Catalyzed Nano-Framework Stabilized High Density Reversible Hydrogen Storage Systems

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METAL HYDRIDE CENTER OF EXCELLENCE

DOE Hydrogen Program
Annual Merit Review
Arlington, VA
June 9, 2008

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

- **Timeline**
  - 7/1/07 Start (signed 9/4/07)
  - 7/1/10 End
- **Budget**
  - $1.26M Total Program
  - DOE: $1.01M
    - SNL: $360k
    - Albemarle: $90k
    - Cost share: 20% (31% UTRC $)
  - FY07: $80k
  - FY08: $480k
- **Barriers Addressed**
  - P. Lack of Understanding of Hydrogen Physisorption and Chemisorption
  - A. System Weight and Volume
  - E. Charging/Discharging Rates

  www.eere.energy.gov/hydrogenandfuelcells/mypp
- **Partner Participation**
  - Sandia National Laboratories
  - Albemarle Corporation
  - Aspen Aerogels

United Technologies

Sandia National Laboratories

aspen aerogels

ALBEMARLE CORPORATION

Objectives

Design & synthesize hydride / nano-framework combinations to improve:

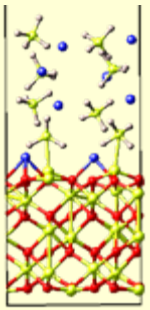
Reversible capacity **Desorption temperature** **Cyclic life**

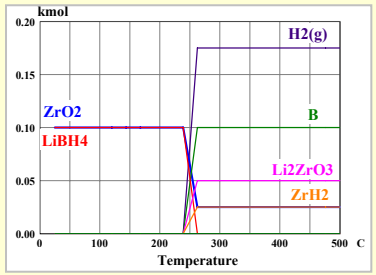
Build upon successes previously demonstrated in the community and *extend to a wider range of doped, functionalized and catalyzed framework chemistries* to:

- *Advance the understanding* of behavior modification by nano-frameworks
- Obtain / maintain *nano-scale phase domains*
- Tune hydride / framework interactions to
  - *Decrease desorption temperature* for highly stable compounds
  - Stabilize high capacity compounds – *ligand elimination*
  - Influence desorption *product formation*
- Activate *H_2 dissociation* on highly dispersed catalytic sites

High Level Approach

Atomistic & Thermodynamic Modeling
Framework design, Material compatibility



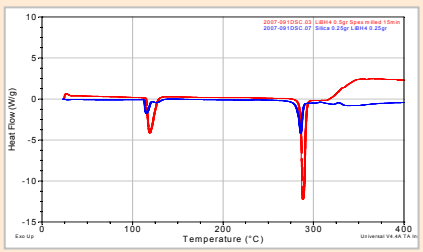


VASP **HSC**

Framework Synthesis

Hydride Synthesis

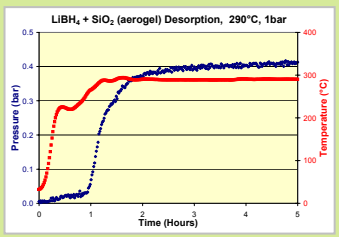
Screening Characterization
Chemical reactivities: DSC, TGA
Framework morphology: BET



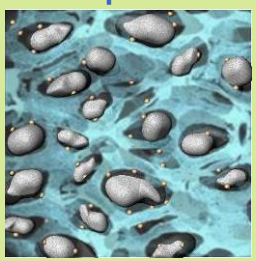
DSC

Down-select

Structure & Performance
SEM, TEM, Sievert's



Hydride Incorporation



Reaction Testing

Detailed Approach

Phase / Task	Phase I Years 1 & 2	Phase II Year 3
First Principles Modeling	Examine hydride / framework interactions. Screen doped / catalyzed / functionalized frameworks.	Evaluate mechanisms of down-selected hydride / framework systems.
Thermodynamic Modeling	Assess chemical compatibility of hydride / framework combinations.	Comparison of bulk scale & nano scale properties.
Nano-Framework Development	Synthesize and characterize uncatalyzed and catalyzed frameworks.	Optimize doped / catalyzed / functionalized framework for down-selected systems.
Hydride Development	Synthesize high capacity hydride materials.	Refine high capacity hydride synthesis methods.
Hydride Incorporation into NFS	Incorporate hydrides into designed frameworks. Characterize properties.	Maximize hydride incorporation into framework for improved capacity.

Iterative design and synthesis of high H_2 capacity systems.

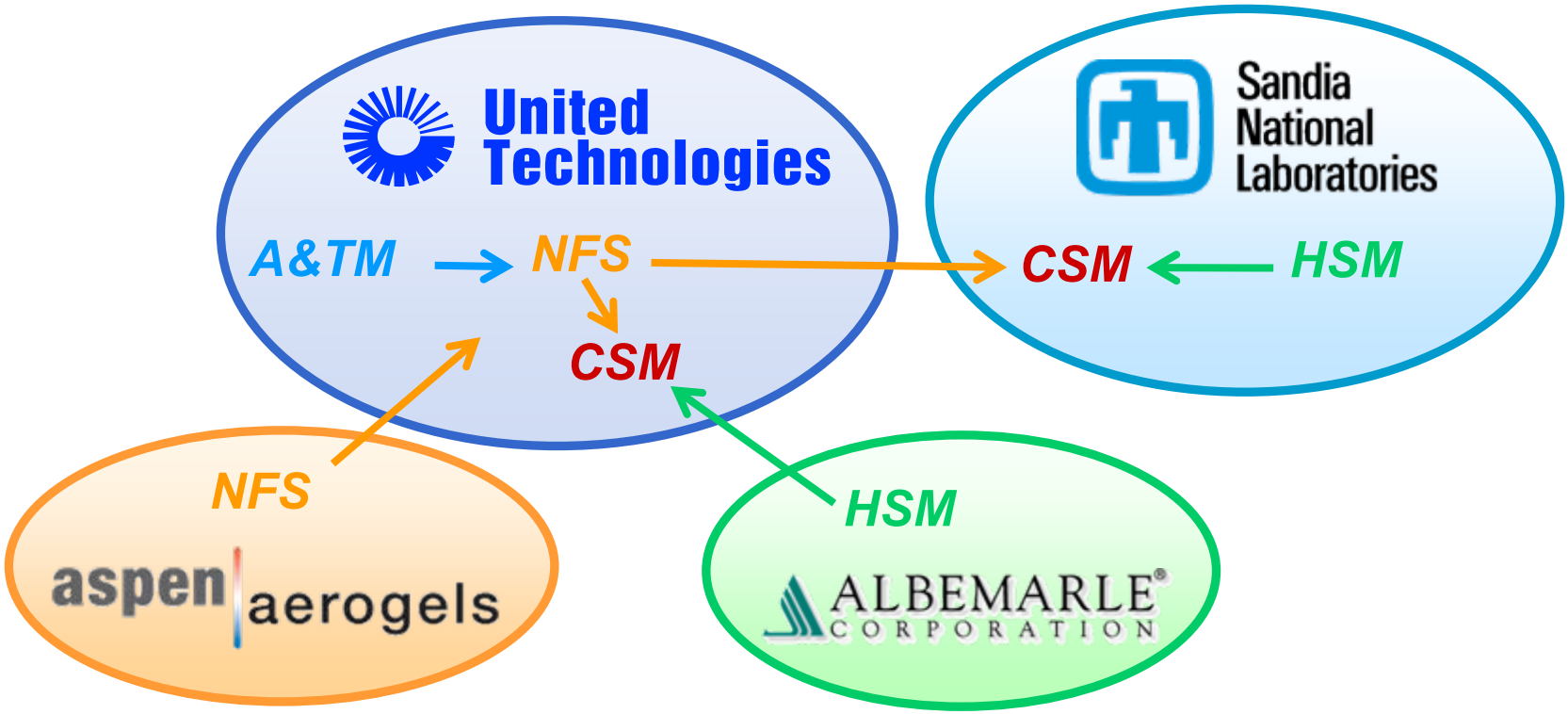
Milestones

Date	Milestone or Go / No Go Decision
2008 Q1	Select advanced nano-framework structure
2008 Q1	Demonstrate synthesis of desired nano-framework structure
2008 Q1	Synthesize top Sandia candidate hydride material
2008 Q2	Synthesize top UTRC / Albemarle candidate hydride material
2008 Q4	Evaluate relative performance of catalysts
2008 Q4	Synthesize optimal catalyzed nano-framework structure
2009 Q1	Demonstrate loading of UTRC / Albemarle hydride into catalyzed framework
2009 Q2	Demonstrate loading of Sandia hydride into catalyzed framework
2009 Q3	Go / No Go on whether to proceed with original plan or redirect based on: > 50% hydride deposition into the CFS Reasonable absorption/desorption behavior for at least one cycle Performance relative to the state-of-the-art material shows promise

