III.C.4 Discovery of Novel Complex Metal Hydrides for Hydrogen Storage through Molecular Modeling and Combinatorial Methods

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Objectives

Discovery of a complex metal hydride through molecular modeling and combinatorial methods, which will enable a hydrogen storage system that meets DOE 2010 performance goals. The deliverables include:

- Delivery of one kilogram of optimized material.
- A potential manufacturing process.
- A design for a hydrogen storage system.
- Accompanying documentation.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- A. Cost
- B. Weight and Volume
- D. Durability
- E. Refueling Time
- M. Hydrogen Capacity and Reversibility
- N. Lack of Understanding of Hydrogen Physisorption and Chemisorption

Approach

- Identify H_2 storage material enabling DOE targets and increase understanding of promoted complex hydrides using:
  - Virtual high throughput screening of new materials & catalysts
  - Combinatorial synthesis & screening
  - Extensive testing, characterization and modeling of leads

- Demonstrate viability for commercial application:
  - Scale-up material meeting targets to 1 kg for samples for independent testing by Southwest Research Institute
  - Identify potential commercial manufacturing route
  - Design H_2 storage system
  - Perform material manufacturing cost estimates

Accomplishments

- Developed an empirical force-field calculation that predicts accurate geometries and thermodynamic functions for alkali hydrides, alkaline earth hydrides, the lithium alanates and the sodium alanates.
- Established an inert-atmosphere laboratory for medium throughput synthesis and testing of promoted complex metal hydrides.
- Established an approach to characterize multiple hydride samples using x-ray diffraction (XRD).
- The medium throughput (8 at a time) assay is operational and validation has begun.
- Developed a design for the high throughput assay (48 at a time).

Planned Work in FY05

- Implement a method to predict the crystal structure of complex hydrides.
- Use molecular modeling to predict which mixture of $NaAlH_4$, $LiAlH_4$ and $Mg(AlH_4)_2$ will be best for hydrogen storage.
- Complete validation of the promoted hydride synthesis.
- Complementing the molecular modeling, begin experimental investigate the Ti/Li-Na-Mg-Al-H system.
- Design and construct the high-throughput synthesis assay.
- Complete validation of the medium throughput assay.
- Initiate screening of novel hydrides and dopants according to the statement of work.

Introduction

Hydrogen can be stored as a chemical compound. Solid hydrides can release hydrogen reversibly under acceptable conditions (for example $LaNi_5H_6$). However, these materials are too heavy and expensive for on-board vehicle applications. Unfortunately, the known reversible metal hydrides which have the desired gravimetric densities, such as MgH_2, require high temperatures to release hydrogen. Currently, there exist no solid hydrides exist which can meet all DOE 2010 hydrogen storage system targets. Recently, it has been shown that the complex hydride $NaAlH_4$ can reversibly absorb hydrogen at lower pressures and temperatures than MgH_2 and has a higher gravimetric capacity and lower cost than $LaNi_5H_6$. Complex hydrides form a new class of reversible hydrides which have not been fully explored. It is possible that a novel complex hydride could have improved properties for on-board hydrogen storage. This project proposes to systematically survey complex hydrides to discover a material which would enable a hydrogen storage system that meets DOE's 2010 goals.

Approach

The team will apply methods of combinatorial chemistry and molecular modeling to discover materials with optimum thermodynamics and kinetics for on-board hydrogen storage. The increased throughput of combinatorial methods enables many more materials and conditions to be investigated for systematic study of the trade-offs between storage capacity and stability. Virtual high-throughput screening (VHTS) exploits the capability of molecular modeling to estimate the thermodynamics on the computer more quickly than can be measured in the laboratory. VHTS will be used to screen complex hydrides to find materials which could meet the DOE system requirements and focus the synthesis effort on making the most

promising materials. Even more importantly, the coupling of combinatorial experiments with molecular modeling of structural and thermodynamic properties will provide insights into the underlying mechanisms of action in these complex materials, permitting the design of hydrogen storage materials which would never have been envisioned otherwise.

Results

(1) Subcontractors

An agreement with Hawaii Hydrogen Carriers has been executed. Agreements with the University of California Los Angeles (UCLA), Ford, and Striatus are being negotiated.

