Novel Synthetic Approaches for the Preparation of Complex Hydrides for Hydrogen Storage

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This presentation does not contain any proprietary or confidential information

METAL HYDRIDE CENTER OF EXCELLENCE

Project ID #
STP19

OAK RIDGE NATIONAL LABORATORY

Project Overview

Timeline

Project Start Date: Initiated FY05

Project End Date: FY09

Percent Completed: New Start

Budget

FY 2005 Budget: $200K

FY 2006 Budget: $200K

Collaboration

ORNL is a partner in the *Metal Hydride Center of Excellence*

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Barriers to Success

The properties of reversible solid state materials will be challenged to meet the goal of demonstrating by 2010 an on-board hydrogen storage system achieving 6 wgt % hydrogen

ORNL will work with MHCoE partners to address:

- Weight and volume
- Cost
- Hydrogen capacity and reversibility
- Lack of understanding of hydrogen chemisorption and physisorption
- Safety

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Critical Technologies for Success

meeting the goals for 2010 will require:

- The development of materials for more compact, light weight, lower cost, safe and efficient storage systems
- Understanding the chemical and physical processes governing the hydrogen-materials interactions to enable the design and discovery of new, higher efficiency, recyclable hydrogen storage materials.
- Designing nanostructured catalyst/support to achieve fast cycling at accessible conditions

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Objectives

ORNL will develop solution–based synthetic methods for preparation of catalyzed alanates and amides of light elements for reversible storage of hydrogen

Collaborate with MHCoE partners to demonstrate a system for the safe and cost-effective storage and delivery of gaseous hydrogen under practical operating conditions that will achieve the DOE/FreedomCAR performance targets for 2010.

Development of synthetic methods in support of MHCoE collaborators

Discovery of new complex metal hydrides

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Approach

Research at ORNL will take advantage of expertise in solution-based synthesis including reactions in liquid ammonia

Synthetic Capabilities: Synthetic methods in solution – vacuum line, Schlenk line, cannula, and glovebox methods to handle oxygen and water sensitive materials.

Characterization Methods: Temperature programmed decomposition, reaction products determined with mass spectroscopy, in-situ X-ray diffraction, IR and Raman spectroscopy, NMR spectroscopy, Sievert's apparatus for P-T-C determination

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Approach (continued)

ORNL will explore materials synthesis of new and known materials using synthetic methods appropriate for scale-up to production and practical application

Alanates have large (~50%) change in lattice dimensions upon hydriding and de-hydriding;

Significant difference in thermal conductivity of hydride and dehydrided material

Nanoscale to mesoscale superstructure will be needed to maintain bed dimensions, allow for heat transfer, and improve kinetics of hydrogen transfer with scale-up

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Approach (continued)

Materials processed by high energy ball milling appear to release and takes up H_2 at a lower temperature than material prepared by solvent processing

Solvent processing will be needed if reactor bed has preformed superstructure

Work with MHCoE partners to understand influence of processing method

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Technical Accomplishments Progress/Results

Funding received in mid-February, 2005

Laboratory space identified for set-up of temperature programmed thermal decomposition apparatus utilizing mass spectrometer for product identification

Equipment ordered: oxygen and water meters for glove box, vacuum pumps, other apparatus

Preparation of Research Safety Summary (RSS) is in progress (at ORNL experimental work cannot begin until RSS approved)

Technician trained on operation of Sievert's apparatus

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Technical Accomplishments (cont)

Limited funding – initially focus on several tasks

Immediate plan in remainder of FY05:

- prepare alanates of Li and Mg using $AlH_3 \cdot OR_2$ as a reactant in ether solvents and incorporate Ti catalyst as organometallic complexes of the form $TiR_{(4-n)}(AlH_4)_n$ where R = alkyl or aryl that is thermally labile
- prepare amides (and imides or nitrides) of Li and Mg in liquid ammonia incorporating Ti catalyst as "TiN" using previously characterized product of the ammonolysis of $Ti(NR_2)_4$ in liquid NH_3