Material Focus & Partner Roles

Hydrogen Storage Material (*HSM*)

- SNL: $Ca(BH_4)_2$ (stable borohydride)
- UTRC / Albemarle: $NaTi(BH_4)_4$*ligand, …
- Compatibility screening / Baseline modeling: $LiBH_4$



A&TM: Atomistic and Thermodynamic Modeling
NFS: Nano Framework Structure
HSM: Hydrogen Storage Material
CSM: Combined Structure & Material

Capabilities – Nano-Framework Development

United Technologies

Autoclave System

- 2200 PSI
- 300°C

Wet Chemistry Laboratory

aspen aerogels

Process Development

Range of chemistries

- Oxides
- Non-oxides
- Polymers, …

Large Scale Manufacturing

- Future cost reduction

Capabilities – Hydride Synthesis / Incorporation

United Technologies

Solid State Processing

- Very rapid, low cost screening
- Limited conditions
- High cost for high volume production

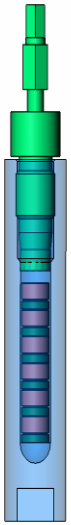
Autoclave System

- Solvated incorporation
- 2200 PSI
- 300°C

Sandia National Laboratories

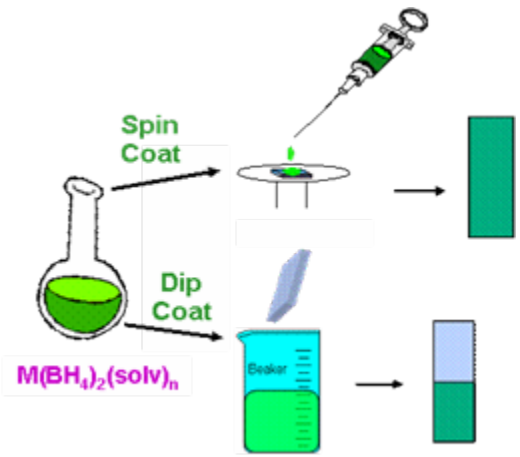
High-Pressure station

- Solid state reactions
- Wide range of P and T <20,000psi, <500°C
- Autoclave with six samples capability



Solvated Hydride Incorporation

- Solvents selected for ease of removal



ALBEMARLE® CORPORATION

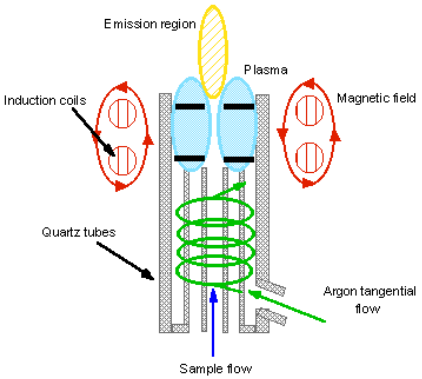
Solution Based Processing Chemical Design & Synthesis

- Excellent control
- High purity products
- Expensive processing
- Cost- effective high volume production

Experimental Methods – Characterization

United Technologies

Inductively Coupled Plasma

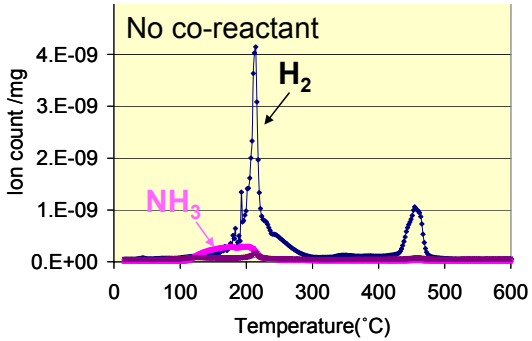


Quantify total metal loading

BET Nitrogen Porosimetry

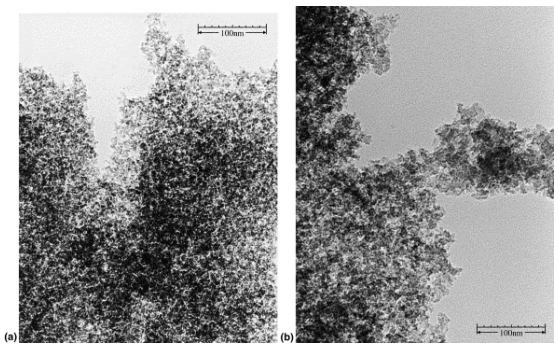
Surface area, average pore size, and pore size distribution

Thermogravimetry-Mass Spectroscopy



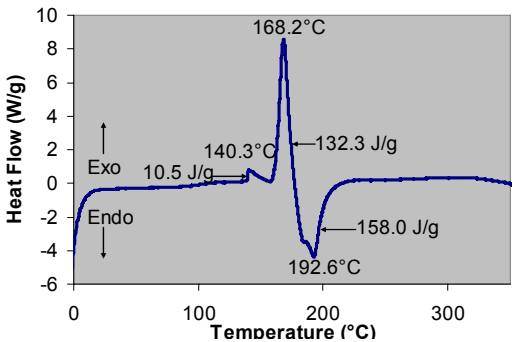
Desorption temperature & species

TEM / High Res SEM



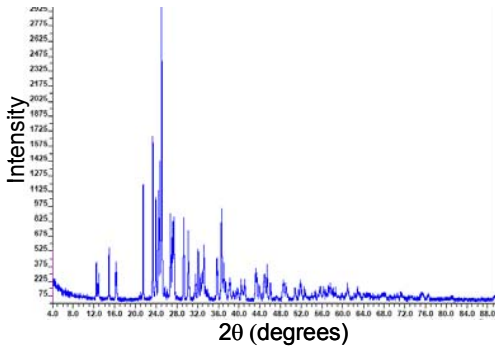
Morphology, catalyst dispersion and size, hydride loading

Differential Scanning Calorimetry



Assess reversibility potential, phase behavior

X-Ray Diffraction



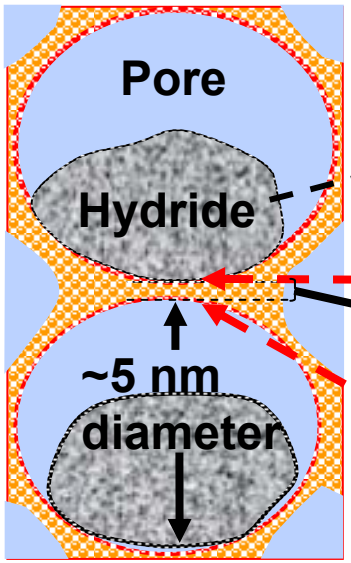
Crystalline structure & phase

* Additional characterization support will be provided by other MHCoE partners

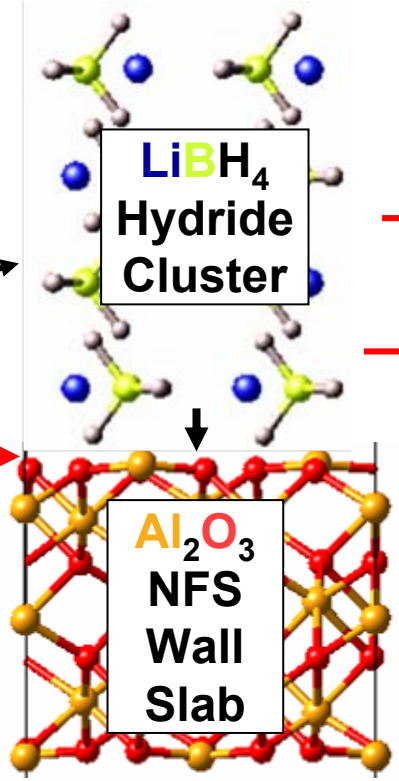
Atomic Modeling of Hydride-NFS Interactions

Concept

Schematic
Filled NFS



Input Models



Baseline System

Role

Conduct atomic modeling to investigate and prescreen:

- Hydride thermodynamics
- Interfacial physi-/chemisorption reactions influence on hydride stability and dehydrogenation
- NFS stability and modification:
  a) Doping to tune reactivity
  b) Loading with H_2 activation catalysts for reversibility
  c) Surface functionalization

VASP (Vienna Ab-initio Simulation Package)	Density Functional Theory Ground State Minimization
Materials Design	Direct Method Lattice Dynamics Thermodynamic Property Prediction