(2) Molecular Modeling of Complex Hydrides

An empirical force-field that predicts accurate geometries and thermodynamic functions for alkali hydrides, alkaline earth hydrides, the lithium alanates and the sodium alanates has been developed. Figure 1 shows a comparison of the predicted heat capacity as a function of temperature for $NaAlH_4$, Na_3AlH_6, $LiAlH_4$ and Li_3AlH_6. This force-field will allow the prediction of thermodynamics of the new phases resulting from mixtures of complex hydrides. The predicted thermodynamics will be used to estimate the Pressure-Composition-Temperature (PCT) curves for complex hydrides. The PCT curves will be used to select the candidate materials for hydrogen storage.

(3) Inert-Atmosphere Laboratory

An inert-atmosphere laboratory has been established with the following components: 4-port synthesis glove box; solvent purification system; common gas manifold to supply low- and high-pressure H_2, N_2, and Ar; vacuum line; large hood for starting material purification and organic synthesis; 2-position high-intensity ball mill; 4-position high-intensity ball mill capable of milling 8 samples at a time; 4-port testing glove box; assay system capable of measuring H_2 desorption from 8 samples at a time.

(4) Synthesis

In order to validate the synthesis and testing methods, samples of $Ti/NaAlH_4$ and $Zr/NaAlH_4$ have been prepared using the ball-milling method.

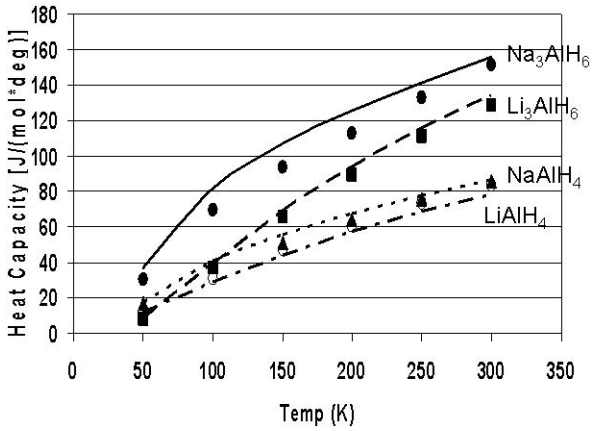

Figure 1. Comparison of Predicted and Experimental Heat Capacities for Complex Hydrides (The theoretical prediction is plotted as a curve. The experimental data is plotted as symbols.)

Subsequent syntheses have focused on doped $NaAlH_4$ using TiH_2, $Ti(OiPr)_4$, $TiCl_4$, ZrH_2, ZrF_4, and YbF_3 with dopant levels ranging from 1-8 mol-% of the $NaAlH_4$. Ball milling was used to mix the dopant and $NaAlH_4$, processing the mixtures at 350 rpm for 30 minutes, with 15 minutes in each direction. For the Ti dopants $Ti(OiPr)_4$ and TiH_2, scanning electron microscopy/energy dispersive x-ray (SEM/EDAX) showed that the dispersion of the Ti was superior for the liquid $Ti(OiPr)_4$ versus solid TiH_2 dopants. Some initial SEM/EDAX work on a high-throughput (48 possible) but low-intensity mix method (compared to ball milling) gave similar results for the solid TiH_2 dopant. The high-throughput/low-intensity approach needs to be tested with liquid dopants to see if the dispersion is comparable to that obtained via ball milling. To follow the reactions, XRD is a useful characterization tool. A high-throughput XRD plate used in other applications was adapted with a polycarbonate film to protect the metal hydrides from the atmosphere. The XRD patterns were collected in one-minute scans on the Bruker Advanced X-ray Solutions General Area Diffraction System (AXS GADDS) diffractometer. Figure 2 shows patterns for $NaAlH_4$ doped with a) TiH_2, b) YbF_3, and c) ZrH_2, all at 8 mol-% levels.

