Design of Novel Multi-Component Metal Hydride-Based Mixtures for Hydrogen Storage

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Overview

Timeline

- Project Start Date: 9/1/08 (Funding started Feb. 09)
- Project End Date: 8/31/13
- 2% complete (one month of funding)

Budget

- Total Budget: $2714K
  - DOE Share: $2160K
  - Contractors Share: $554K
- Funding for FY08: $75K
- Funding for FY09 $450K

Barriers

- Barriers addressed
  - P. Lack of Understanding of Hydrogen Physisorption and Chemisorption
  - A. System Weight and Volume
  - E. Charging/Discharging Rates

Partners

- Northwestern University
- UCLA
- Ford Motor Company
- Project lead: Northwestern University

Relevance - Project Objectives

- 3 Materials Classes (chemical, metal/complex, physisorptive) divided into DOE Centers of Excellence
- **Our project: <u>Combine</u> materials from <u>distinct categories</u> to form novel multicomponent reactions**
- Systems to be studied include mixtures of complex hydrides and chemical hydrides [e.g. $LiNH_2+NH_3BH_3$] and nitrogen-hydrogen based borohydrides [e.g. $Al(BH_4)_3(NH_3)_3$].
- These types of combinations have only recently begun to be explored – initial results look very promising!
- PIs have extensive experience in H_2 storage research, from materials and automotive perspectives

Relevance: Motivation for Novel Combinations- I

High-capacity hydrogen storage in lithium and sodium amidoboranes

ZHITAO XIONG[1], CHAW KEONG YONG[1], GUOTAO WU[1], PING CHEN[1,2]*, WENDY SHAW[3], ABHI KARKAMKAR[3], THOMAS AUTREY[3], MARTIN OWEN JONES[4], SIMON R. JOHNSON[4], PETER P. EDWARDS[4] AND WILLIAM I. F. DAVID[5]

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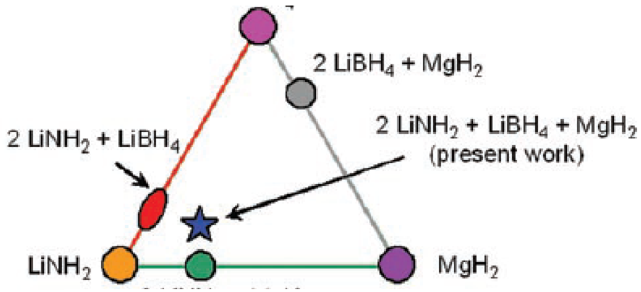
- **Combinations of NH_3BH_3 (a chemical hydride) with LiH or NaH (metal hydrides)** → novel alkali metal amidoborides, $LiNH_2BH_3$ and $NaNH_2BH_3$, which release a large amount of hydrogen at 90ºC, ~10.9 and 7.5 wt.%.
- Similar results found at Ford for combinations of NH_3BH_3 with other metal/complex hydrides
- Very promising results open a wealth of possibilities involving combinations of NH_3BH_3 with other metal hydrides and complex hydrides.
- The number of such combinations is enormous, and hence a systematic method of screening for promising reactions is required.

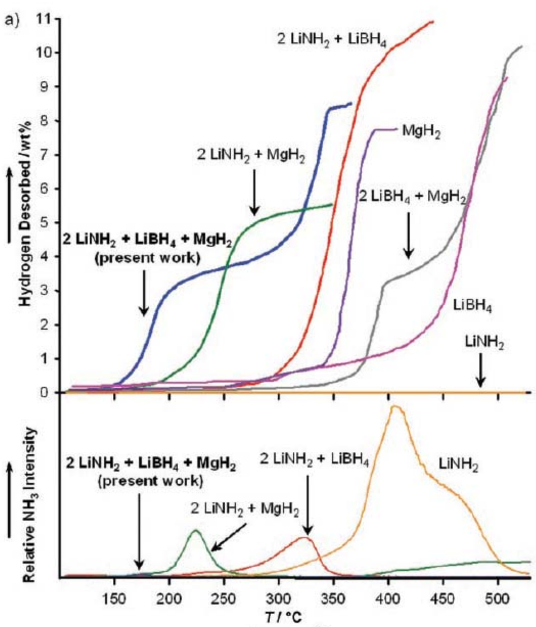
Relevance: Motivation for Novel Combinations- II