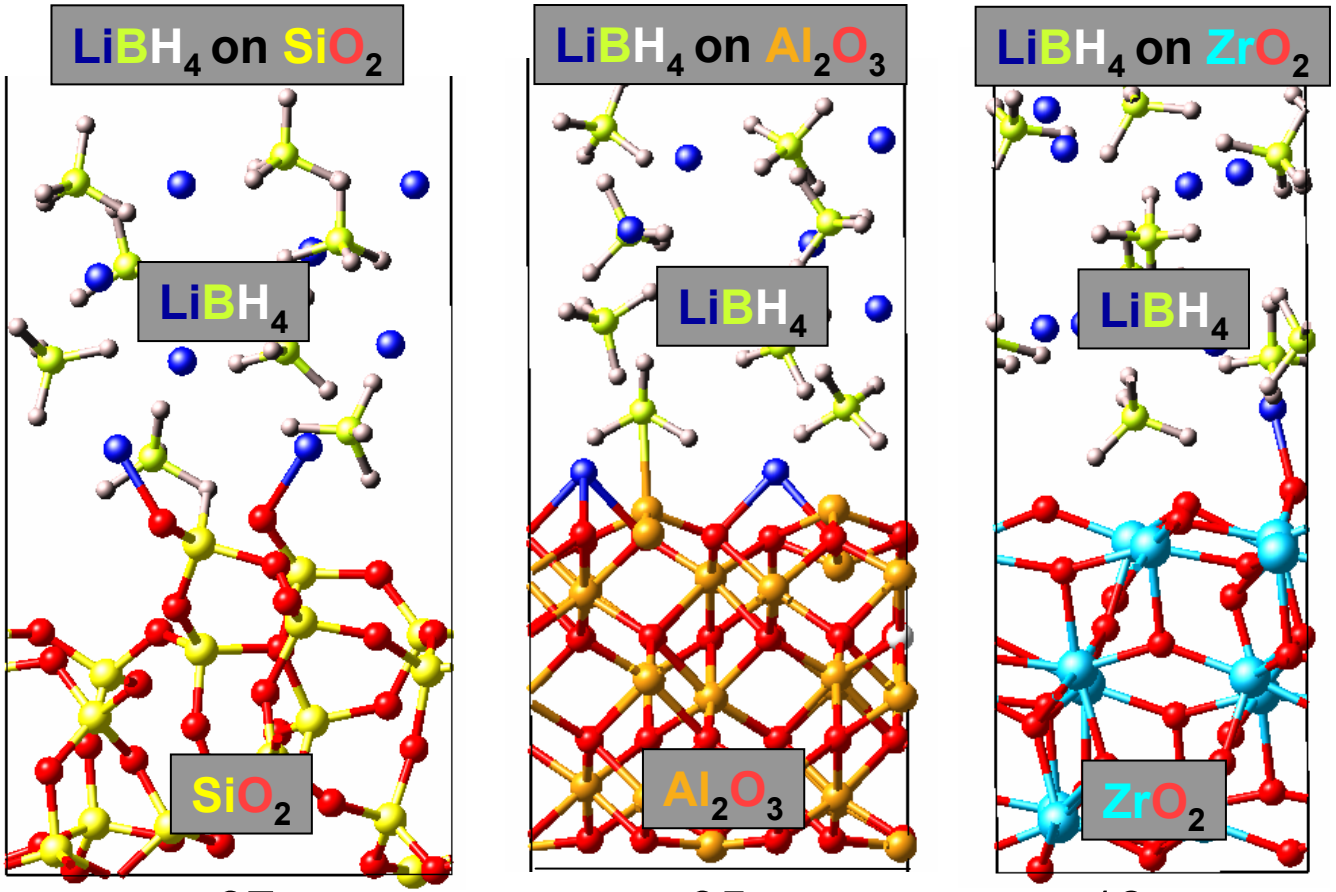
Mechanistic simulations guide NFS down-selection, design and modification.

Screening of NFS Stability and Hydride Interactions

Strategy:
Guide experiments by determining promising as well as unfavorable system characteristics.

Baseline System:
$LiBH_4$ is highly stable. Balance reversibility by increasing dehydrogenation product interaction with NFS.

Adhesion to NFS
ΔH_{adh} (kJ/mole $LiBH_4$)
(- =favorable)



-37
(strong binding

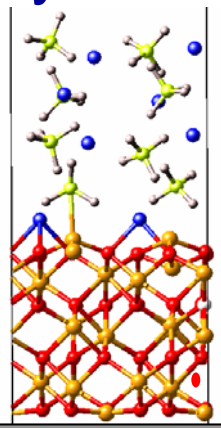
-35
←→

-18
weak binding)

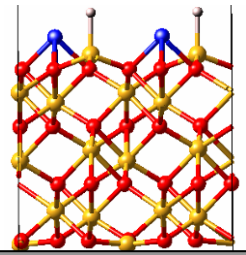
ZrO_2 NFS predicted to have low reducibility in an H_2 atmosphere and weaker tunable interfacial associative interactions with $LiBH_4$.

Hydride Physi-/Chemisorption Interactions w/ NFS

Fully Charged Discharged

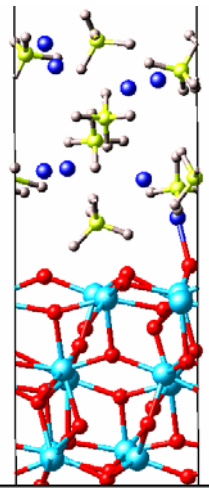


Adsorbed Li & H enhance discharge

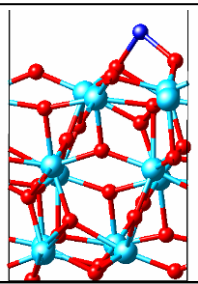


$LiBH_4$ on Al_2O_3

2Li & 2H on Al_2O_3



Equally strong Li-O bond in charged and discharged states



$LiBH_4$ on ZrO_2

Li on ZrO_2

Ground State Dehydrogenation Reaction Predictions	**ΔH_{deh} kJ/mole $LiBH_4$**
$8LiBH_4$ w/o NFS → 8 LiH + 8B + $12H_2$ ★	+114
$8LiBH_4$ / Al_2O_3 → Al_2O_3∗2Li∗2H + 6LiH+8B +$12H_2$	+100
$8LiBH_4$ / ZrO_2 → ZrO_2∗Li+ 7LiH + 8B + $12.5H_2$	+112

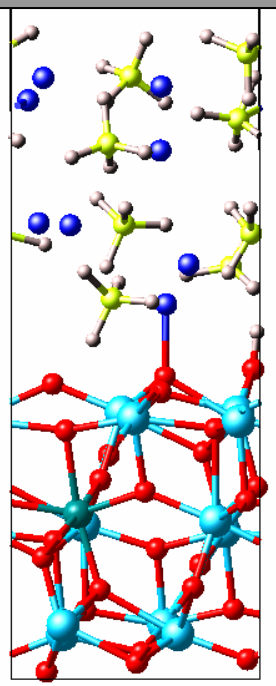
∗ = Adsorbed

★ Experimental thermodynamic ΔH_{deh} at 298 K:
100 kJ/(mole $LiBH_4$), HSC v. 5.1.
104 kJ/(mole $LiBH_4$), Smith and Bass, *J. Chem. Eng. Data* **8** (1963) 8.

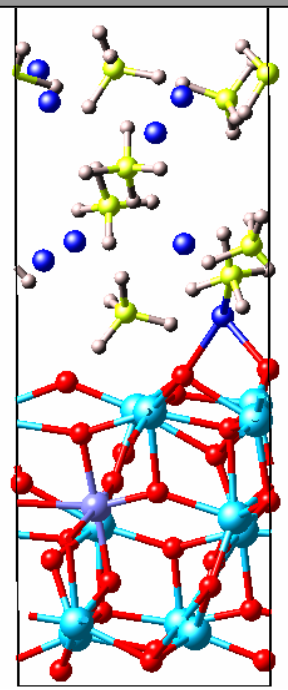
- Dehydrogenation influenced by product adsorption on NFS surface.
- $Ca(BH_4)_2$/NFS under investigation.

