METAL HYDRIDE CENTER OF EXCELLENCE

Development and Evaluation of Advanced Hydride Systems for Reversible Hydrogen Storage

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Project ID
ST34

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Timeline

- Project start date: April, 2005
- Project end date: Dec., 2009
- 60 % complete

Budget

- Expected total project funding:
    - $1.859M (DOE)

- Funding received in FY07
    - $400K (DOE)
- Funding received for FY08:
    - $487.2K (DOE)

Barriers/System Targets

- A. System Weight and Volume
    - 2010 Targets: 6 wt.% & 45 gH/L
- D. Durability/Operability
    - 2010 Target: Life of 1000 cycles
- E. Charging/Discharging Rates
    - 2010 Target: Fill time of 3 min for 5 kg H_2
- P. Lack of Understanding of Hydrogen Physisorption and Chemisorption

Partners

- Participant in DOE MHCoE – collaborations with partners in all five sub-group Projects [primarily with Caltech, NIST, GE Global, U. Hawaii, SNL, U. Utah, HRL, ORNL in FY-07 & FY-08]

- Washington U. and Caltech in support a DOE/BES H_2 Storage Project on solid state NMR studies of light element hydrides

- International: IFE (Norway), Tohoku U. (Japan), and AIST (Japan)

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Objectives & Milestones of JPL in MHCoE

Develop and demonstrate light-metal hydride systems that meet or exceed the 2010/2015 DOE goals for on-board hydrogen storage

(1) Validation of storage properties and reversibility in light element hydrides
- Nanophase, destabilized hydrides based upon LiH, MgH_2, & $LiBH_4$
- Complex hydrides (e.g., amides/imides, borohydrides, & AlH_3-based hydrides)
- Samples provided by numerous MHCoE partners

(2) Support developing lighter weight and thermally efficient hydride storage vessels.

FY07/FY08 Milestones:

- **Evaluate behavior of destabilized MgH_2/$LiBH_4$ and Li-Sc-B-H systems against targets:**
  - ➢ **Reversibility**
  - ➢ **Kinetics**
  - ➢ **H_2 storage parameters (i.e., capacities, pressures, etc.)**
- **Characterize phases & chemical bonding via MAS-NMR (Caltech) to better understand basic chemisorption processes.**
  - ➢ **Li amides/imides/alanates**
  - ➢ **Borohydrides**
  - ➢ **Other hydrides provided by MHCoE partners**
- **Have postponed extended cycling tests to assess lifetime potential & durability since no destabilized/catalyzed hydrides was found with viable kinetics and reversibility to justify this commitment.**

JPL Has Been Supporting Many MHCoE Projects

DOE/EERE

Metal Hydride Center of Excellence (MHCoE)
Coordinating Council
Sandia National Laboratory (SNL)- Lead Laboratory

Project Groups

A
Destabilized Hydrides

- **Stanford (POC)**
- Caltech
- **JPL**
- UIUC
- U. Hawaii
- U. Pitt/CMU
- HRL
- U. Utah
- Intematix
- NIST

B
Complex Anionic Materials

- **SNL(POC)**
- GE
- U. Hawaii
- UIUC
- **JPL**
- ORNL
- NIST
- UNR
- Utah
- UTRC

C
Amides/ Imides (M-N-H)

- **Utah (POC)**
- GE
- UNR
- ORNL
- U. Hawaii
- **JPL**
- Caltech
- SRNL

D
Alanes (AlH$_3$)

- **BNL(POC)**
- SRNL
- U. Hawaii
- SNL
- UIUC
- UNB
- **JPL**

E
Engineering Analysis & Design

- **SRNL(POC)**
- NIST
- **JPL**
- GE
- SNL

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Perform Analysis and Characterization of Selected Hydrides to Explain Fundamental Processes:

- Volumetric measurements are used to determine hydrogen storage capacities and equilibrium pressures on destabilized nanophase and complex metal hydrides.
- Magic Angle Spinning - Nuclear Magnetic Resonance (MAS-NMR) measurements being performed at Caltech Solid State NMR Facility (Dr. Son-Jong Hwang, lead) to assess the phase compositions and chemical bonding parameters.
- Examinations of structures by neutron scattering and diffraction, etc. in collaboration with MHCoE partner NIST.
- Using Raman spectroscopy measurements at Caltech to determine mechanisms of desorption processes .
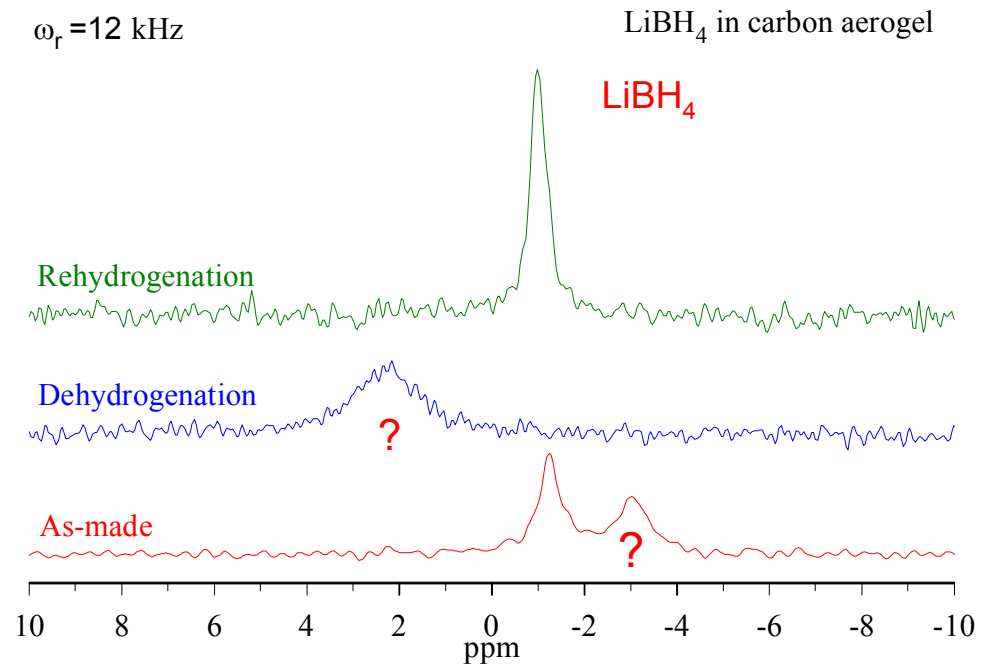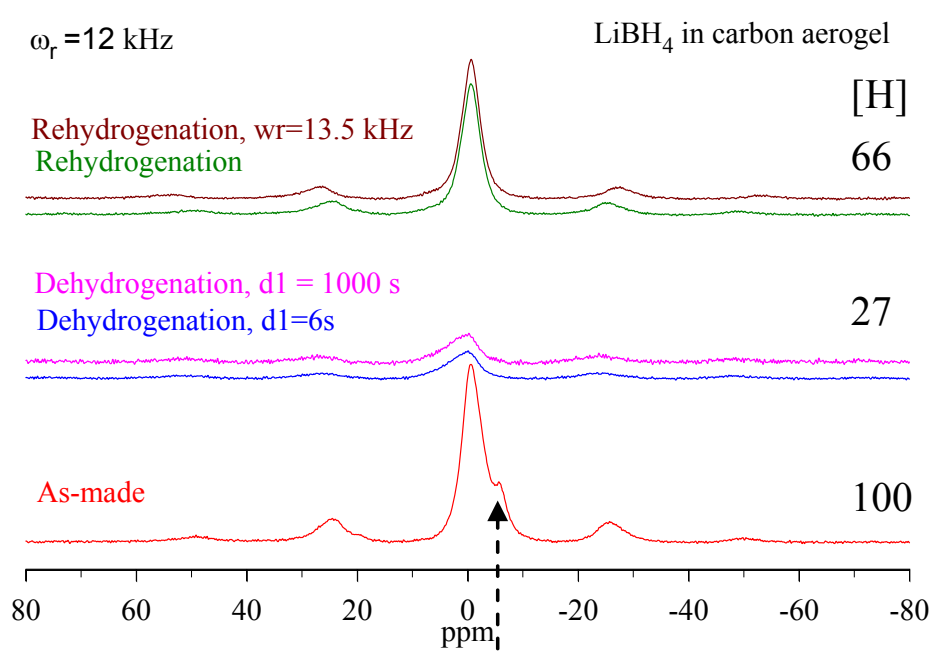- Interacting with MHCoE theory teams (i.e., U. Pittsburgh, GA Tech, and UMSL) on phases and destabilization behavior.

