IV.A.6 Advanced Hydrogen Storage Materials Development

Ragaiy Zidan (Primary Contact),
Ray Schumacher and Donald Anton
Savannah River National Laboratory
Hydrogen Technology Research Laboratory,
Bldg 999W-2
Aiken, SC 29803
Phone: (803) 725-1726; Fax: (803) 652-8137
E-mail: Ragaiy.zidan@srnl.doe.gov

DOE Technology Development Manager:
Carole Read
Phone: (202) 586-3152; Fax: (202) 586-9811
E-mail: Carole.Read@ee.doe.gov

Start Date: October 1, 2005
Projected End Date: September 30, 2010

Objectives

Identify rechargeable hydrogen storage media with a gravimetric capacity of 7.5 wt% or greater

- Identify new complex compounds in the $(Na,Li,Mg)Tm(AlH_4)_i$ system through the use of molten state processing techniques.
- Develop photo-enhanced hollow glass microspheres capable of storing and readily discharging hydrogen.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen 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
(P) Lack of Understanding of Hydrogen Physisorption and Chemisorption.

Technical Targets

This project has two tasks (i) the discovery of new materials through the combination of known metal alanate materials at elevated temperatures and pressures, and (ii) development of optically enhanced hydrogen diffusion in hollow glass microspheres (HGMs). Insights gained from these studies will be applied toward the synthesis of hydrogen storage materials that meet the following DOE 2010 hydrogen storage targets:

- Specific energy: 2 kWh/kg
- Energy density: 1.5 kWh/L

Accomplishments

- Alanate Development Through Molten State Processing
  - Molten state processing (MSP) was successfully demonstrated.
  - Kinetics of $NaAlH_4$ was enhanced due to higher catalyst homogeneity.
  - Compositions of $(Na,Li,Mg)AlH_4$ synthesized.
  - Elemental substitution of Na, Li and Mg demonstrated in formation of $NaMgH_3$ and Na_2LiAlH_6 via MSP.
  - Compositions of $(Na,Li,Mg)(Ca,K)AlH_4$ synthesized.
  - Elemental substitution of Li, K, and Mg was shown in formation of K_3AlH_6.
  - Compositions of $(Na,Mg,Fe)(AlH_4)_x$, $(Li,Mg,Ni)(AlH_4)_x$ were synthesized via MSP at 100 bar/190°C.
- Hollow Glass Microspheres
  - Samples of doped HGMs and glass synthesized.
  - Vessel designed to withstand hydrogen pressure and temperature for charging HGMs – designed and fabricated.

Introduction

Alanate Development

Sodium alanate continues to be the best candidate as a low temperature (<120°C) hydrogen storage compound. It is limited to a theoretical capacity of 5.5 wt%, and only significantly lower capacitates have been achieved to date. New materials and systems need to be invented having >7.5 wt% hydrogen in order to meet the high hydrogen storage goals required for commercialization. This project will investigate mixed alanates such as $(Na, Li, Mg, Ti)AlH_4$ synthesized at elevated temperatures and pressures in order to create and identify new compounds.

HGMs

Storage of high pressure hydrogen in HGMs can improve safety because it distributes the hydrogen in micro capsules and will not release hydrogen until needed. Glass microspheres can store hydrogen at pressures of up to 10,000 psi. One of the main limitations at present is that high temperatures of up to 400°C are required to release the hydrogen from the glass microspheres. Prof. Jim Shelby at Alfred University has discovered a phenomenon of photo-induced hydrogen diffusion in glasses, which will be investigated in this project.

Approach

Alanate Development

The MSP approach will be used to fuse various alanate complexes in an attempt to identify new compounds having >7.5 wt% reversible hydrogen capacity. Sodium alanate and other hydrides are molten at elevated temperatures and pressures. These conditions promote high atomic mobility, enabling full liquid state mixing of substitutional species into the alanate lattice and possible alteration of alanate stoichiometry to form new complex hydride compound phases. This method utilizes a unique facility that can be safely pressured with up to 680 bar (10 ksi) of hydrogen at temperatures up to 300°C. Under these conditions the substituents will be introduced to the hydride complexes at or close to the molten state. This method will allow for the formation and production of new catalyzed complex hydrides that may not otherwise be produced using chemical methods or mechanico-chemical milling methods. The mass production of these compounds with minimum use of wet chemistry will also be developed. This synthesis method has the potential to be robust and can be easily scaled-up for producing large quantities of complex hydrides.