NFS Doping Alters Hydride Dehydrogenation

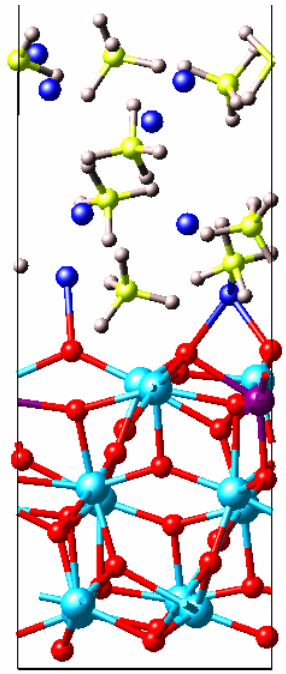
$LiBH_4$ on Sc-doped ZrO_2



$LiBH_4$ on Ti-doped ZrO_2



$LiBH_4$ on V-doped ZrO_2



Ground State $LiBH_4$ Dehydrogenation Reaction Predictions on NFS★	ΔH_{deh} kJ/ mole $LiBH_4$
ZrO_2	+112
$Zr_{0.92}Sc_{0.08}O_2$	+85
$Zr_{0.92}Ti_{0.08}O_2$	+125
$Zr_{0.92}V_{0.08}O_2$	+120

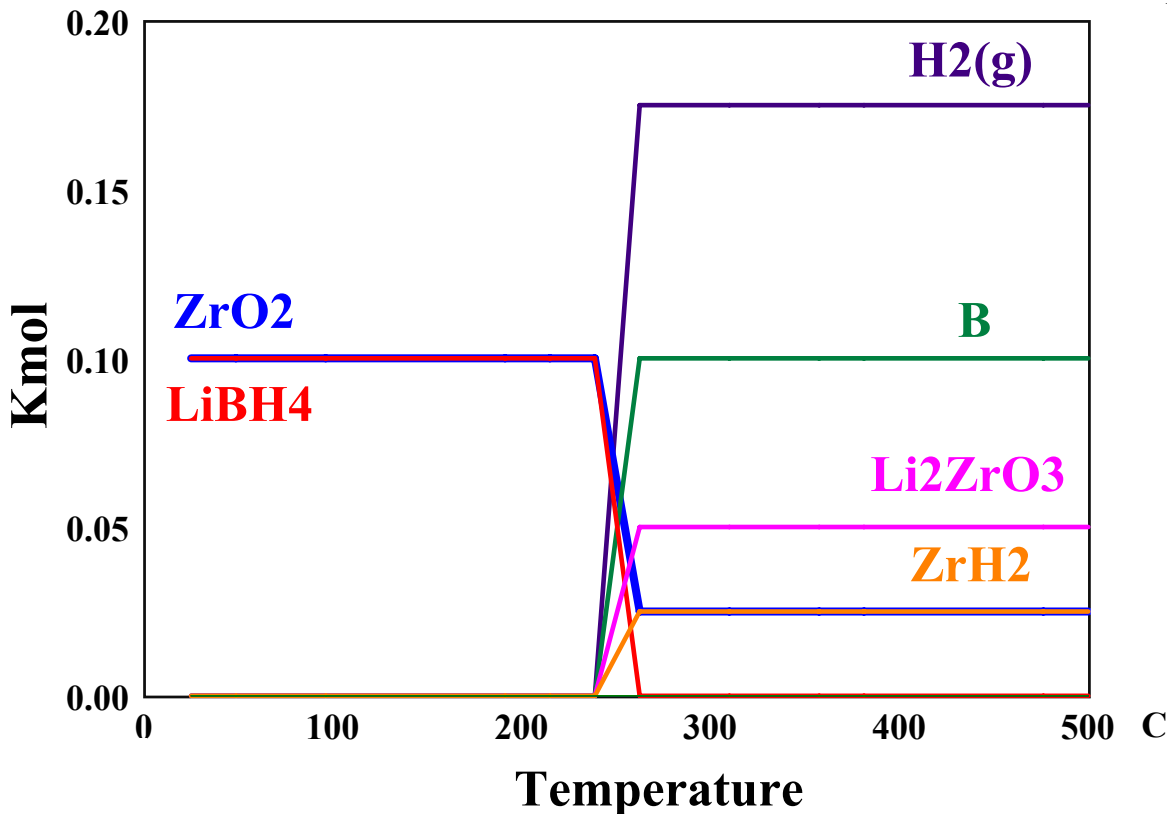
★Calculated for favorable discharge to single adsorbed *Li on surface.

- Dopants substituted in most favorable position.
- Increased hydride interactions with increased typical formal dopant valence.

NFS dopants used to balance both lattice stability and electronic NFS/hydride interfacial interactions. Sc predicted to enhance $LiBH_4$ dehydrogenation.

Thermodynamic Modeling - NFS / Hydride Compatibility

Predicted reaction from thermodynamics motivates additional modeling and experimental efforts.



Examined additional compositions to determine NFS stability and system reversibility with borohydrides:

- 5 Oxides
- 3 Carbides
- 1 Nitrides

Objective: Use thermodynamic modeling in combination with experimentation to guide design of stable framework compositions.

Thermodynamic Modeling – Potential Oxide Reduction

Example: Possible hydride reactivity with NFS

- Only $LiBH_4$ thermodynamic data initially available in HSC Software
- Oxides may be susceptible to reduction
- SiO_2 was reported as catalyst for $LiBH_4$ dehydrogenation[1], but has shown thermodynamic instability

$$4LiBH_4 + 3SiO_2 = 2Li_2O{*}SiO_2 + Si + 4B + 8H_2(g)$$

$$\Delta G_{298K} = -49.286 \text{ kJ}$$

- *Currently conducting thermodynamic evaluations of $Ca(BH_4)_2$ / NFS interactions*

Methods to prevent oxide reduction and examine the possibility of boronic acid formation are being explored.

1. A. Züttel, S. Rentsch, P. Fischer, P. Wenger, P. Sudan, Ph. Mauron, Ch. Emmenegger, "Hydrogen Storage Properties of LiBH4", J. Alloys and Compounds 356 (2003)

Nano-Framework Materials Development

Initial focus on oxide and carbon materials:

- Xerogels (SiO_2, Al_2O_3, ZrO_2): 5nm & >300m^2/g

Xerogel

- Cryogels (Al_2O_3): 5 - 20nm & >300m^2/g

Cryogel

- SiO_2 Aerogels: 17nm & > 550m^2/g

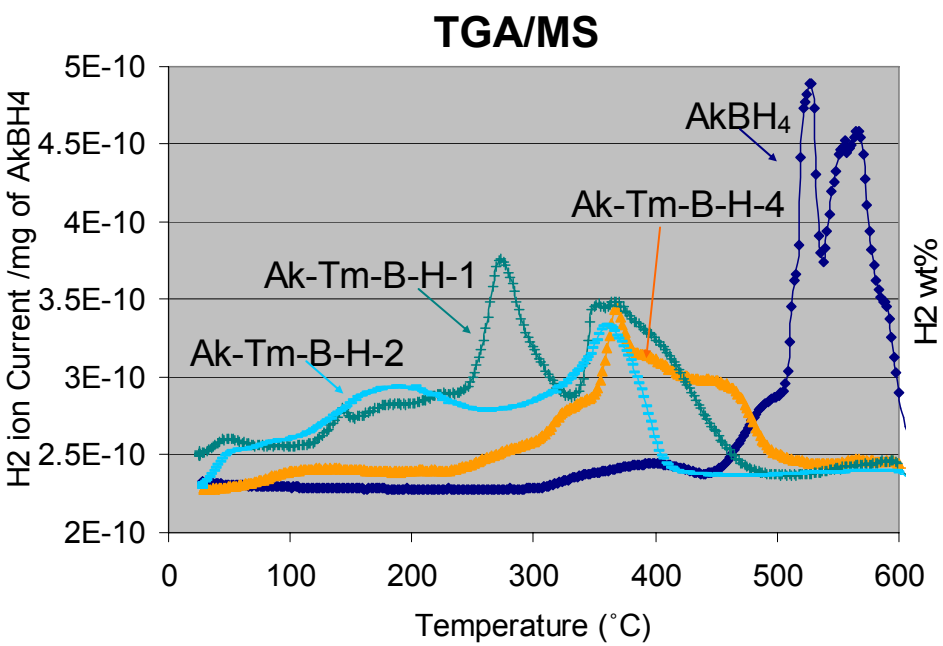
SiO_2 Aerogel

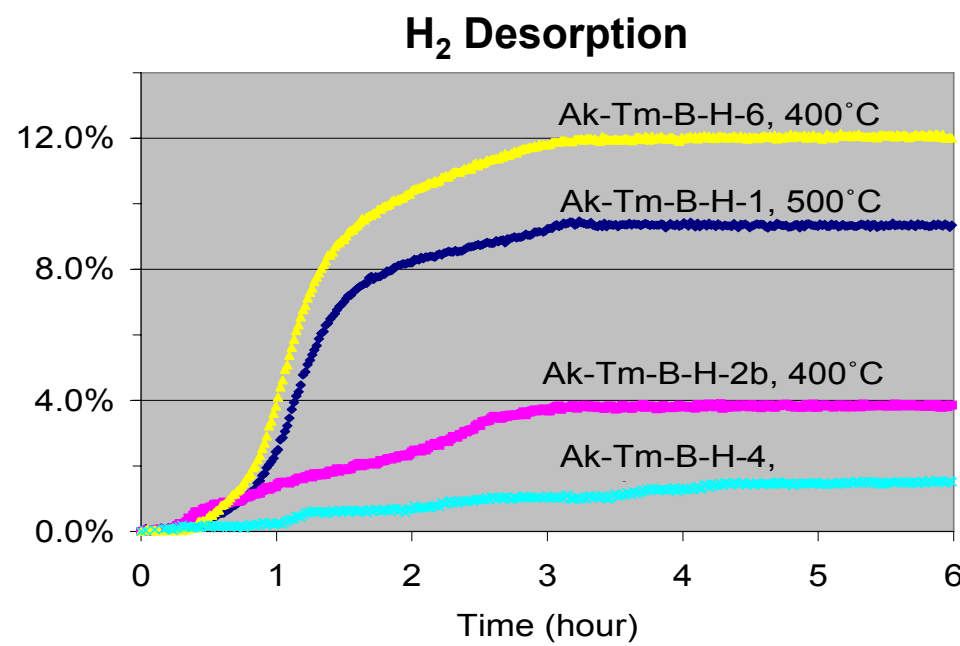
- Carbon Aerogel: 10 - 25nm & >600m^2/g

Carbon Aerogel

Hydride Development

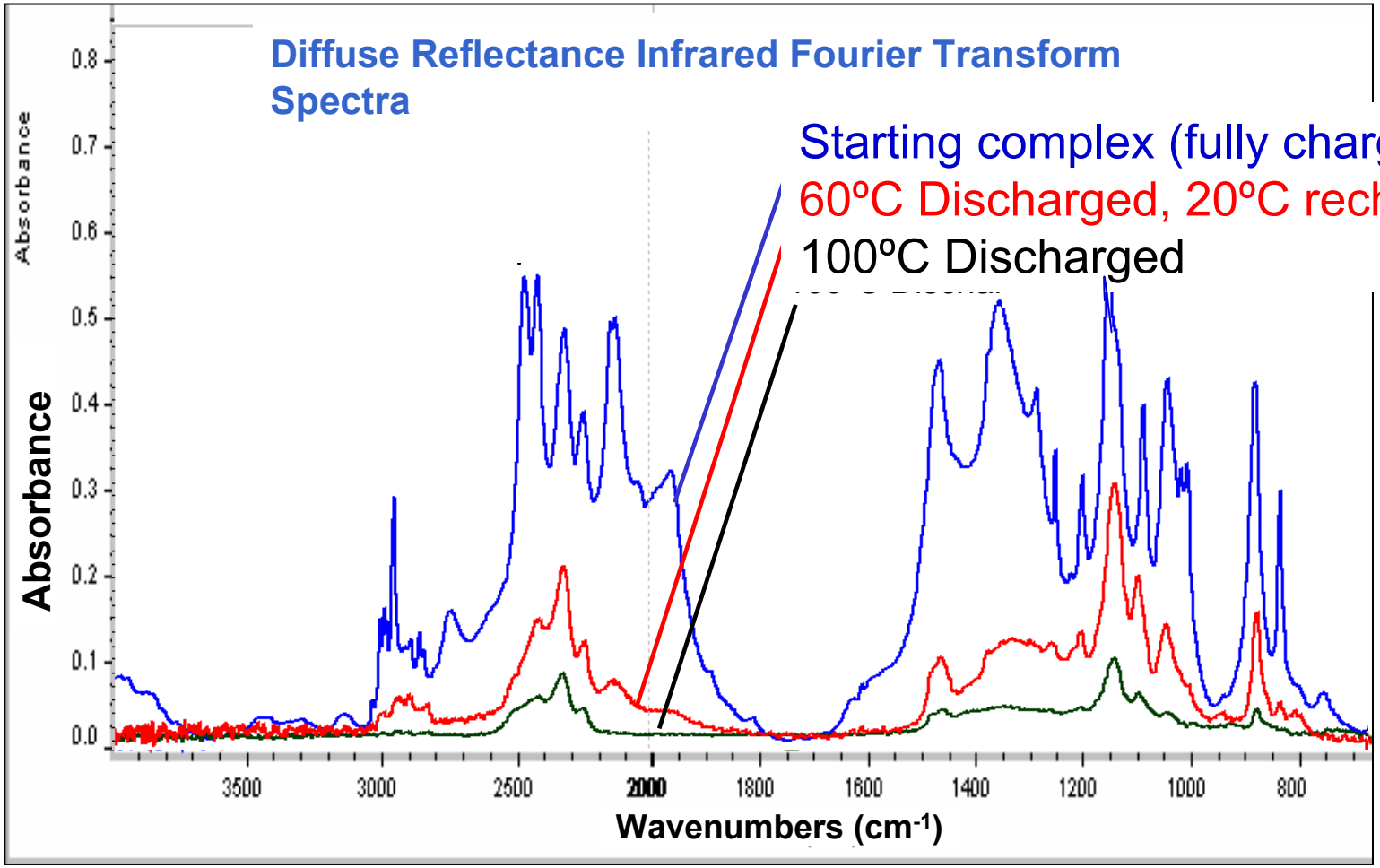
- Metal borohydrides, Alkaline (Ak)-Transition metal (Tm)-B-H, were developed under contract DE-FC36-04GO14012.
- Multistep reactions significantly lower dehydrogenation onset temperatures and improved kinetics. Only trace B_2H_6/B_3H_9 detected in the outgas.





For compounds with limited reversibility, the NFS will inhibit irreversible segregation thus improving reversibility.

$NaTi(BH_4)_4$*ligand – Up to 7.3 wt% H_2 Endothermic

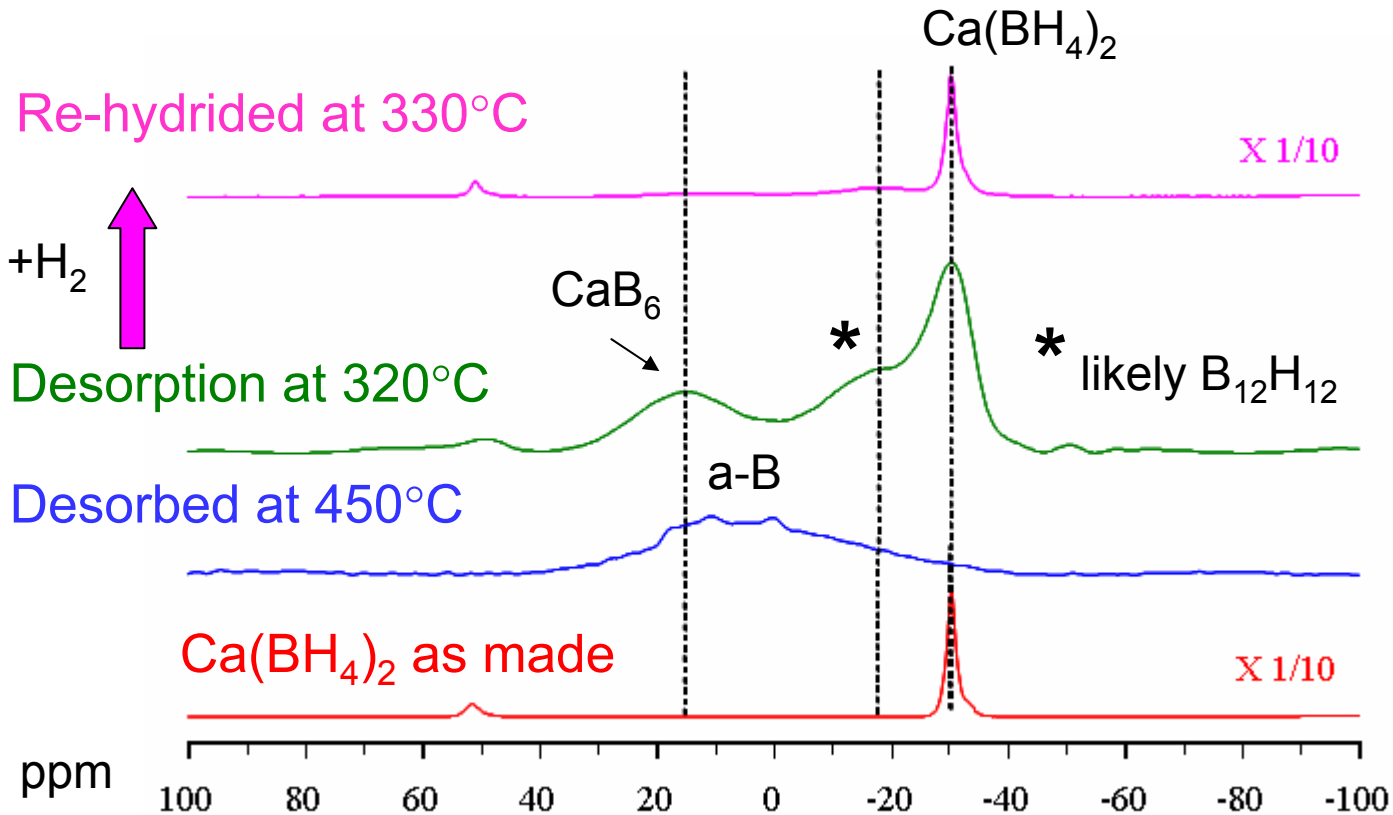


Down-selected $NaTi(BH_4)_4$ based on potential for reversibility, low desorption temperature and possible solution based incorporation.