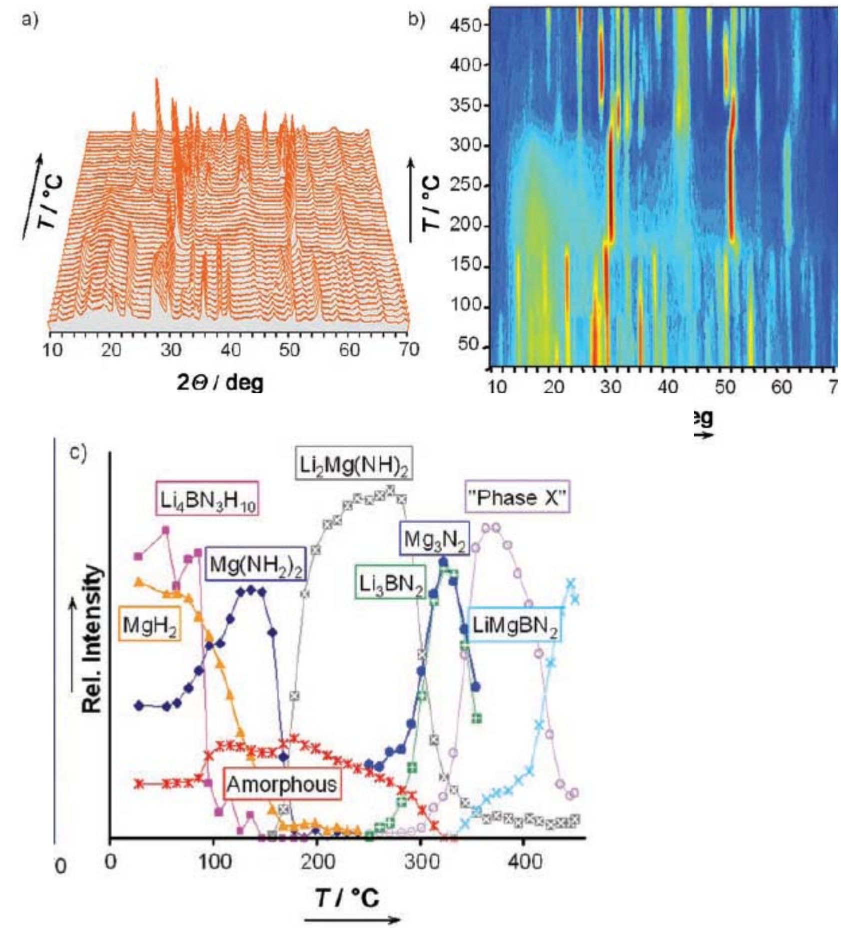
- **Nitrogen-hydrogen based borohydrides** (e.g., ammoniated metal borohydrides) researched extensively twenty years ago [Konoplev 1985, Kravchenko 1990], but have not received much attention as hydrogen storage materials. Recent GE [Zhao 2007] work has shown $Mg(BH_4)_2{\cdot}(NH_3)_2$ has enhanced properties. Discovery by GM/Oxford/Toyota groups of $Li_4(BH_3)(NH_2)_3$ another successful example in this area.
- Ammoniated metal borohydrides are actually quite common: Li, Na, Al, Mg, Ca, Be, Zn, Sc, Y La, Zr, Cr, and Co [Kravchenko 1990]. Most of these remain largely unexplored for hydrogen storage applications.
- NH_3 is a well known poison for PEM fuel cells (but not H2ICE), so we will carefully monitor for both H_2 and NH_3 release.