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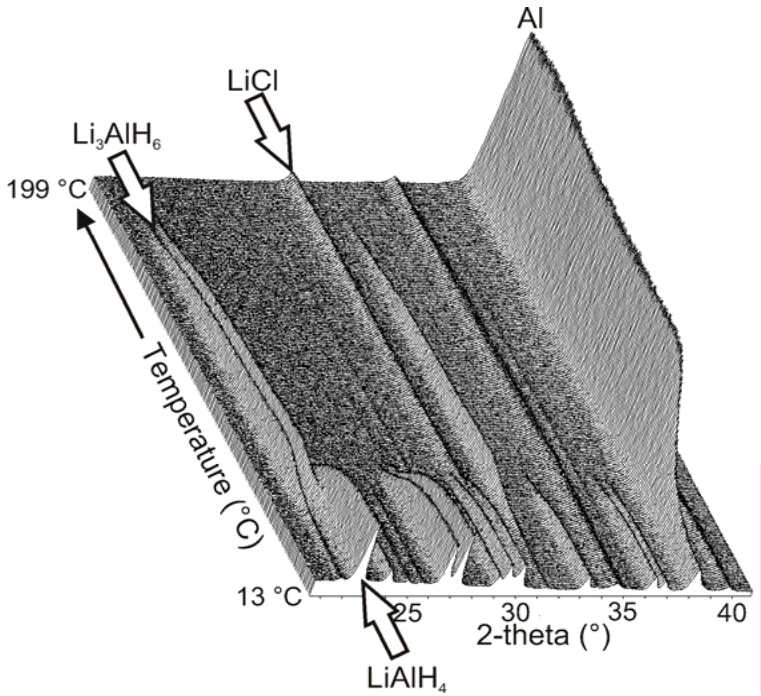
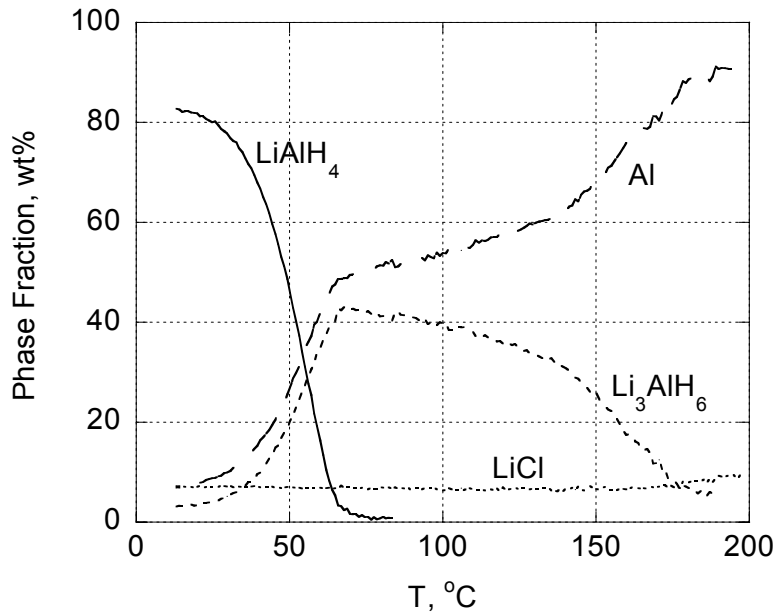
Results – Prior Work

Hydrogen Release from $LiAlH_4$





D. S. Easton, J. H. Schneibel, and S. A. Speakman, submitted for publication

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Future Work

SNL success with Mg modified Li amide suggest that multi-element metal hydrides may be needed to meet 2010 goals; solution based processing may facilitate preparation

Subtask 1.1 - Development of Synthetic Methods

Support collaborators with synthetic methods that can be scaled up; materials identified in combinatorial, theoretical studies FY06 and FY07

Subtask 1.2 - Discovery of New Complex Metal Hydrides

Process for preparation of alanates from $AlH_3 \cdot OR_2$ as precursor; Mg in combination with alkali metal – FY06

Preparation and properties of metal borohydrides; investigate borohydrides of Al, Mg, and Zr - FY07

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Publications and Presentations

D. S. Easton, J. H. Schneibel, and S. A. Speakman, “Factors affecting hydrogen release from lithium alanate ($LiAlH_4$),” submitted for publication

(work sponsored by ORNL LDRD funds)

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Summary of Research Tasks

Task Description	2005	2006	2007	2008	2009
Develop synthetic methods in support of MHCoE partners	X	X	X	X	X
Discover New Metal Hydrides	X	X			
Scale-up Synthesis			X	X	X

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