Hydride Material – $Ca(BH_4)_2$

$$CaB_6 + 2CaH_2 + 10\ H_2 \rightarrow 3Ca(BH_4)_2 \text{ @700bar, 400°C, 48hours}$$

^{11}B MAS NMR and XRD show re-formation of $Ca(BH_4)_2$ after re-hydriding at 330°C and 100 bar



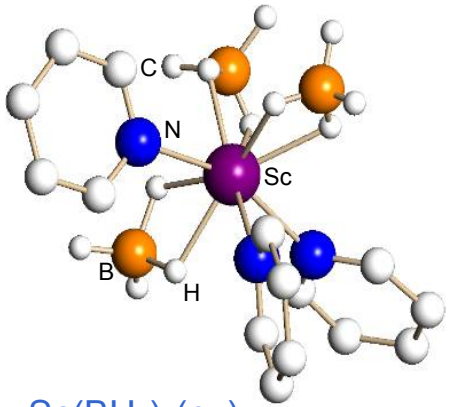
Bowman, Hwang, Kim, Reiter, Zan Rönnebro

See more details on $Ca(BH_4)_2$ in ST36, Ronnebro, Majzoub

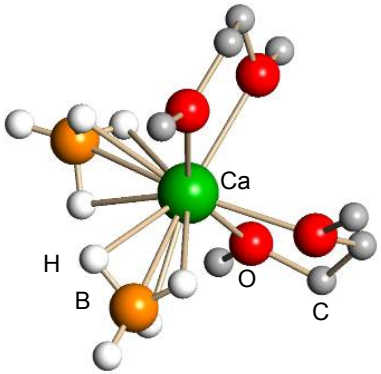
Solvated Synthesis of Metal Borohydrides

$$MX_n + n\ NaBH_4 \xrightarrow{solv} M(BH_4)_n(solv)_x$$

MX_n = $ScCl_3$, $TiCl_4$, $ZrBr_4$, CaI_2; solv = THF, DME or MeOH



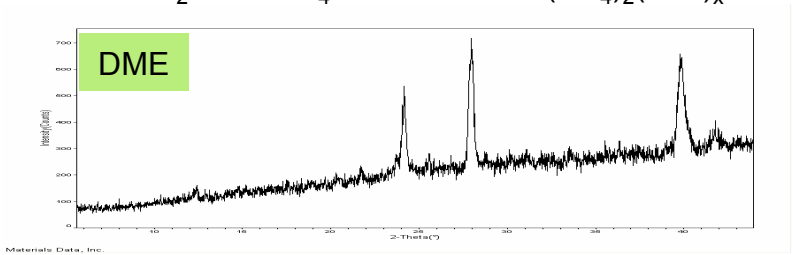
$Sc(BH_4)_3(py)_3$

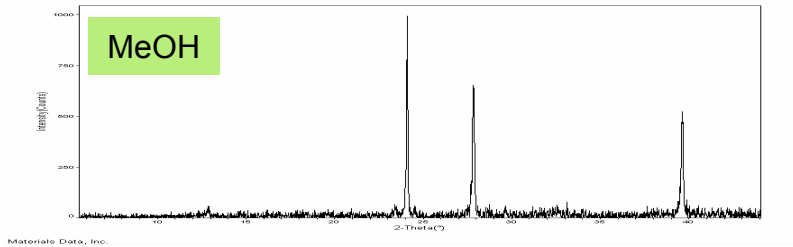


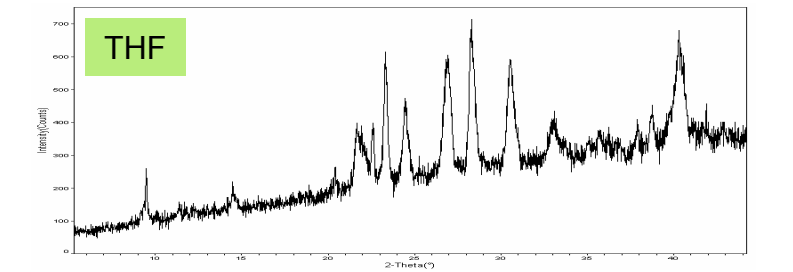
$Ca(BH_4)_2(DME)_2$

- single crystal X-ray diffraction confirms $Ca(BH_4)_2(DME)_2$ was synthesized. Used for deposition studies, with THF adduct looking the most promising

$$CaI_2 + 2NaBH_4 \xrightarrow{solv} Ca(BH_4)_2(solv)_x$$







Solution deposition of MBH onto silica substrate illustrates that deposition by this method will be possible. However, contamination with NaX by product appears to be problematic. Schemes to further purify the MBH from the NaX are underway.

Solvent-free Synthesis of Metal Borohydrides

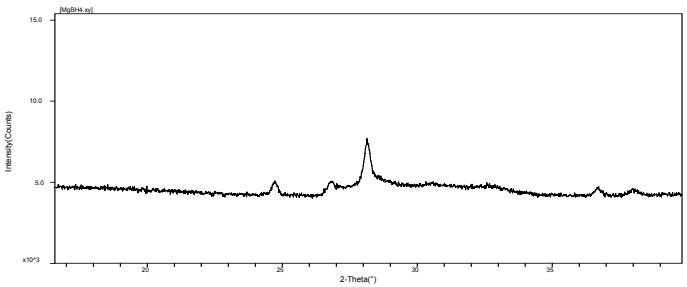
$$AlBr_3 + 3\ NaBH_4 \xrightarrow{tol} Al(BH_4)_3 + 3\ NaBr$$

$$2\ Al(BH_3)_3 + 3\ Ca(NR_2)_2 \xrightarrow{tol} 3\ Ca(BH_4)_2 + 2\ Al(NR_2)_3$$

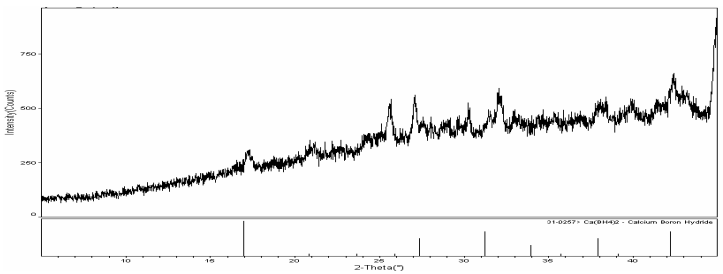
$$2\ Al(BH_3)_3 + 3\ MgR_2 \xrightarrow{tol} 3\ Mg(BH_4)_2 + 2\ AlR_3$$

Zanella et al. Inorganic Chemistry 2007 (ASAP).

$2\ Al(BH_3)_3 + 3\ MgR_2$ in tol



$AlBr_3 + 3\ LiBH_4 + 2/3\ Ca(NR_2)_2$ in tol/reflux



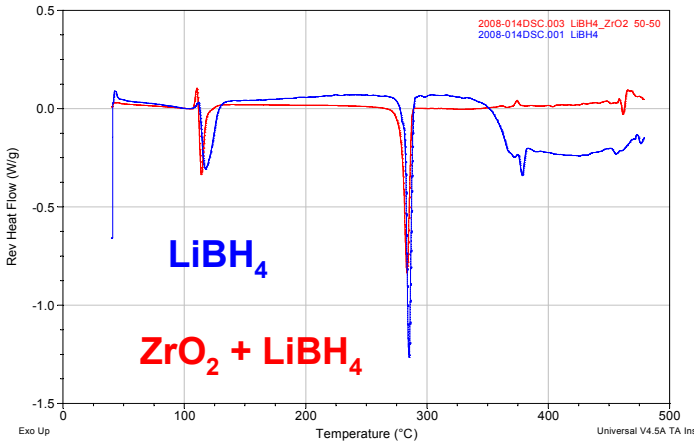
Identification of final materials not consistent with known PXRD patterns of $Mg(BH_4)_2$ or $Ca(BH_4)_2$. Contamination by Br indicates additional work to purify final product necessary. Sequential stepwise characterization of intermediates underway.

Hydride / Framework Compatibility Screening

Press Pellet

Melt LiBH4 (290°C, 190Bar)

Compatibility screening ⇒ DSC



DSC screening to determine reaction compatability of framework with hydride.

