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## High Throughput Screening of Nanostructured Hydrogen Storage Materials

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### Program Scope

Our project combines high throughput combinatorial materials synthesis, high throughput screening along with fundamental studies to identify high capacity hydrogen storage materials with fast sorption and desorption kinetics. The project was initiated in September 2005. This extended abstract reports our research targets, the progress achieved and future plans.

Our program aims at the development of nanostructured metastable hydride materials that are capable of storing hydrogen based on both chemisorption and physisorption mechanisms, and with fast sorption and desorption kinetics, enabled by the small size and good heat transfer characteristics. In the early phases of this program the following targets have been identified:

- Development of combined synthesis and high throughput screening methods for discovery of nanostructured metastable metal and complex hydrides.
- Development of nanoporous hydride materials with integrated chemisorption and physisorption characteristics through the synthesis of nanocomposite materials with fine-tuning of the process conditions.
- Development of materials characterization techniques that are compatible with the combinatorial synthesis approach.
- Development of models and simulations for increasing our fundamental understanding of size effects on the thermodynamics, kinetics of hydrogen sorption and desorption, and heat transfer processes in nanostructured hydrogen storage materials.

### Recent Progress

#### (a) Synthesis of metastable hydride materials

Metal hydrides are solid alloys, some of which are capable of storing larger amounts of hydrogen at ambient temperatures and at much lower pressures than can be achieved with gaseous or liquid hydrogen. Hydrogen is a highly reactive element and is known to form hydrides with thousands of metals and alloys. However, there are some metals that do not form stable hydrides, such as iron and nickel. Metal hydrides are typically composed of metal atoms with a host lattice and hydrogen atoms that are trapped in the interstitial sites. Many of these compounds,  $MH_n$ , show large deviations from ideal stoichiometry and they can exist as multiphase systems, for example,  $\alpha$ -phase where only some hydrogen atoms are adsorbed, and  $\beta$ -phase where the hydride is fully formed (e.g.,  $Mg_2Ni$  forms hydrides of  $Mg_2NiH_{0.3}$  and  $Mg_2NiH_4$ ).

Most metals and complex hydrides, however, suffer from high thermal stability (hydrogen desorption temperatures  $> 250^\circ C$ ) and/or slow kinetics, which prevent these materials from being used in practice, as for example for automotive applications. The challenge with stable high capacity hydride materials is therefore to develop destabilization approaches that lower the enthalpy for hydride formation and to increase the kinetics. We aim to search for nanostructured

metastable hydrides that consist of atoms or molecules arranged in a higher energy state than expected for the most stable configuration. Kinetics will be increased by nanostructures, as discussed further in the next section. The metastable nature is a result of an energy barrier between the higher energy state and the stable lowest energy state of the material, and this barrier can also be tuned by nanostructures. The fundamental mechanism behind destabilizing hydride materials is to modify a material's atomic configuration, and thus the hydrogen-binding environment, by introducing structural and/or compositional disorder. This can be achieved by applying non-equilibrium materials synthesis methods, incorporating substitution and doping elements, adding catalysts, as well as using nanostructures such as nanoparticles. The purpose of substitution/doping using elements that do not form stable hydrides is for structural and compositional destabilization in the bulk of the material, while catalyst addition is to promote surface modification that can be done during the last stage of the hydride synthesis process.

In the past six months, we have completed calibration of a new laser pyrolysis system and successfully synthesized Mg and binary MgNi nanoparticles using the combinatorial laser pyrolysis method. Figure 1 shows a library of Mg-Ni nano-powders obtained under two laser pyrolysis conditions and four elemental ratios of Mg to Ni. The ability to synthesize Mg and Mg-Ni nanoparticles and to incorporate them into nanoporous structures is an important first step in our quest to use nanostructured metastable hydrides to enhance hydrogen storage.

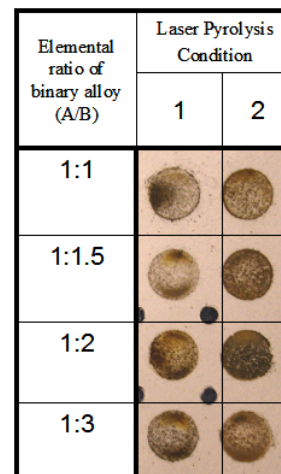


Figure 1 Pictures of synthesized Mg-Ni nanoparticles.