Relevance: Motivation for Novel Combinations- III

- Recent collaborative work by PI's has demonstrated enhanced properties from <u>combinations of materials</u>





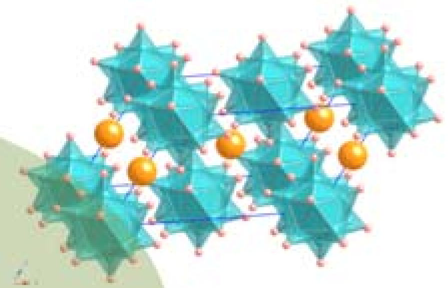


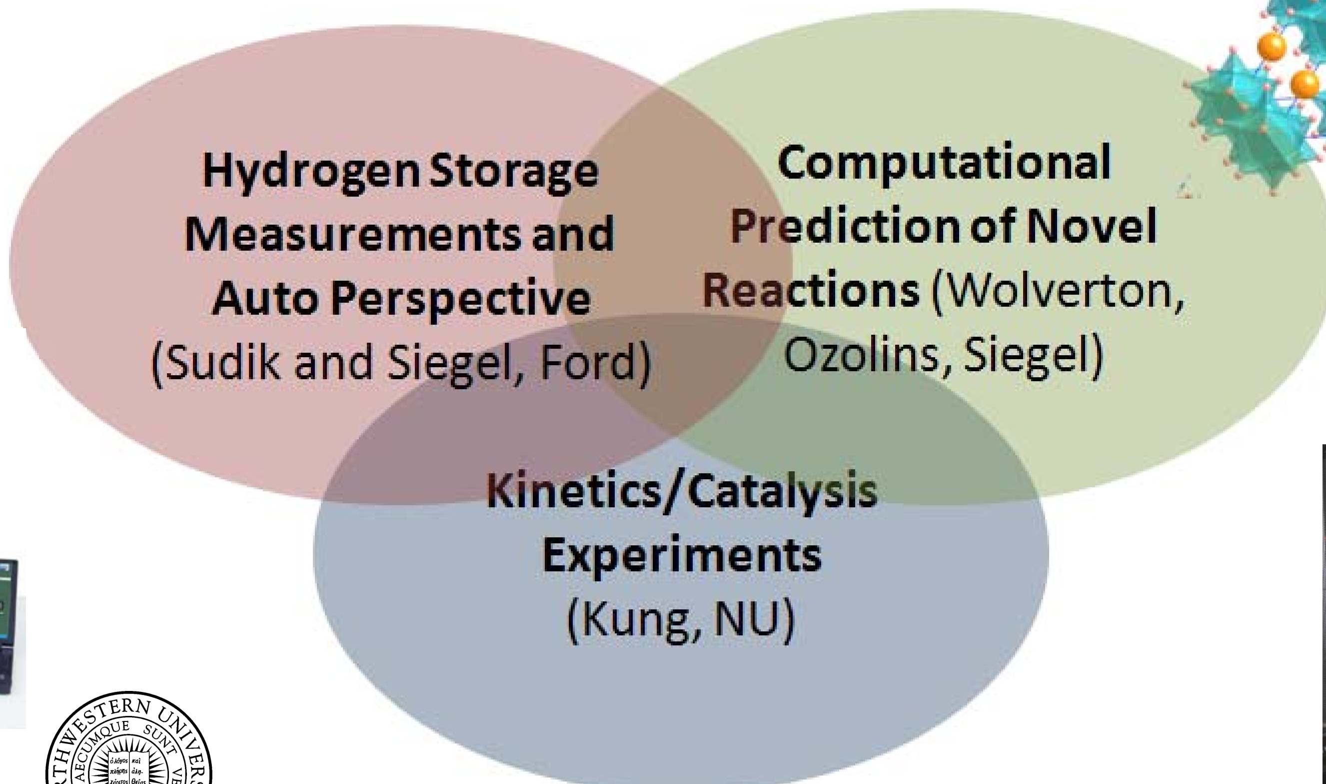
Yang, Sudik, Siegel, Wolverton, Ozolins et al., Angew. Chem. Int. Ed., 47, 882 (2008).