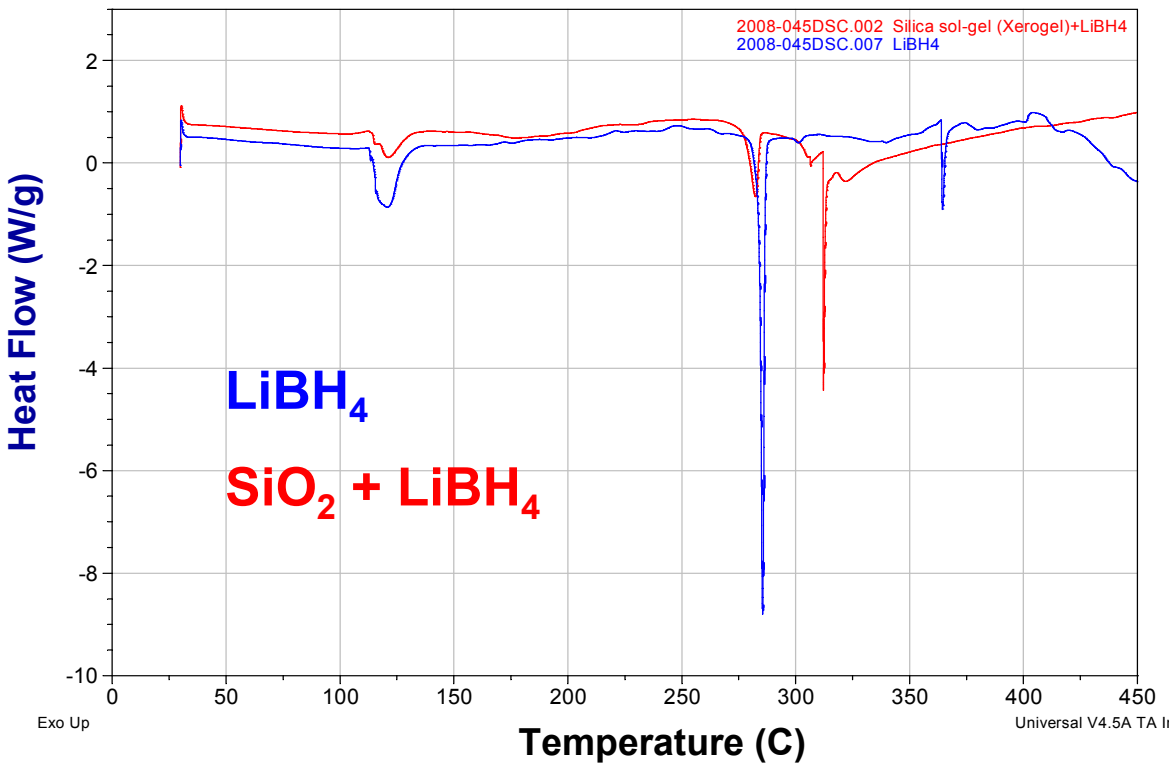
$LiBH_4$ use for initial compatibility screening because of high reactivity, availability, and existing thermodynamic data.

Compatibility Screening – SiO_2 + $LiBH_4$

Potential Reaction Pathway

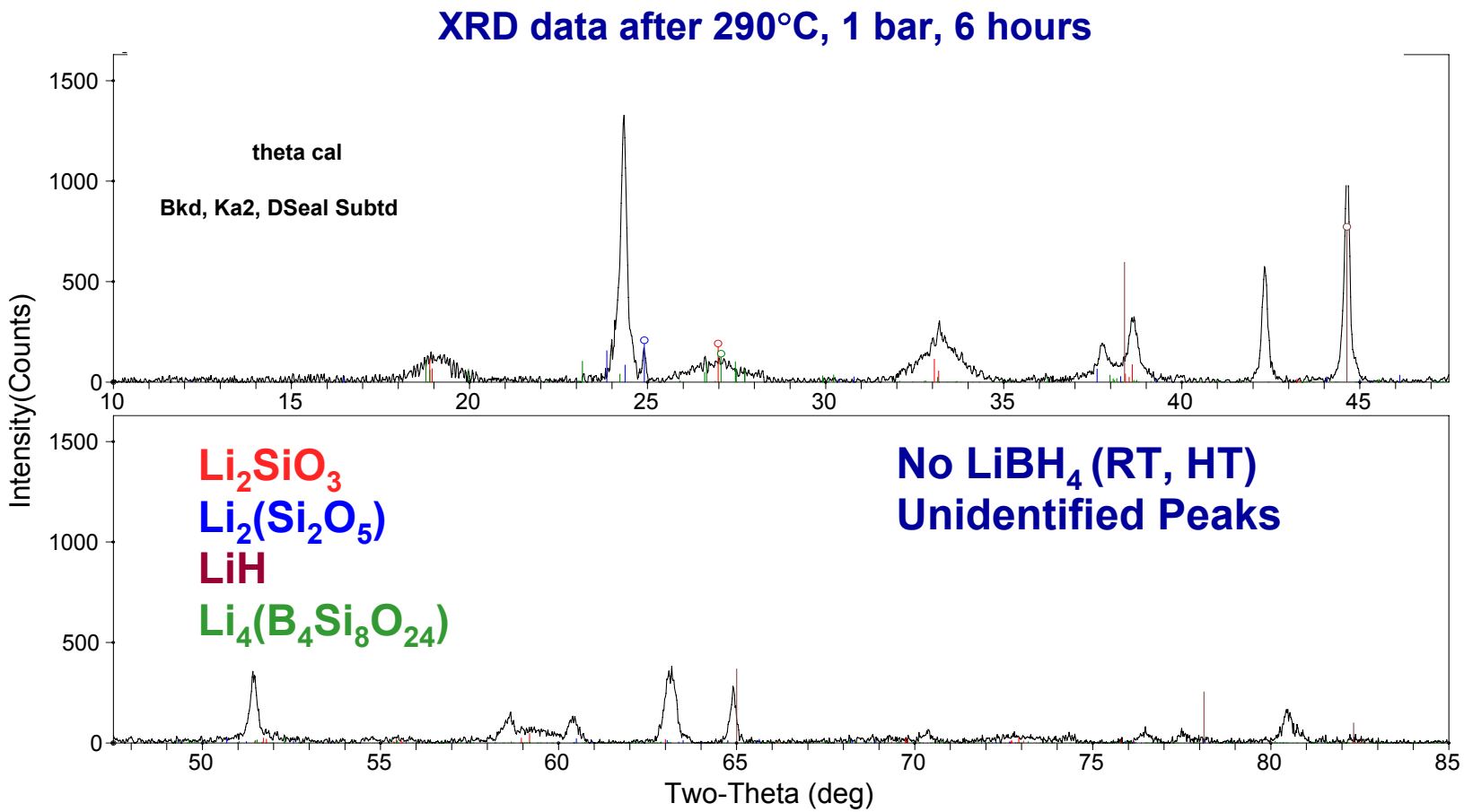
$4LiBH_4 + 3SiO_2 \rightarrow 2Li_2O{*}SiO_2 + 4B + Si + 8H_2(g)$

ΔG_{298K} = - 49.286 KJ



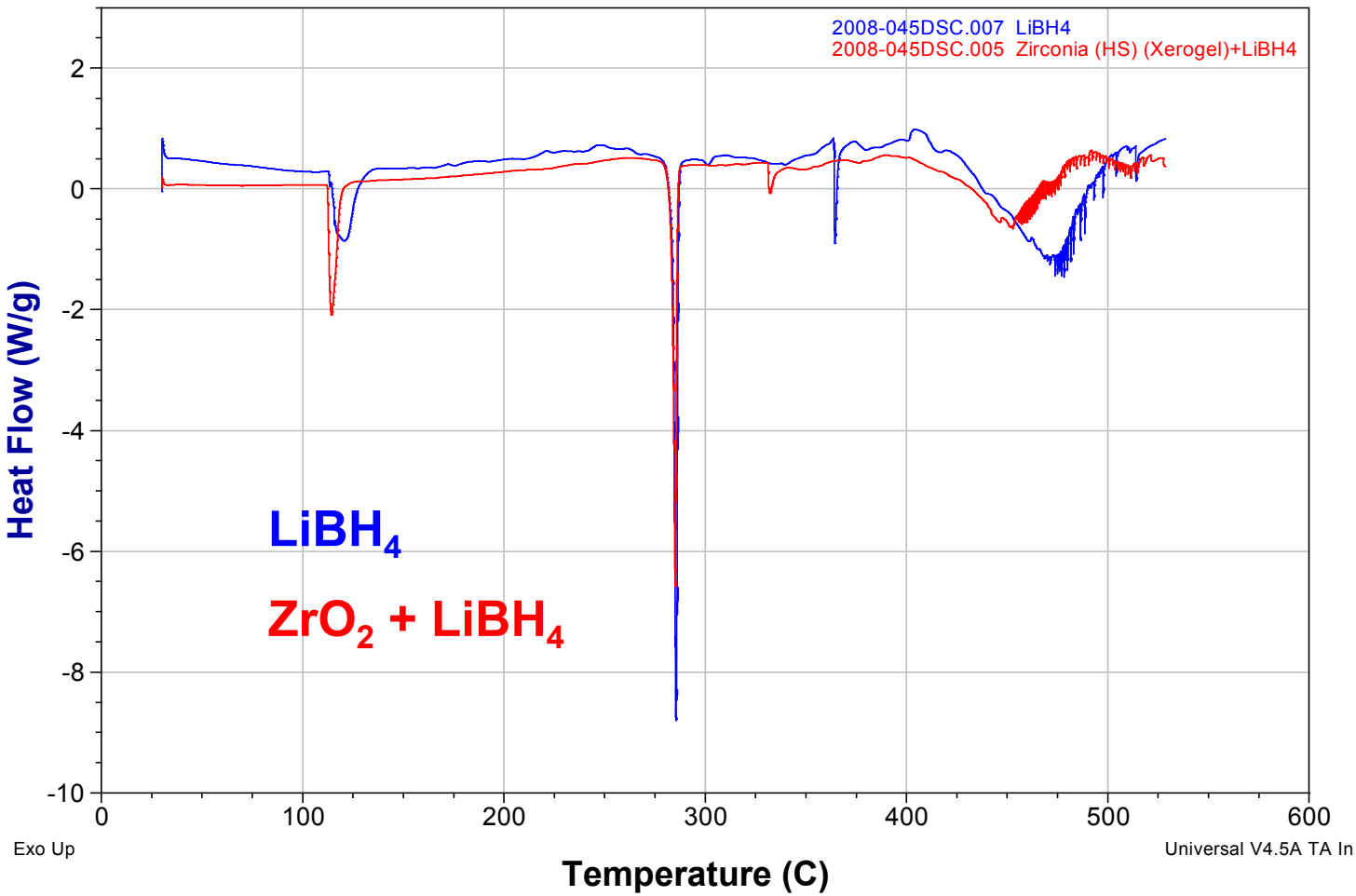
Possible non-reversibility suggested via thermodynamic assessment. DSC shows split peak at 280-300°C suggesting reaction event.