HGMs

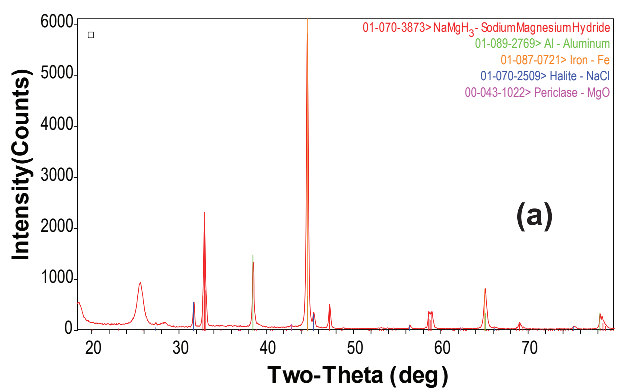
Glass forms including HGMs with different compositions and dopants will be produced and charged with hydrogen at different pressures. The release of hydrogen from these hydrogen loaded samples will be studied with photo induction and with heat, and the results compared. The loading and releasing of high pressure hydrogen will be repeated and assessed, along with possible effects on performance and physical conditions of the microspheres. A sufficient quantity of selected hollow glass microspheres will be produced and a proof-of-principle hydrogen storage device fabricated and tested. Hydrogen loading and release performance of the storage device will then be evaluated.

Results

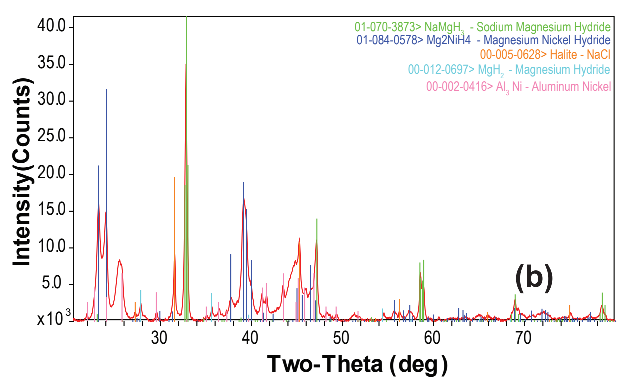
Alanate Development

Compositions containing various ratios of the metallic elements as $(Na,Mg,Fe)(AlH_4)_x$ and $(Li,Mg,Ni)(AlH_4)_x$ were synthesized via MSP at 100 bar/190°C. Neither Ni nor Fe were observed to form high hydrogen containing compounds as anticipated. The iron containing compositions resulted in essentially unreacted iron as shown in the x-ray diffraction spectra given in Figure 1a. Here the product of mixing $NaAlH_4$ and MgH_2 results in the formation of $NaMgH_3$ plus free aluminum. This has been observed previously and reported as a possible 3.75 wt% reversible reaction. Figure 1b shows the x-ray spectra for sodium alanate combined with the reversible hydride Mg_2NiH_4. Utilization of this relatively high temperature reversible hydride was found to be an ideal method of introducing Ni which does not have a stable room temperature hydride phase. Other attempts to introduce Ni powders led to minimal incorporation of this metal in any form similar to the iron containing samples described previously. In this case, however, incorporation of Ni in the hydride resulted in formation of the product phase Al_3Ni. This would lead to a reversible reaction as given in Figure 1b having a theoretical weight fraction of 3.3 wt%.

Compositions containing Li were not observed in many of the products. These compositions must have resulted in materials having either amorphous phases containing lithium or crystalline products as of yet unidentified which are masking by the other products. To definitively determine this, a new x-ray source, Co, is required and currently being obtained. The new source



$NaAlH_4+MgH_2+Fe$ =MSP=> $NaMgH_3+Al+Fe+{}^3/_2H_2$



$3NaAlH_4+Mg_2NiH_4$ =MSP=> $2NaMgH_3+Al_3Ni+NaH+{}^9/_2H_2$

FIGURE 1. X-Ray Diffraction Spectra of Na,Mg,Al and Na,Mg,Ni Quaternary Materials Following MSP Processing

will change the incident radiation wavelength so as to separate the peaks of the different products.

