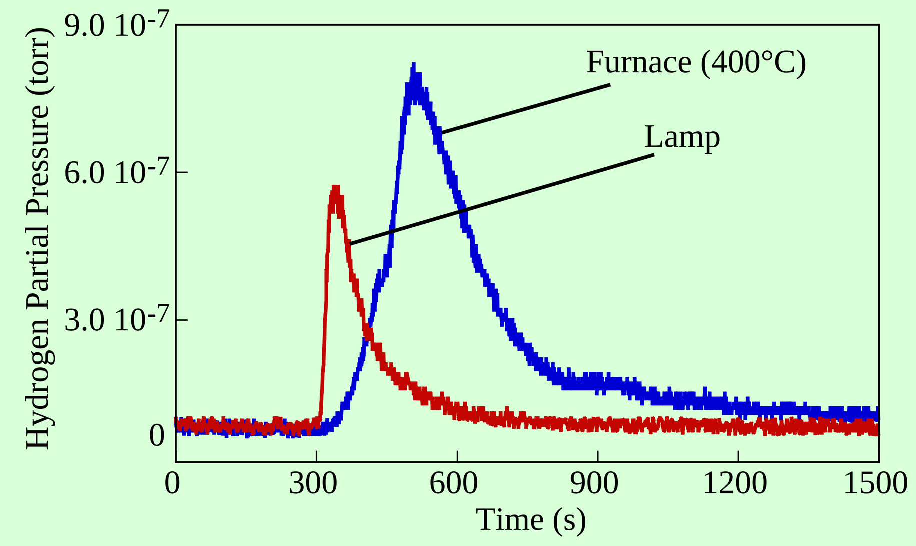
Glasses are prepared from reagent grade raw materials or by doping commercial glass frit. Samples are cut to ≈ 1 mm thick, ≈ 1.5 g of which are saturated at 500°C under ≈ 710 torr of H_2. Saturated glasses are outgassed under high vacuum while H_2 release is detected using a mass spectrometer. H_2 is removed by furnace heating or by exposing the glass samples to a 250W incandescent lamp at 300 seconds. The area under the full outgassing curve corresponds to the quantity of H_2 released and represents the H_2 solubility.



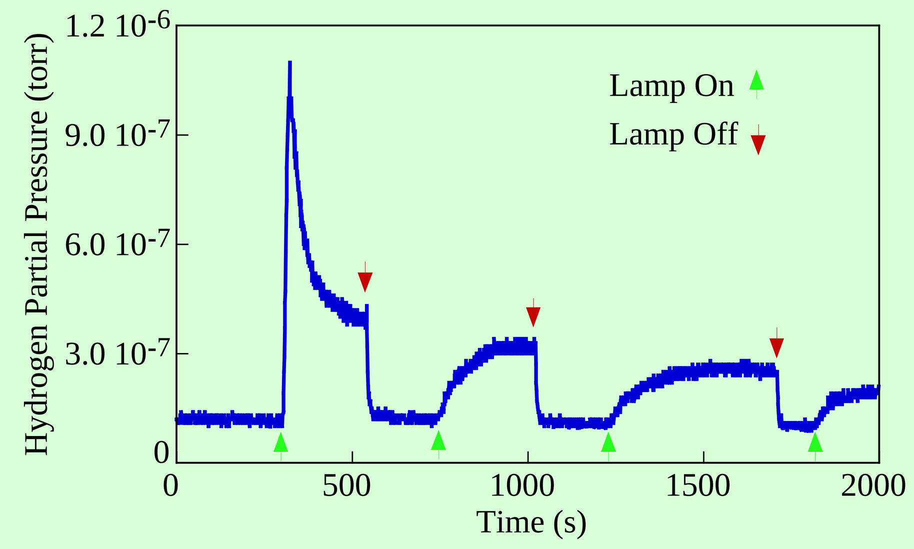
Conclusions

H_2 outgassing is enhanced by the absorption of light in doped glasses and represents an improvement in poor hydrogen release rate difficulties as compared to heating using a furnace. Fe_3O_4 additions to high-permeability glasses provide the most immediate photo-induced response, although NiO is the most effective dopant (ions/cm^3 basis). CGW 7070, a low alkali, borosilicate glass exhibits the best hydrogen outgassing response. H_2 release is proportional to lamp intensity above a threshold. Thus, adjusting the lamp voltage represents a method of obtaining controlled H_2 release. In addition, the rapid response is especially favorable for the microsphere storage concept, where applications may require H_2 to be supplied on demand. H_2 reaction results in higher Fe^{2+}/Fe^{3+} ratio and increased [OH], promoting higher H_2 yield due to increased infrared absorption. This behavior suggests that the iron-doped microsphere performance would improve with repeated use.