#### (b) Mesoporous silica scaffolds for enhancing the $MgH_2$ release kinetics

The use of nanostructures serves multiple functions. Nanoporous structures tune the thermodynamics by incorporating destabilizing metals or catalysts onto a composite material, enhance the kinetics by increasing the diffusivity and reducing the diffusion distance, and increasing the reaction surface area. In addition, nanoporous structures offer mechanical durability, a property that ensembles of nanoparticles do not have. Nanoporous materials with high internal surface densities can also be exploited for physisorption. At Berkeley, experiments have been carried out on hydrogen storage in aerogels and preliminary results showing up to approximately 2% hydrogen storage at 20 Bar (Figure 2) have been achieved.

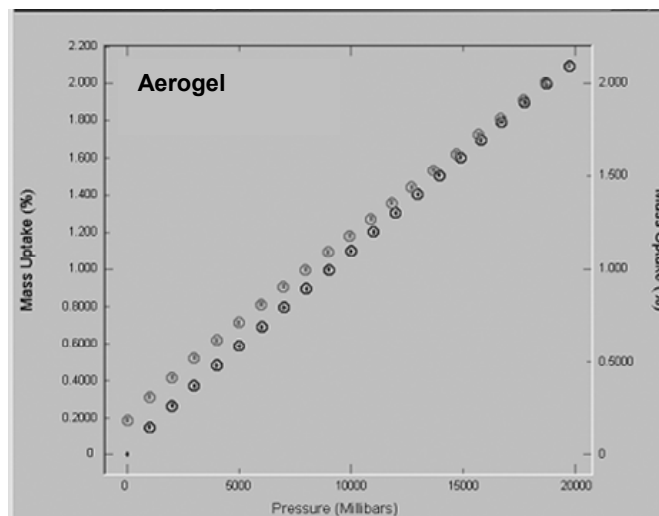


Figure 2 Hydrogen sorption results in pure aerogel.

At North Carolina State University (NCSU), Magnesium hydride ( $\text{MgH}_2$ ) powders and two other types of metal nanoparticles (100 nm) have been successfully incorporated into nanoporous silica aerogels. During aerogel synthesis, water is required for the hydrolysis of silicon alkoxide (TEOS) and water is also produced in the condensation or gelation step. We have modified a well established aerogel synthesis route to eliminate the residual water after hydrolysis and we have greatly minimized  $\text{MgH}_2$  dehydrogenation by rapid condensation and solvent exchanges.

A selected type of nanoparticle that can be used to catalyze the  $\text{MgH}_2$  decomposition has also been incorporated into the gels. We have developed a new synthesis procedure for the preparation of the selected metal nanoparticles which employs metal displacement reduction. The resulting aerogels are heavily loaded with nanoscale metal particles (1-50 nm). This “in-situ” technique provides much greater loading of metal nanoparticles than the conventional “wet impregnation” techniques and allows all metal precursors to be removed through solvent exchanges. Figure 3 shows three synthesized samples and preliminary results for their kinetics. The results of Figure 3 clearly show that  $\text{MgH}_2$  embedded in an aerogel with metal catalysts has a faster kinetics. We anticipate that the use of a silica nanoporous scaffold and nanostructured  $\text{MgH}_2$  will facilitate  $\text{MgH}_2$  decomposition at a significantly lower temperature than  $\text{MgH}_2$  alone and that the addition of selected catalytic metal nanoparticles to the scaffold will further reduce the  $\text{H}_2$  release temperature and enhance the kinetics of the hydrogen release.

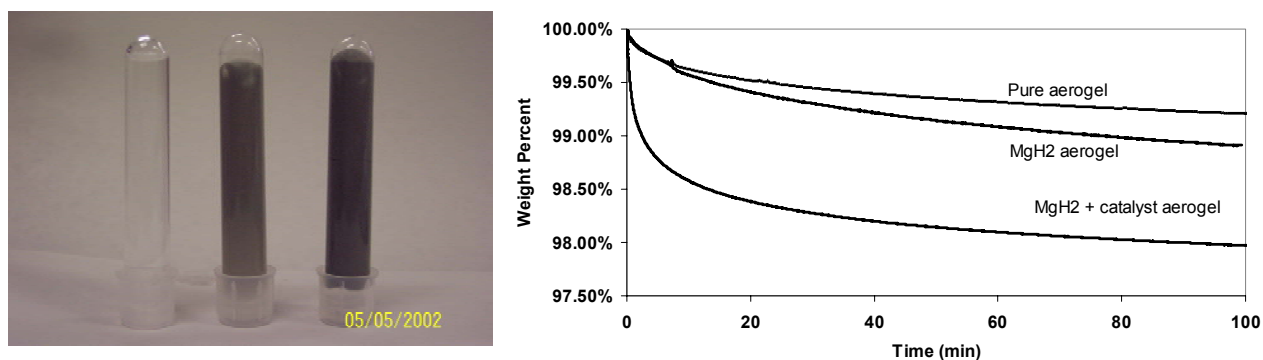


Figure 3 Nanocomposite  $\text{MgH}_2$  and preliminary results of the kinetics. Left Vial - pure aerogel (no additives); Middle Vial - aerogel with embedded  $\text{MgH}_2$  powder (~50 wt%); Right Vial - aerogel with  $\text{MgH}_2$  (~50 wt%) and a catalyst with the size of 100nm (~2 wt%). Data in the right figure show an improvement in the kinetics of nanocomposite  $\text{MgH}_2$  material with regard to the control of the amount of hydrogen released and the time constant for the release.