Project A: NMR Studies of H_2 Reactions with LiBH$_4$ in Carbon Aerogel (CA) Scaffolds

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Sample ID (HRL)	Chemical species	Processing Description
SO542-113-59	LiBH$_4$/CA	As-made in 25 nm carbon Aerogel (44.7 wt%)
SO542-113-59-used	LiBH$_4$/CA	Dehydrogenation at 400 ºC
SO542-113-59-used-a	LiBH$_4$/CA	Rehydrogenation at 100 bar H$_2$, at 400 ºC for 2 hours

HRL_SO542_1H

^{1}H MAS NMR

HRL_SO542_6Li_bd

^{6}Li MAS NMR

ω_r = 12 kHz

LiBH$_4$ in carbon aerogel

[H]

Rehydrogenation, wr=13.5 kHz
Rehydrogenation
66

Dehydrogenation, d1 = 1000 s
Dehydrogenation, d1=6s
27

As-made
100

ω_r = 12 kHz

LiBH$_4$ in carbon aerogel

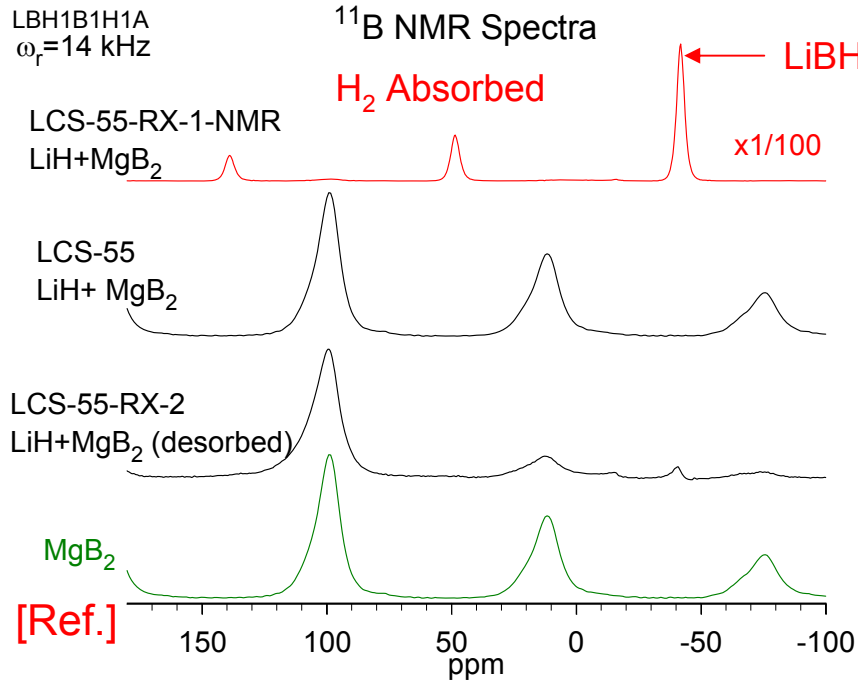LiBH$_4$

Rehydrogenation

Dehydrogenation
?

As-made
?

- Two proton peaks in the as-made sample indicate distinct hydrogen species within the scaffold where the bulk LiBH$_4$ peak recovers while the other unknown peak (at -5 ppm) disappears after cycling.

- ^{6}Li NMR spectrum for LiBH$_4$ on CA scaffold also suggest two different sites. The -3 ppm peak might be Li ions interacting with the surface. Re-hydrogenation gives the LiBH$_4$ phase without the -3 ppm peak.

- Partial reversibility of LiBH$_4$ was noted in ^{11}B spectra (not shown) – some B$_{12}$H$_{12}^{2-}$ species & B formed.

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MAS-NMR Determined Phase Formation & Reversibility in Destabilized $LiBH_4/MgH_2$

"$MgH_2 + 2LiBH_4 = 2LiH + MgB_2 + 4H_2$"

J. J. Vajo, et al., J. Phys. Chem. B **109** (2005) 3719

Samples	Code	Treatment	Comments
$LiH + MgB_2$	LCS-55	As ball milled	From J. Vajo [HRL]
$LiBH_x + MgH_2$	LCS-55: RX-1	Absorbed H_2	Saturated hydrides
$MgB_2 + LiH + LiBH_x$	LCS-55: RX-2 + SiO_2	Desorbed H_2: diluted for NMR	Incomplete desorb reaction

^{11}B NMR Spectra

LBH1B1H1A
ω_r=14 kHz

H$_2$ Absorbed

LCS-55-RX-1-NMR
LiH+MgB$_2$

LiBH$_4$
x1/100

LCS-55
LiH+ MgB$_2$

LCS-55-RX-2
LiH+MgB$_2$ (desorbed)

MgB$_2$

[Ref.]