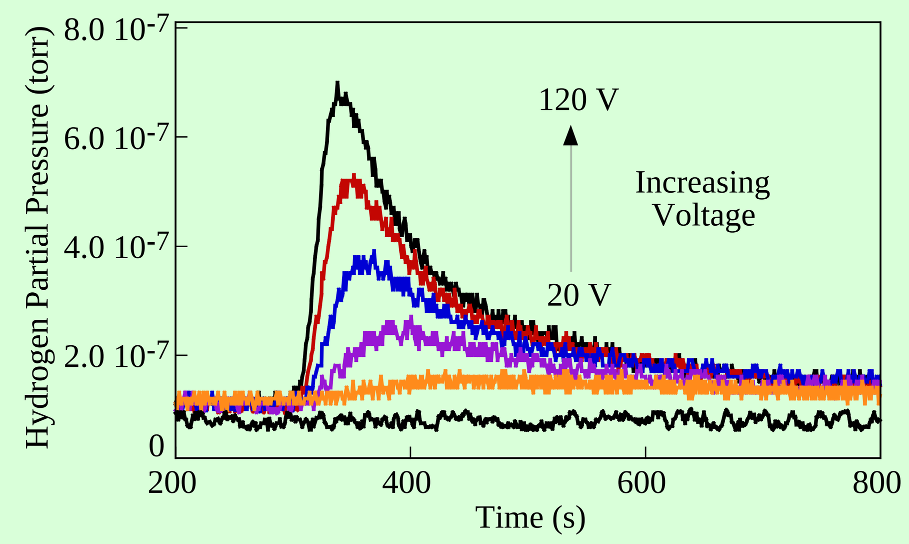
Experimental Results



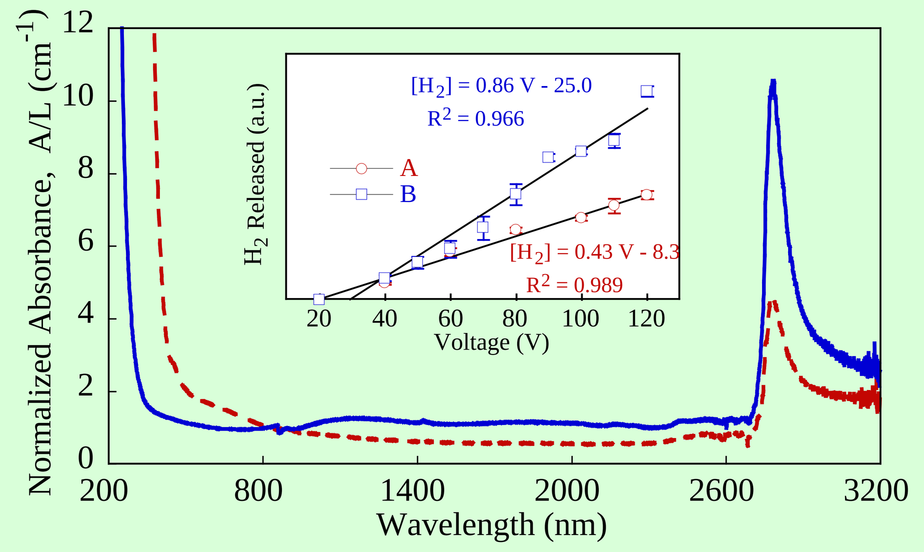
Lamp exposure results in faster H_2 outgassing as compared to furnace heating. Note the immediate onset of H_2 release upon exposure at 300 seconds. Data shown are for 0.5 wt% Fe_3O_4 doped 7070.



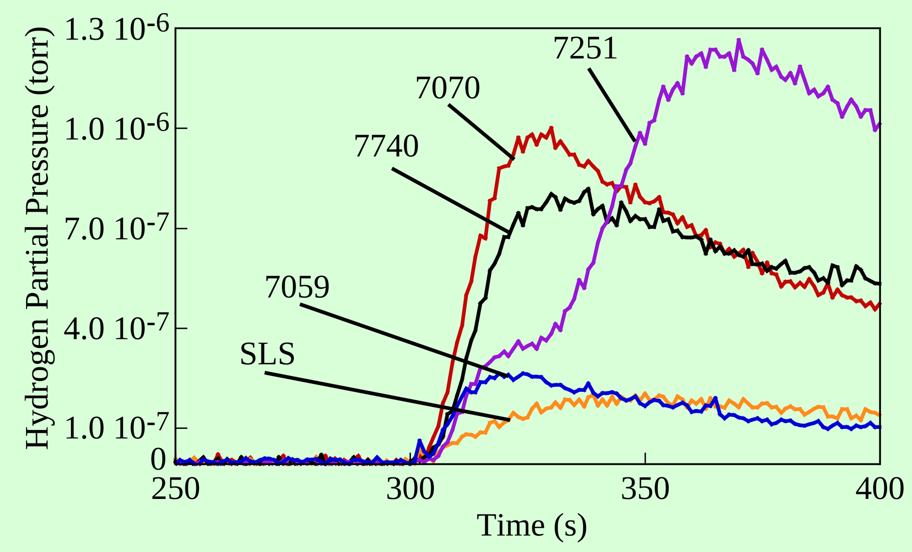
H_2 release rapidly decays to background when the lamp is turned off but is quickly reestablished when the lamp is turned back on. Data shown for 2.0 wt% Fe_3O_4 doped 7070.