(5) Testing

The medium throughput assay has been installed in a dedicated glove box, and shake-down has been completed. Validation using known doped hydrides

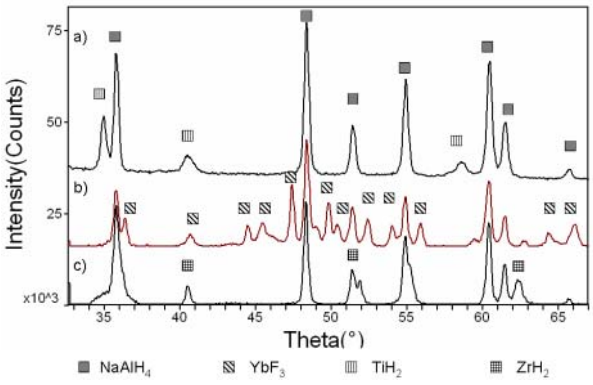

Figure 2. XRD Patterns of a) TiH_2, b) YbF_3, c) ZrH_2-Doped $NaAlH_4$ Taken through Protective Polycarbonate Film

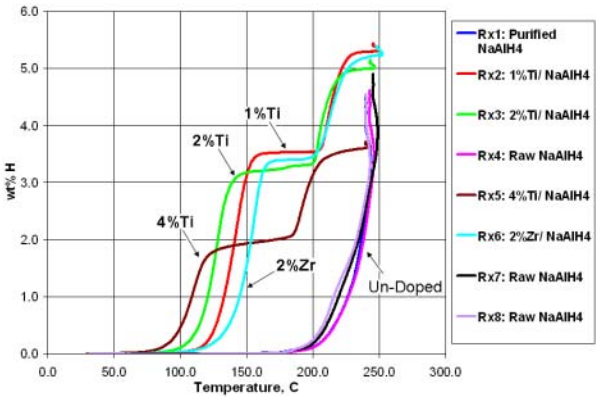

Figure 3. First-Cycle Desorption for 8 Hydride Samples Analyzed in a Single Run

is currently in progress. The following test protocol is being used:

(a) Desorption to 240°C to measure the initial H_2 content;
(b) Re-hydriding at 125°C and 1000 psig H_2 for 16 hours, followed by
(c) A second desorption to 240°C to measure reversible H_2 content.

H_2 evolution for samples of un-purified $NaAlH_4$ (3 samples), purified $NaAlH_4$, 1 mol-% Ti/$NaAlH_4$, 2 mol-% Ti/$NaAlH_4$, 4 mol-% Ti/$NaAlH_4$, and 2 mol-% Zr/$NaAlH_4$ was measured in a single run. The doping was performed by ball milling $NaAlH_4$ with $Ti(OiPr)_4$ and Zr-fluoride. The H_2 evolution versus temperature for the as-synthesized materials is shown in Figure 3. The H_2 evolution for the second

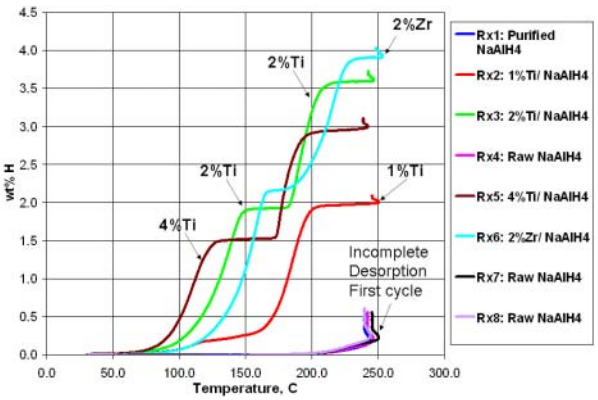

Figure 4. Second-Cycle Desorption for 8 Hydride Samples Analyzed in a Single Run

desorption, after re-hydriding, is shown in Figure 4. These results show, in agreement with literature data, that increasing the concentration of Ti lowers the temperature for H_2 desorption and that there is an optimum in the reversible H_2 content near 2 mol% Ti.

Conclusions

- Empirical force-fields can be used to predict structures and thermodynamic functions of complex hydrides. This will facilitate the prediction of properties of complex hydrides. The predicted thermodynamics will allow us to estimate the pressure-composition-temperature (PCT) curves of novel complex hydrides and select target materials for hydrogen storage.
- The experimental capability for medium throughput synthesis and testing of doped hydrides has been established and experiments are in progress.

FY 2004 Publications/Presentations

1. "Discovery of Novel Complex Metal Hydrides for Hydrogen Storage through Molecular Modeling and Combinatorial Methods," presentation to the H_2 Storage Tech Team Meeting, March 18, 2004, Detroit, MI, by J.J. Low.

2. "Discovery of Novel Complex Metal Hydrides for Hydrogen Storage through Molecular Modeling and Combinatorial Methods," presentation to the 2004 HFCIT Annual Program Review, May 24-27, 2004, Philadelphia, PA, by J.W. Adriaan Sachtler.