ω_r=12 kHz

— Bloch decay
— CPMAS; p15=500us

LiBH$_4$

MgB$_2$

Li$_2$B$_{12}$H$_{12}$

^{11}B MAS & CPMAS of Desorbed LCS-55 RX-2
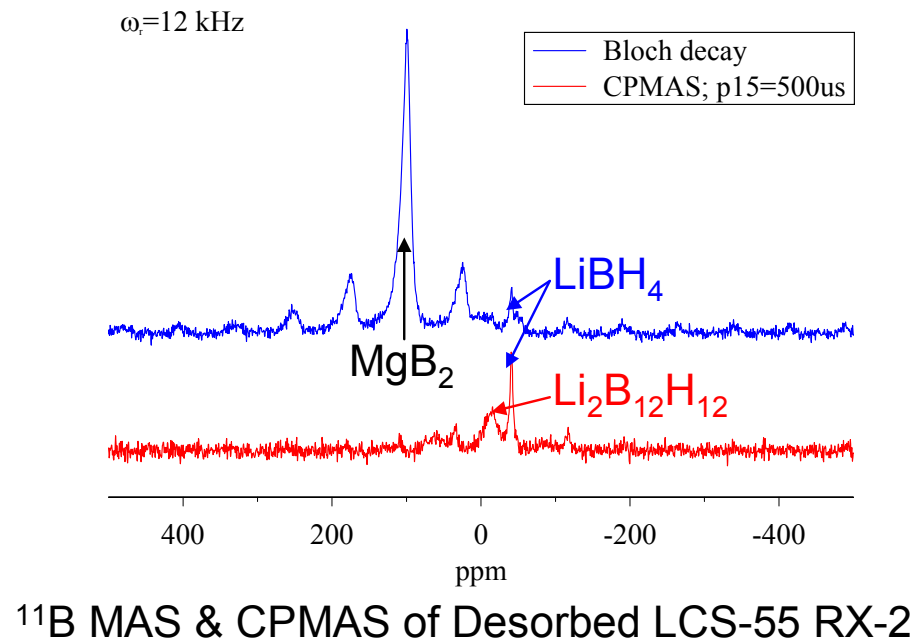
NMR shows residual amounts of $B_{12}H_{12}^{-2}$ along with $LiBH_4$: Incomplete reversibility under these cycling conditions.

Reaction down selected to "No-Go", except for Aerogel scaffolding studies (HRL).

JPL Objectives:

Support phase characterizations and bonding properties for new borohydrides [i.e., $Mg(BH_4)_2$, $Ca(BH_4)_2$, & $LiSc(BH_4)_4$] and their desorption processes via NMR measurements in collaboration with Caltech, SNL, GE Global, NIST, U. Hawaii.