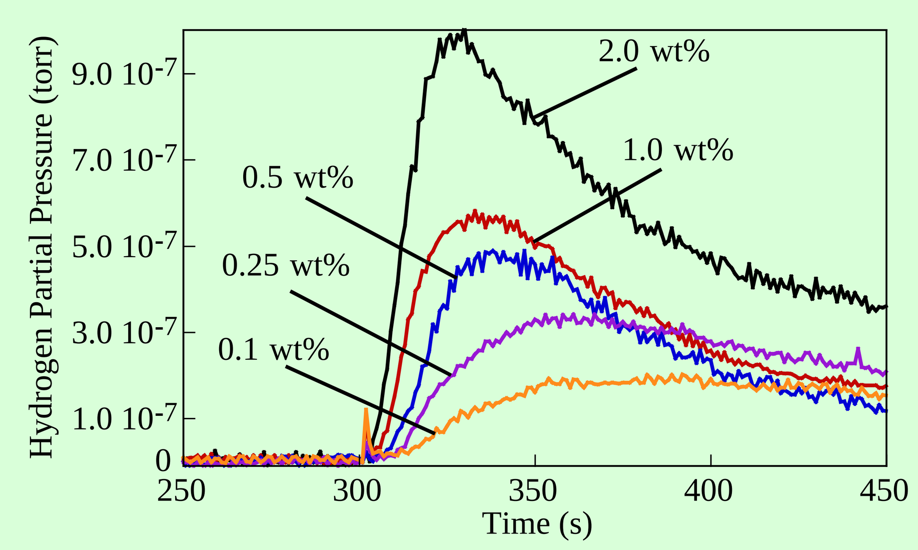
The effect of lamp intensity on the H_2 outgassing response was investigated using a variable transformer to control lamp voltage. The response is proportional to voltage above a threshold of 20 V, below which no H_2 release occurs. Data shown are for 0.5 wt% Fe_3O_4 doped 7070.



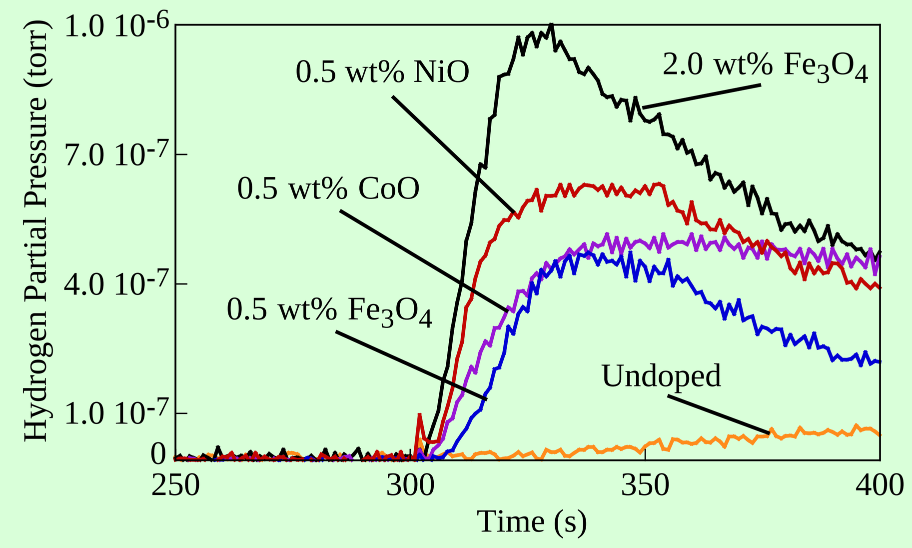
H_2 reaction during saturation treatments promotes increased Fe^{2+}/Fe^{3+} in 0.5 wt% Fe_3O_4 doped 7070 as UV-Vis-NIR spectra indicate. The dashed curve is for unreacted samples (A) while the solid line is for reacted samples (B). The H_2 yield improves with reaction (inset) for a given voltage.