### (c) Modeling

The MIT team has been engaged in modeling the effects of size on the thermodynamics and kinetics for physisorption and chemisorption. Efficient hydrogen storage materials should have a small enthalpy of formation. Our preliminary study shows that the enthalpy of reaction can be tuned by exploiting the size effect, potentially leading to a smaller enthalpy of formation and thus less heat released during the sorption processes, and conversely, less heat addition required in the dehydration process. We are also studying the kinetics of hydrogen diffusion through nanopores using Monte Carlo simulation and diffusion through the solid, aiming at identifying conditions under which the kinetics for both the gas phase and solid phase transport can be balanced.

### (d) Characterization

The Berkeley team has completed a setup including an infrared camera integrated with a new hydride testing chamber for high throughput characterization of combinatorial metal hydride samples based on infrared reflectivity measurements. Fabrication of microcantilever array for

qualitative weight measurements is in progress at the Berkeley microfabrication laboratory. The MIT team is also developing laser pump-and-probe techniques for fast screening of the thermal conductivity of combinatorial synthesized materials. The technique could also probe the ultra-fast non-equilibrium hot electrons, electron phonon interaction and phonon transport to gain fundamental understanding of the electronic and thermal properties at the material interface. Better understanding of the structure of the hydrogen binding at the interface will in turn help in synthesizing better hydrides. Figure 4 shows some preliminary signals we obtained from the system.

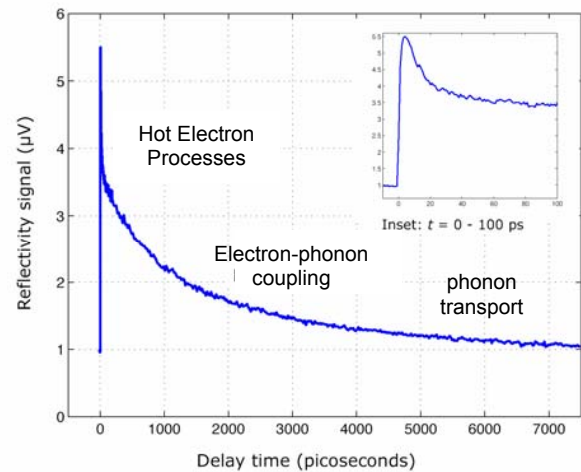


Figure 4 Pump-and-probe techniques for characterization of thermal and electronic properties. Upper right: Zoom on the first 100ps of the decay.

### Future Plans

For better understanding of the effects of particle or grain size on the thermodynamic properties of potential hydrogen storage materials, an accurate determination of the surface energy and reaction enthalpy at the nanoscale is essential. In the future we plan to carry out modeling studies, followed by first principles calculations to determine such quantities. We will continue the development of Monte Carlo simulation schemes for gas phase transport, and eventually combine these with first principle simulation studies of adsorption processes at interfaces. Thermal properties of nanoporous structures will also be modeled, aiming at a balanced development of materials with good kinetics and good heat transfer.

For combinatorial metal hydride material synthesis, by replacing Ni with other element(s), we will move from fabricating nanoscale Mg-Ni alloy system to screening Mg-X and Mg-X-Y alloys in the second half of this fiscal year. We will continue with the development of high throughput characterization approaches, including the laser pump-and-probe technique for fast screening the thermal and electronic properties of candidate materials, the infrared reflectivity measurements, and the microcantilever technique. Our current focus is on improving the sensitivity of the three different characterization systems.

For the development of nanostructured porous hydride materials, we will synthesize a series composition-controlled nanocomposite metal hydrides by integrating aerogels or other nanoporous matrix scaffolds with different destabilized hydride materials, starting from nanoscale  $\text{MgH}_2$  embedded with selected metal catalysts to achieve the desired chemisorption properties. We will also tune the pore size to optimize the joint physisorption and fast kinetics requirements.

### Publications

1. B. P. Mosher, S. S. Mao, G. Chen, and T. Zeng, Investigation of Hydrogen Storage and Absorption/Release Kinetics in Nanocomposite Metal Hydride and Nanoscaffolds, Presented at MRS (Material Research Society) Spring Meeting, San Francisco, April 2006.