Approach

Our approach involves a powerful blend of:

1) H2 Storage measurements and characterization, 2) State-of-the-art computational modeling, 3) Detailed catalysis experiments, 4) In-depth automotive perspective





NORTHWESTERN UNIVERSITY

UCLA

Ford

Approach: Project Organization

Organization	Roles and Responsibilities
Northwestern University (Wolverton and Kung)	• Overall project and technical management (Wolverton) • Lead effort in first-principles calculations of NH_3BH_3 mixtures (Wolverton) • Lead effort in identifying new storage reactions (Wolverton) • Lead effort in experimental studies of new catalysts and catalytic activity (Kung) • Experimental characterization of hydrogen storage materials (Kung)
Ford (Siegel and Sudik)	• Collaborate in computational studies (Siegel) • Consult on material selection and testing (Sudik and Siegel) • Lead effort in material synthesis and measurements of H_2 storage properties (Sudik)
UCLA (Ozolins)	• Lead effort on first-principles calculations of ammoniated borohydrides • Lead first-principles studies of reaction kinetics and design of catalysts

Approach: Milestones/Go No-Go Decision Point

- By the end of the 3rd year, complete DFT thermodynamics calculations [Wolverton, Ozolins, Siegel] **Milestone**
- By the end of the 3rd year, complete experimental studies of desorption temperature, capacity and purity on remaining compositions. [Sudik] **Milestone**
- **Go/No-go decision** (end of Year 3): Identify a mixed materials system that experimentally desorbs 8.5 wt% H2 and has measured or predicted first-principles thermodynamics enabling operation in a reversible storage window between -40 and 80C and 1 and 700 bar. [All]

Approach: Experimental Capabilities

- Ford's hydrogen storage research laboratory is designed for handling, synthesizing, & processing diverse materials, including those which require air/water-free conditions

Synthesis, Handling, & Processing Equipment:

- MBraun Labmaster 130 gloveboxes
- Controlled energy-temperature mixer mills
  - Spex 8000, Spex Freezer, Fritsch P7, Retsch MM301
- High- and low-pressure manifolds
  - High: vacuum to 200 bar (Ar, N_2, NH_3, H_2)
  - Low: vacuum to 1 bar N_2 (Schlenk line)
- Tube and muffle furnaces
- Arc-melting furnace (>3000ºC) (Thermal Tech. LLC)

MBraun Labmaster Glovebox

Spex High-Energy Ball Mill

Approach: Experimental Capabilities

❖ Extensive characterization and property evaluation instruments available on-site for identification of reaction phases and determination of principal hydrogen storage properties

Phase Characterization Apparatus:

- *In situ* variable temperature & static PXRDs (SCINTAG XDS2 and X1)
- *In situ* variable temperature & static IR spectrometers (Mattson Inst.)

Property Evaluation Instruments:

- TPD-MS built in-house (MKS PPT MS)
- Setaram high-pressure DSC (max. 900ºC; 400 bar H_2)
- Setaram PCT Pro-2000 apparatus (max. 400ºC; 200 bar H_2)
- Several volumetric water displacement burettes