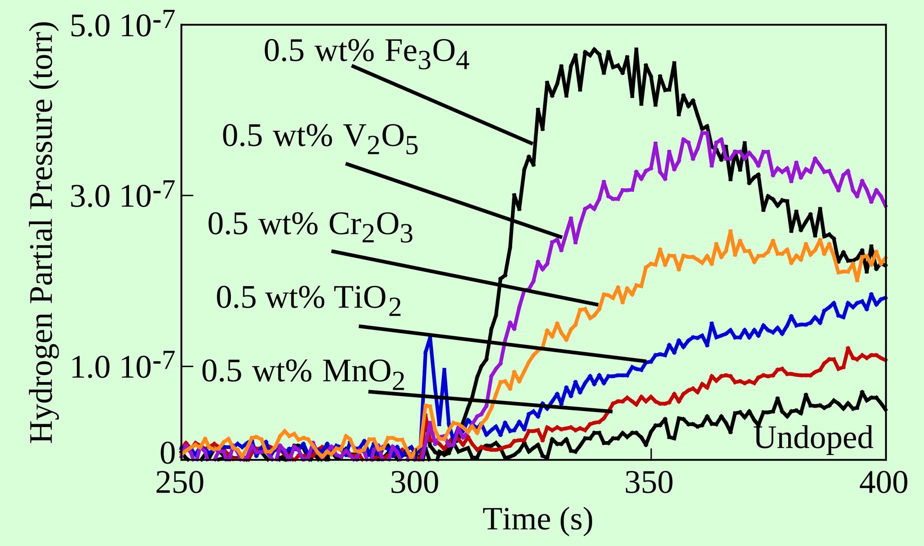
The effect of base glass on the onset of H_2 release upon lamp exposure is shown for glasses containing iron oxide. CGW 7070, a phase-separated borosilicate glass outperforms the other base glasses due to its high permeability matrix phase.



The effect of Fe_3O_4 concentration on the onset of H_2 release with lamp exposure is shown for 7070 with 0.1, 0.25, 0.5, 1.0 and 2.0 wt% Fe_3O_4. The H_2 outgassing response becomes more favorable with increasing dopant concentration.

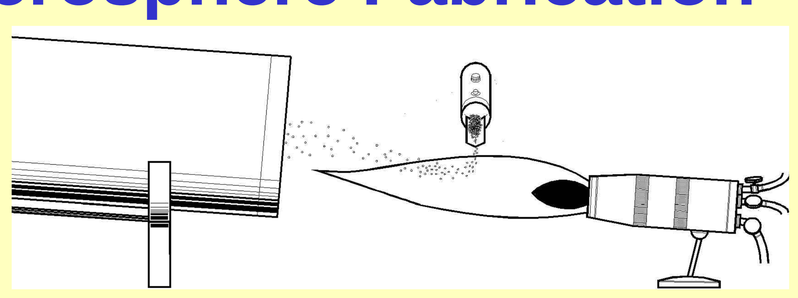


The effect of dopant on the onset of H_2 release upon lamp exposure is shown for 7070 with 0.5 wt% NiO, CoO and Fe_3O_4. The undoped glass exhibits the poorest response, while NiO provides the most immediate response. The 2.0 wt% Fe_3O_4 doped glass is included for comparison.

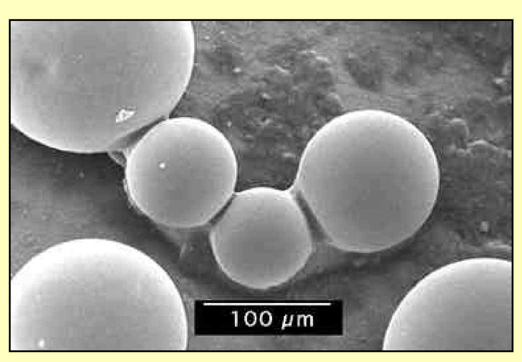


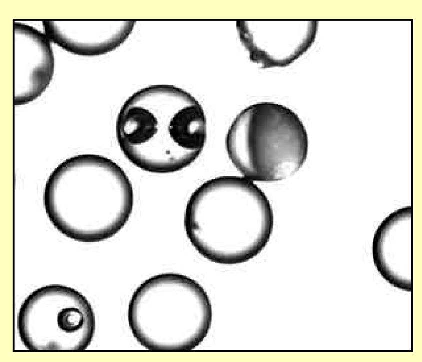
The H_2 response upon lamp exposure is less favorable for 7070 with 0.5 wt% of either V_2O_5, Cr_2O_3, TiO_2, or MnO_2. However, all dopants provide better outgassing response as compared to the undoped glass. The 0.5 wt% Fe_3O_4 doped glass is included for comparison.

Microsphere Fabrication



The 2.0 wt% Fe_3O_4 doped 7070 glass was used to demonstrate spherodization. Glass frit was dropped into the flame of an oxy-methane torch. The frit was successfully spherodized and the spheres were collected. Torch schematic courtesy of M. Hall.





A scanning electron microscopy image (300X, left) shows the varying size of spheres produced. Surface damage was present on some spheres as shown in the optical microscopy image (400X, right).

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