Compatibility Screening – SiO_2 + $LiBH_4$



After discharge $LiBH_4$ is decomposed but unidentified peaks exist.
Conclusion: SiO_2 is reactive with hydride and unsuitable for NFS.

Compatibility Screening – ZrO_2 + $LiBH_4$

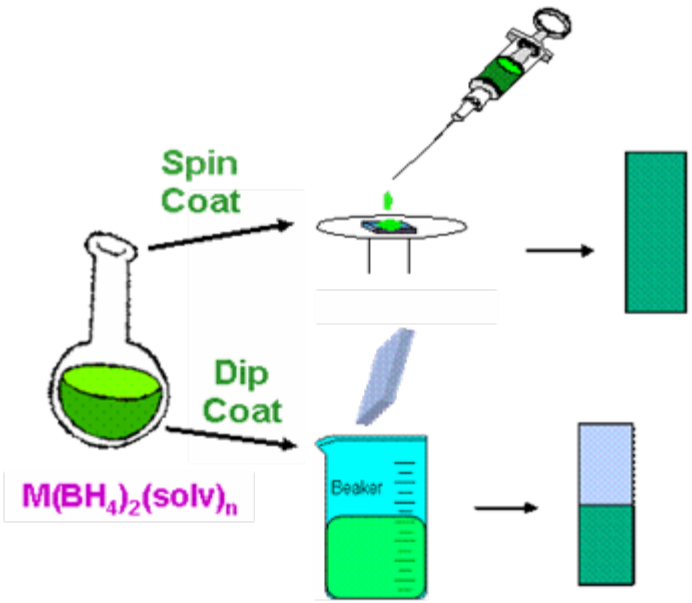


DSC of ZrO_2 + $LiBH_4$ is similar to $LiBH_4$, suggesting that ZrO_2 is stable and non-reactive in the presence of this strongly reducing hydride.

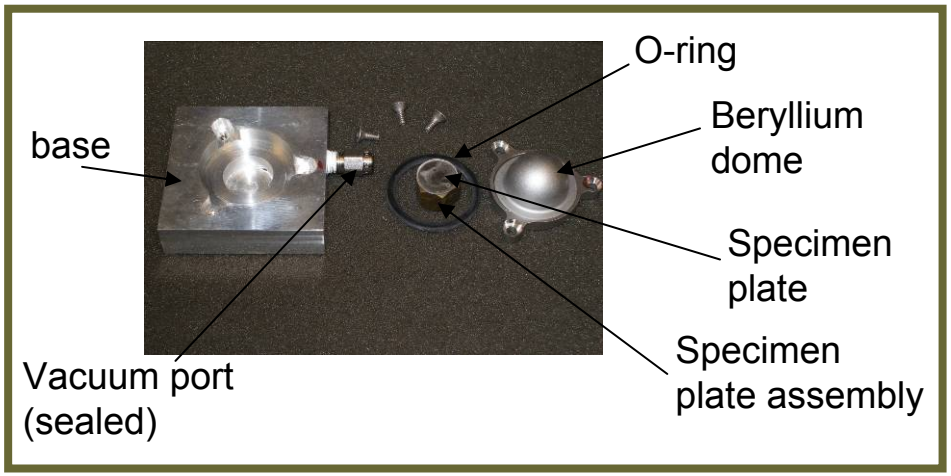
Solvated Hydride Incorporation

Solution coating of ceramic (SiO_2 initially) substrate with metal borohydride.

Solution Deposition



BeD-XRD



Analyze air-sensitive materials.

Solvent selection is critical:

- Stability in synthesis and deposition
- Binding to surface is appropriate
- Volatile enough to be removed prior to BH_4 decomposition

Project Summary

Improve reversibility of high capacity hydride candidates by developing advanced NFS chemistries through combined modeling and experimentation.

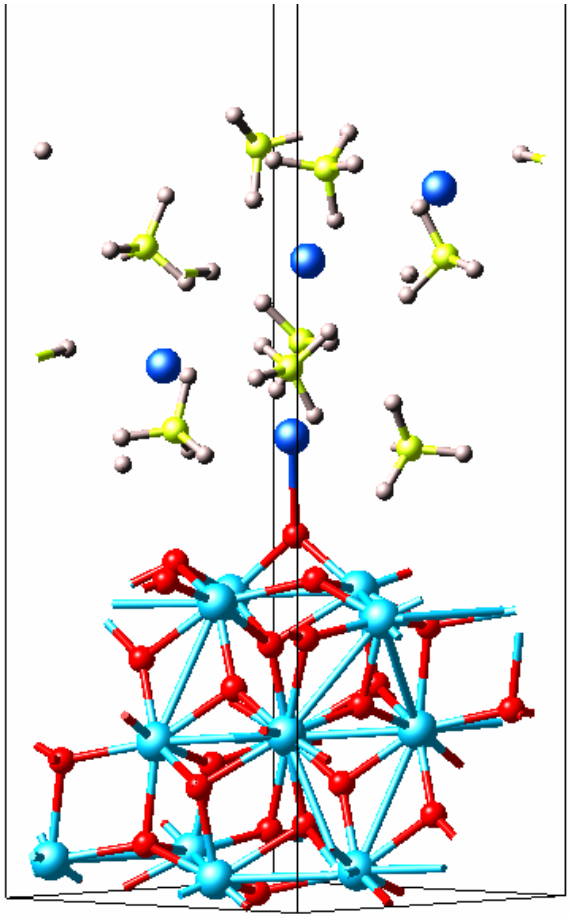
Modeling

- Simulations show interfacial NFS interactions can alter stability of hydride and discharged products.
- Dopants balance both NFS lattice stability and electronic NFS/hydride interfacial interactions.

Framework and Hydride

- Initial nano-framework structures have been synthesized (ZrO_2, Al_2O_3, SiO_2, TiO_2, Carbon).
- Multiple suitable oxide candidates have been identified. ZrO_2 selected because of low reducibility.
- Compatibility screening reactions with $LiBH_4$ have been performed.
- UTRC / Albemarle focus on ligand stabilized: $NaTi(BH_4)_4$*ligand
- Sandia focus on stable borohydride: $Ca(BH_4)_2$

Future Plans



$Ca(BH_4)_2$ on ZrO_2

Atomistic Modeling

- Simulate $Ca(BH_4)_2$ and $NaTi(BH_4)_4$*ligand hydride interactions with ZrO_2 NFS.
- Virtually tune doped NFS to balance hydride stability and dehydrogenation.
- Virtually develop doped, functionalized, catalyzed NFS to enhance reversibility.

Framework and Hydride

- Evaluate initial oxide (ZrO_2) aerogel.
- Continue to assess oxide, modified carbon and other alternative framework materials.
- Examine support interactions with selected $NaTi(BH_4)_4$*ligand and $Ca(BH_4)_2$.
- Evaluate doped, heterogeneously catalyzed and functionalized nano-frameworks.