$Mg(BH_4)_2$ Decomposition Pathway
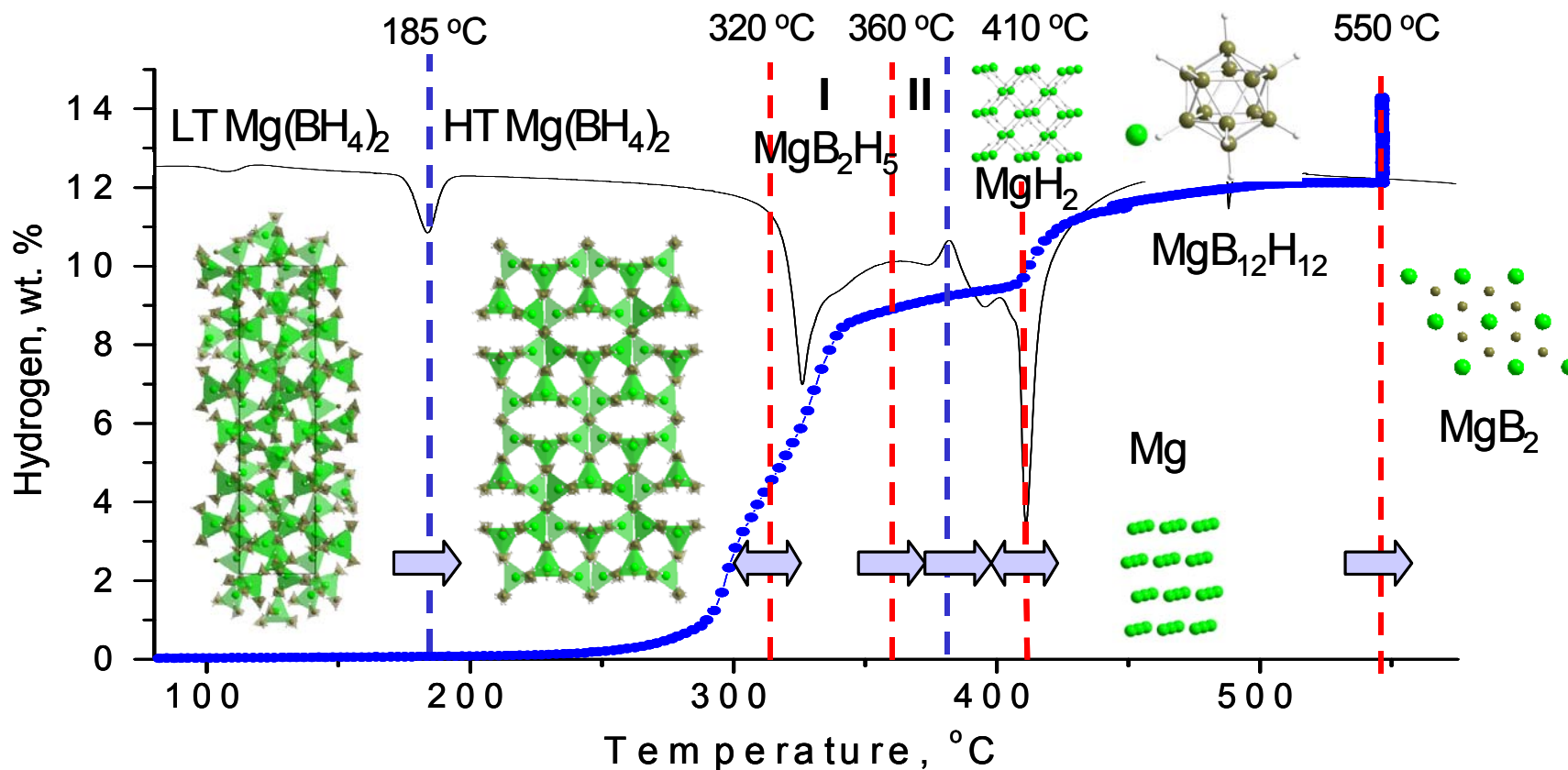
NMR has been a key method to establish phase identification!