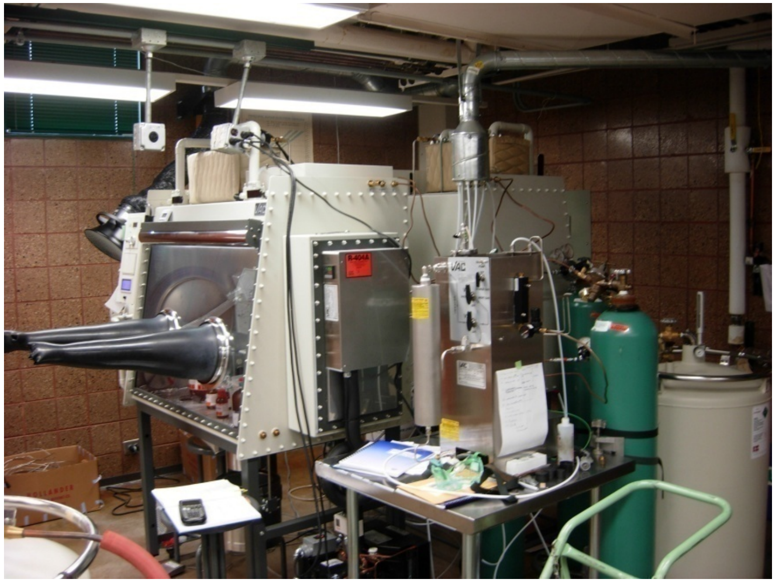
Setaram PCT Apparatus

Setaram High Pressure DSC

Approach: Experimental Capabilities

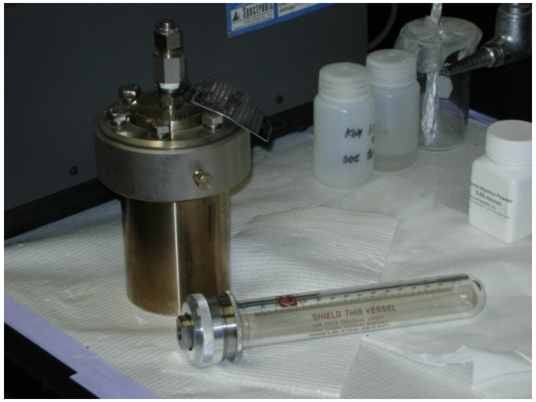
Facility to handle air-sensitive materials at Northwestern

•Glove boxes



• Schlenk lines

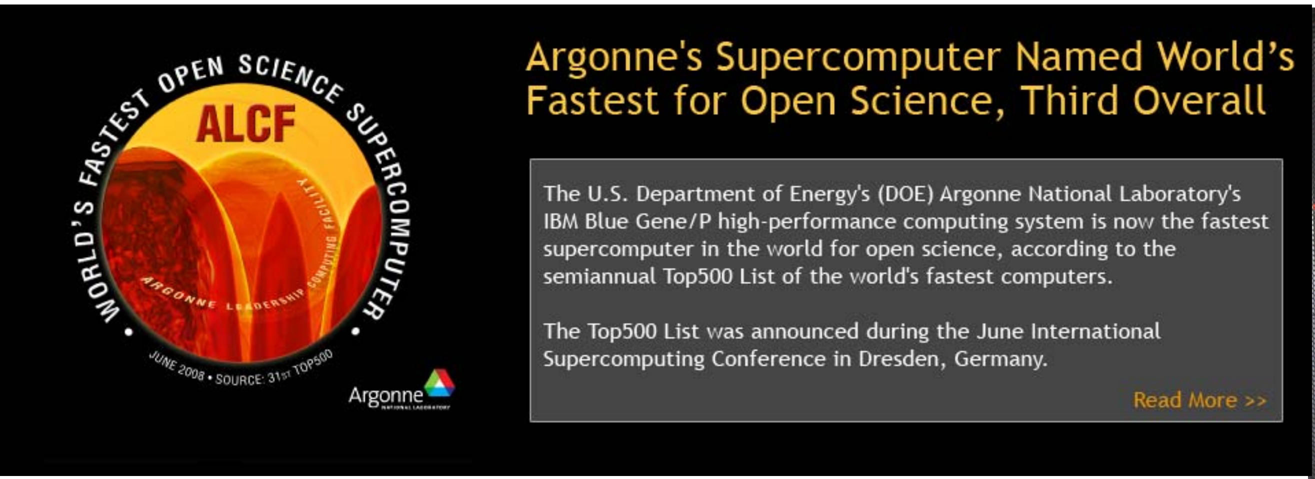
• Pressure reactors



Approach: Computational Resources

Wolverton and Ozolins (DOE INCITE Program):
1,000,000 CPU Hour Award on Argonne Blue Gene