HGMs

An experimental station has been set up at SRNL that is capable of loading glass microsphere samples with hydrogen up to 10,000 psi, at temperatures up to 400°C. Ten samples, five glass chips and five hollow microspheres, have been loaded with hydrogen at 1,500 psi and 400°C. Four of the five microsphere samples retained their physical appearance after hydrogen loading (see Figure 2). The 5th sample, which had extremely thin walls and was about 70% lighter than the other samples, did show a small amount of breakage. Some of these hydrogen loaded microsphere samples have been tested for hydrogen release behavior under both photo-induced and heated conditions at Alfred. The results confirmed the very important observation that photo induction alone can release the hydrogen rapidly.

Conclusions and Future Directions

Alanate Development

Attempts to fuse combinations of alkaline metal, alkaline earth metals and group VIII transition metals into alanate complexes has been unsuccessful in forming new complex compounds having high hydrogen capacity thus far. Emphasis will shift to fusing alkaline metal and alkaline earth alanates with group V, VI and VII transition metals. This will include incorporation of V, Cr and Mn into $(Na,Li,Mg)AlH_4$ compositions utilizing MSP. Thus far, work has been limited to MSP processing of alanate compounds. Future work will extend to MSP processing of quaternary "alloying" of $(Na,Li,Mg)NH_4$ & $(Na,Li,Mg)BH_4$ to determine its efficacy in these alternate complex hydride systems. The higher pressure/high temperature processing will be extended to include high pressure solute charging of alanates, boranes and amides.

HGMs

Results to date confirmed that hollow glass microspheres of special compositions can be loaded with high pressure hydrogen and the hydrogen can be released using photo induction alone. Microspheres with more variation in composition and in fabrication parameters will be produced and loaded with hydrogen with increasing pressures of up to 10,000 psi. The loaded samples will then be evaluated for hydrogen release and durability. Among the most important goals of this project are to gain a basic understanding of the photo-induced hydrogen diffusion phenomenon and to generate performance data for design, fabrication and demonstration of a proof-of-principle hydrogen storage device.

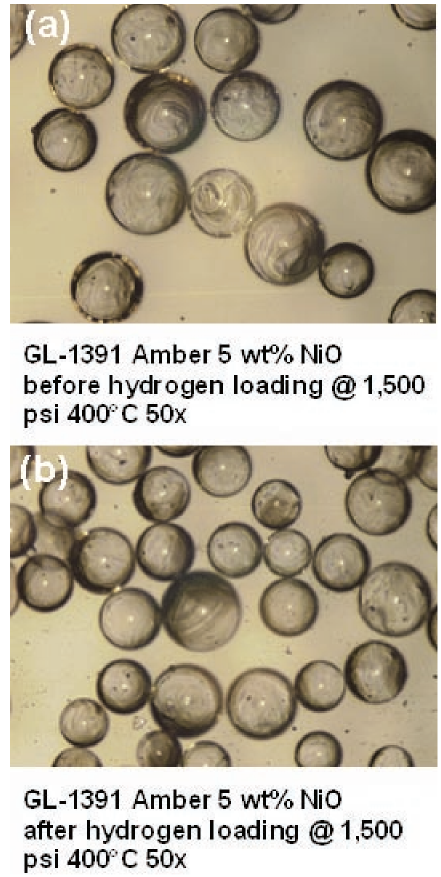


FIGURE 2. Hollow Glass Microsphere Before (a) and After (b) Hydrogen Filling

FY 2006 Publications/Presentations

1. "Development and Characterization of Novel Complex Hydrides- Synthesized via Molten State Processing" Material Research Society, Proceeding Fall Meeting Nov. 28 - December 2, 2005.

2. "Effect of graphite as a co-dopant on the dehydrogenation and hydrogenation kinetics of Ti-doped sodium aluminum hydride" *Journal of Alloys and Compounds,* Volume 395, Issues 1-2, 31 May 2005, Pages 252-262.

3. "Synthesis and crystal structure of Na_2LiAlD_6" *Journal of Alloys and Compound*, Volume 392, Issues 1-2, 19 April 2005, Pages 27-30.

4. "Synergistic effects of co-dopants on the dehydrogenation kinetics of sodium aluminum hydride, *Journal of Alloys and Compound*" Volume 391, Issues 1-2, 5 April 2005, Pages 245-255.

5. Complex Hydrides for Hydrogen Storage, Patent Number 20040105805, Allowed.