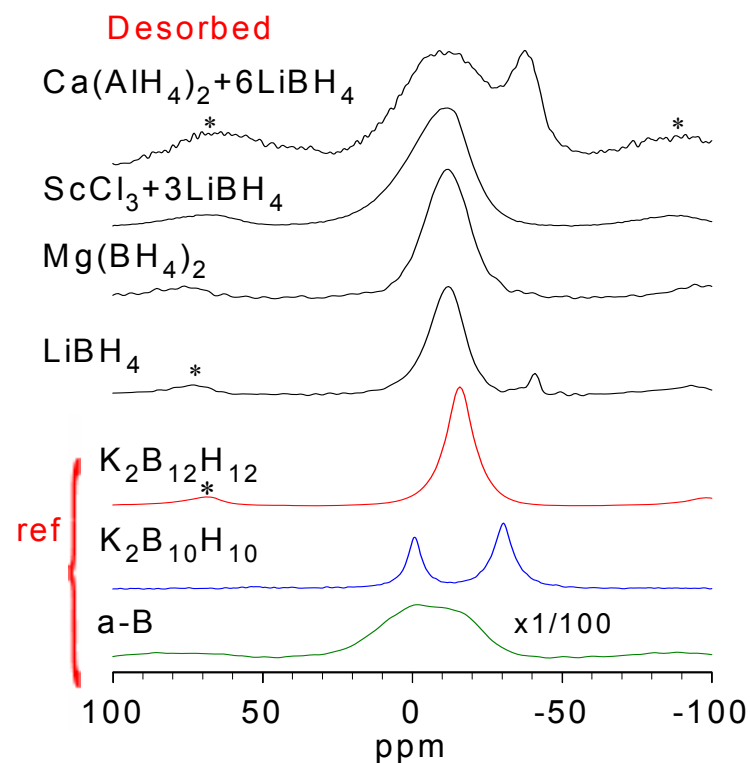# Desorption Behavior of Borohydrides

$$(1)\; LiBH_4 \rightarrow LiH + B\ (\text{amorphous}) + 1.5H_2\uparrow$$

$$(2)\; M(BH_4)_n \rightarrow MH_x + n\text{"a-B"} + (2n-x/2)H_2\uparrow$$
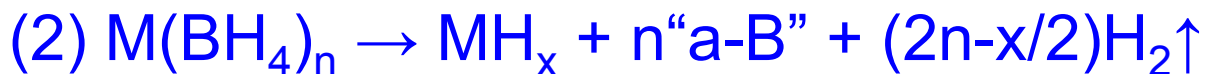
Boron phases NOT identifiable via X-ray/Neutron diffraction ("Amorphous")

Solid state ^{11}B NMR identified the formation of $M_{2/n}B_{12}H_{12}$ phases as major intermediate species in hydrogen desorption reaction of various $M(BH_4)_n$ systems before further conversion to either MB_n or $B+MH_n$.

$$\bigcirc = B\text{-}H$$
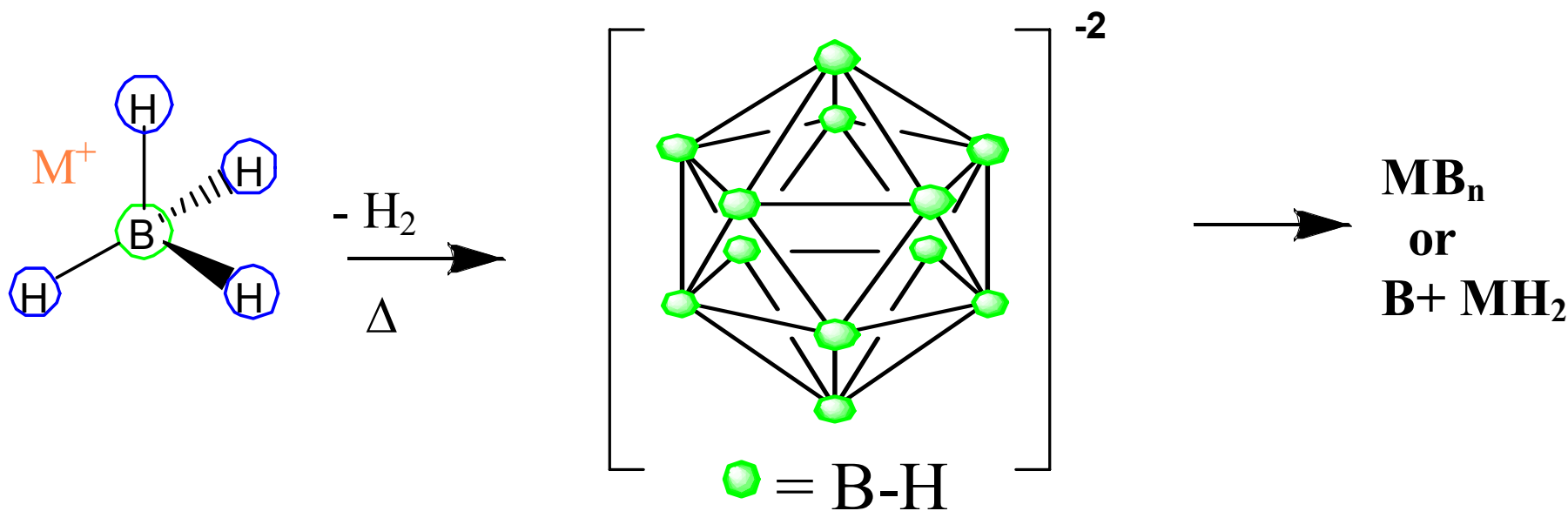
S.-J. Hwang, R. C. Bowman, Jr., J. W. Reiter, J. Rijssenbeek, G. L. Soloveichik, J.-C. Zhao, H. Kabbour, and C. C. Ahn, *J. Phys. Chem. C Letters* **112** (2008) 3164-3169.