Wolverton Group (NU)
3 Opteron/Infiniband Clusters
> 700 total cores



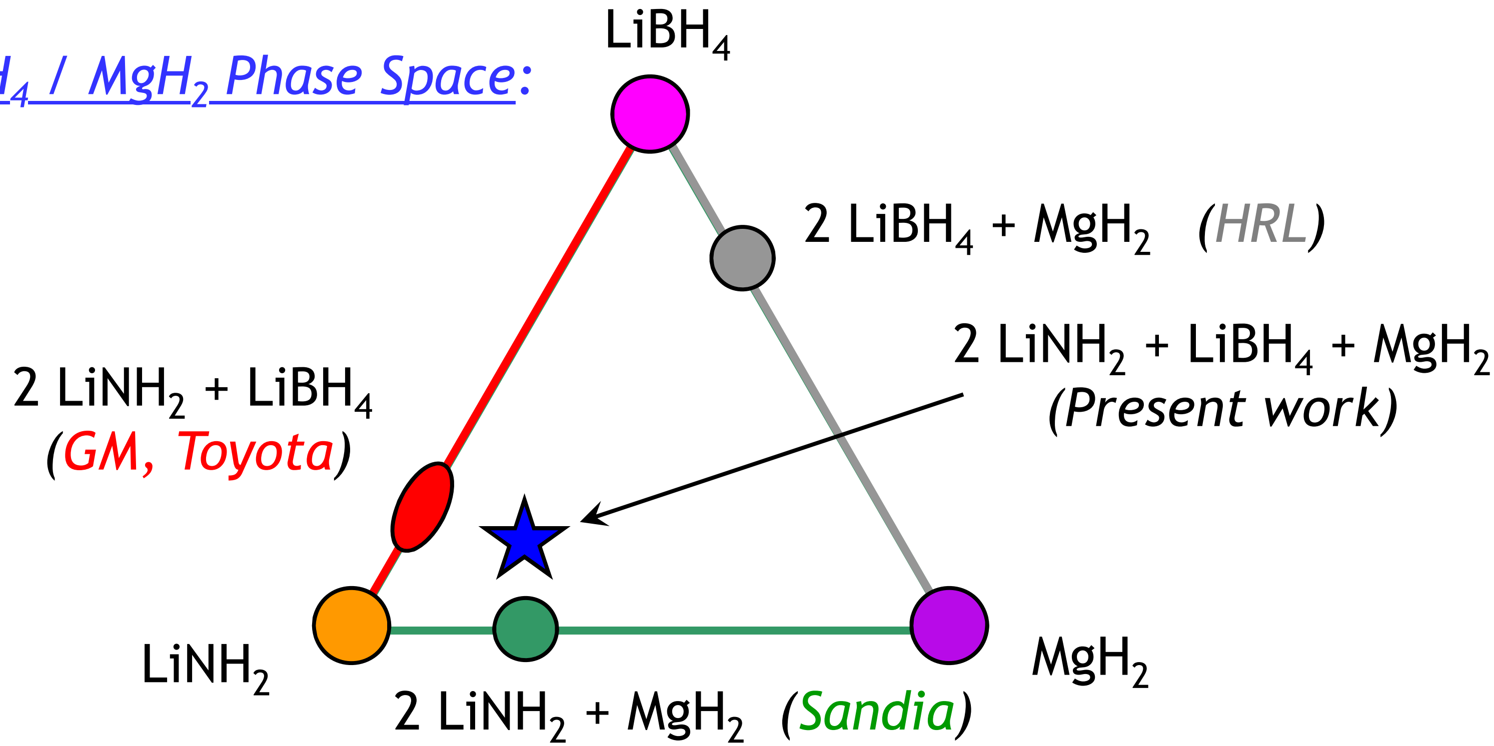
Ozolins Group (UCLA)
1 Opteron/Infiniband cluster
1 Xeon/Infiniband cluster
~ 350 total cores

Technical Accomplishments: Prior Work

Why *combinations* of compounds?

Improved kinetics

LiNH$_2$ / LiBH$_4$ / MgH$_2$ Phase Space:

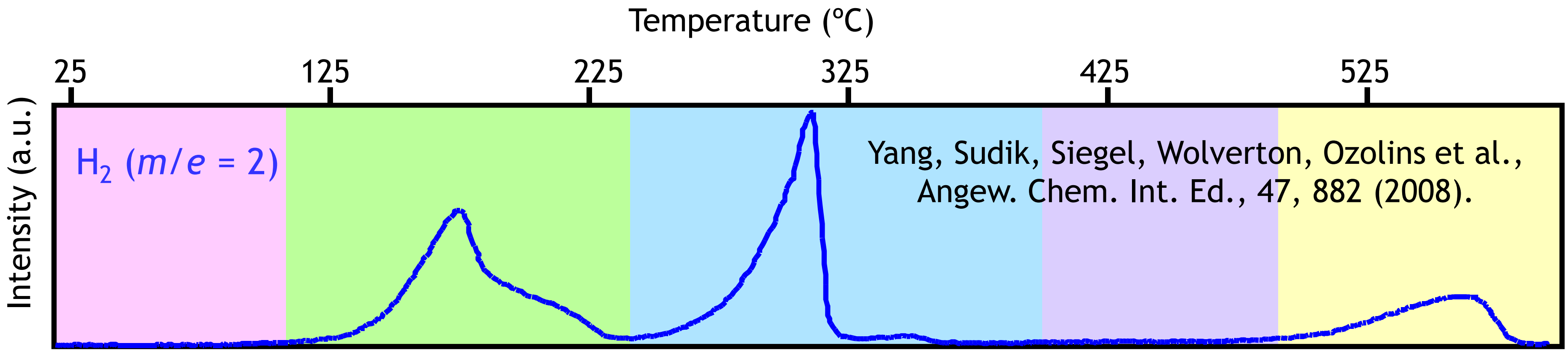


Sequence of decomposition reactions Is "self-catalyzing"

Product of initial reaction serves as nucleation center for subsequent reactions

Yang, Sudik, Siegel, Wolverton, Ozolins et al., Angew. Chem. Int. Ed., 47, 882 (2008).

Technical Accomplishments: Prior Work



Step	Reaction	Conversion	Obs. (Theo.) H_2 Release (wt.%)	ΔH_{calc} (kJ/mol)	E_a (kJ/mol)
Milling	$3\ LiNH_2 + LiBH_4 \Rightarrow Li_4BN_3H_{10}$	1	-	-12	-
	$2\ Li_4BN_3H_{10} + 3\ MgH_2 \Rightarrow 3\ Mg(NH_2)_2 + 2\ LiBH_4 + 6\ LiH$	x	-	-207	-
Heating < 110° C	$2\ Li_4BN_3H_{10} + 3\ MgH_2 \Rightarrow 3\ Mg(NH_2)_2 + 2\ LiBH_4 + 6\ LiH$	y	-	-207	
1st Peak	$2\ Li_4BN_3H_{10} + 3\ MgH_2 \Rightarrow 3\ Li_2Mg(NH)_2 + 2\ LiBH_4 + 6\ H_2$	1 - x - y	4.0 (4.3)	80	119
Shoulder	$Mg(NH_2)_2 + 2\ LiH \Leftrightarrow Li_2Mg(NH)_2 + 2\ H_2$	x + y		96	-
2nd Peak	$3\ Li_2Mg(NH)_2 + 2\ LiBH_4 \Rightarrow 2\ Li_3BN_2 + Mg_3N_2 + 2\ LiH + 6\ H_2$	1	4.2 (4.3)	-13	184
Heating > 400° C	$2\ Li_3BN_2 + Mg_3N_2 + LiBH_4 \Rightarrow 3\ LiMgBN_2$ (Phase X) $+ 4\ LiH$	1	-	-173	-
	$LiMgBN_2$ (Phase X) $\Rightarrow LiMgBN_2$ (Tetragonal)	1	-	-	-
3rd Peak	$2\ LiH \Rightarrow 2\ Li + H_2$	1	2.1 (2.1)	84	-

Technical Accomplishments: Prior Work

Demands on H2 Storage Systems

- Multiple stringent criteria:
  - High gravimetric density
  - High volumetric density
  - Target equilibrium pressures & temperatures
    - recharge/release between 1 and 700 bar and -40 to +80 ^{o}C
  - High rates of hydrogen release and absorption

Composition & Structure (high gravimetric density, high volumetric density)

Reactions & Thermodynamics (target equilibrium pressures & temperatures)

Kinetics (high rates of hydrogen release and absorption)

Technical Accomplishments: Prior Work

Computational Capabilities
Part I: Structure Prediction

How can we predict crystal structures of new materials?

- Database searching
  - Alanates, Borohydrides
- Enumeration
  - Li_2NH, MgNH, $Li_4Mg(NH)_3$, ...
- Genetic algorithms
  - MgNH
- Prototype Electrostatic Ground States (PEGS)
  - Alanates, Borohydrides, $X_nB_{12}H_{12}$, ...

Technical Accomplishments: Prior Work

Computational Capabilities
Part II: Grand Canonical Linear Programming

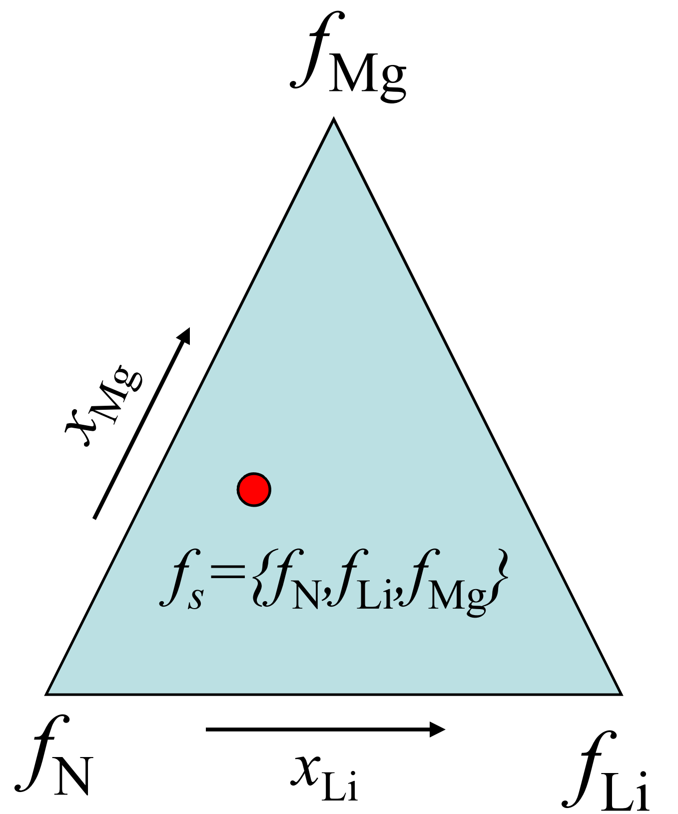
In the presence of H_2 gas, the total free energy is:

$$G(T) = \sum_i x_i G_i(T) - \frac{\mu_{H_2}(p,T)}{2} \sum_i x_i n_H^i = \min$$

- x_i mole fraction of phase "*i*" (unknown)
- n_s^i number of atoms of type "s" per f.u. of phase "*i*"
- G_i Gibbs energy of phase "*i*" (from first-principles)
- μ_{H_2} chemical potential of H_2, $\mu_{H_2} = \mu_0 + RT\log(p/p_0)$

G(T) is minimized keeping non-H compositions fixed:

$$f_s = \sum_i x_i n_s^i = \text{const} \quad \text{for} \quad s \neq H.$$



Linear programming yields phase fractions $x_i(p,T)$.

A. Akbarzadeh, V. Ozolins, and C. Wolverton, Advanced Materials **19**, 3233-3239 (2007)

Technical Accomplishments: Prior Work

Computational Capabilities
Part III: Kinetics

Elucidate rate-limiting steps for hydrogen release:

- Diffusion
  - $NaAlH_4$, Na_3AlH_6, $LiNH_2$, H in Al
- Surface & interface kinetics
  - $NaAlH_4$
- Kinetics in liquids
  - $Li_4BN_3H_{10}$

Technical tools:

- Large-scale *ab initio* MD
- Transition state calculations (NEB, etc.)

Collaborators

PI's/co-PI's

Chris Wolverton (Northwestern, lead)
Harold Kung (Northwestern)
Vidvuds Ozolins (UCLA, subcontract)
Andrea Sudik (Ford, no-cost collaborator)
Don Siegel (Ford, no-cost collaborator)

Outside Collaborators:

E. Majzoub (UMSL)
J. Yang (Ford)
G. Ceder, N. Marzari (MIT)
C. Brown (NIST)

Summary

- New project focused on design of novel multi-component mixtures for hydrogen storage
- Focus on mixtures of materials from two distinct classes (e.g., reversible + irreversible)
- Systems to be studied include mixtures of complex hydrides and chemical hydrides [e.g. $LiNH_2$+NH_3BH_3] and nitrogen-hydrogen based borohydrides [e.g. $Al(BH_4)_3(NH_3)_3$]
- Powerful blend of: 1) H_2 Storage measurements and characterization, 2) State-of-the-art computational modeling, 3) Detailed catalysis experiments, 4) In-depth automotive perspective