In collaboration with Caltech and GE, $LiBH_4$, $Mg(BH_4)_2$, $LiSc(BH_4)_4$, $Ca(AlH_4)_2$-$LiBH_4$, studied by ^{11}B magic angle spinning (MAS) and cross-polarization magic angle spinning (CPMAS) after hydrogen desorption reactions at ~400 ºC .

Desorbed

$Ca(AlH_4)_2 + 6LiBH_4$

$ScCl_3 + 3LiBH_4$

$Mg(BH_4)_2$

$LiBH_4$

$K_2B_{12}H_{12}$

$K_2B_{10}H_{10}$

ref

a-B   x1/100

100   50   0   -50   -100
ppm

Des-$Mg(BH_4)_2$

Des-$LiBH_4$

ref- $K_2B_{12}H_{12}$

-10   -12   -14   -16   -18   -20
ppm

^{11}B CPMAS NMR spectra of desorbed materials (contact time = 0.05 ms). Ref. spectra: amorphous boron (a-B, note the scale change (1/100)), $K_2B_{10}H_{10}$, and $K_2B_{12}H_{12}$ added for comparison.
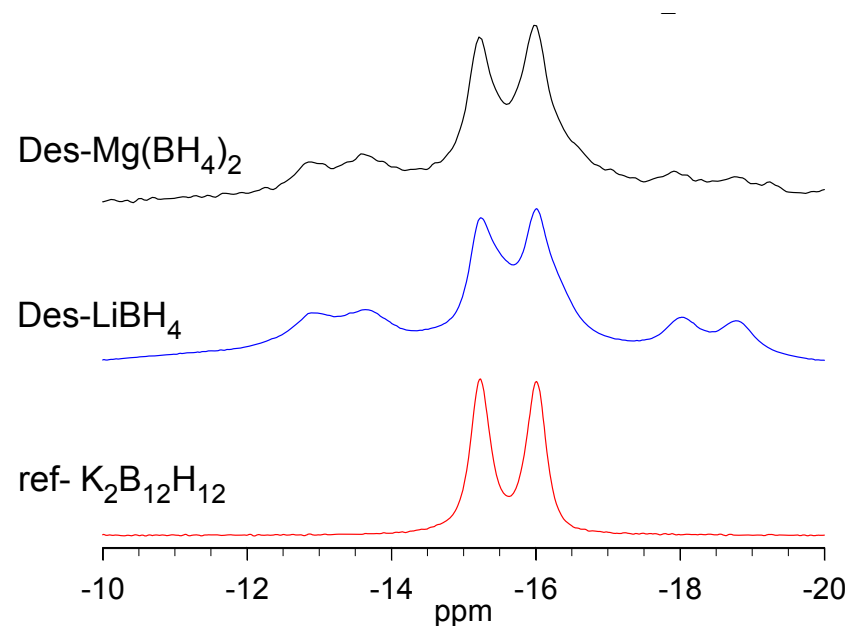
**^{11}B solution NMR spectra after powders from desorption reactions were dissolved in H_2O.**
- **Ref: $K_2B_{12}H_{12}$ compound dissolved in water.**
- **$[B_{12}H_{12}]^{-2}$ unit present in the dissolved $LiBH_4$ and $Mg(BH_4)_2$ decomposition products.**
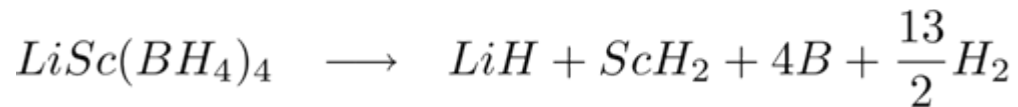- **J(B-H) = 125 Hz is confirming signature of B-H chemical bond in $[B_{12}H_{12}]^{1-2}$ unit**
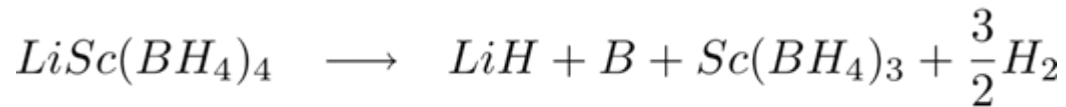
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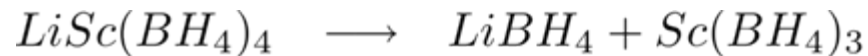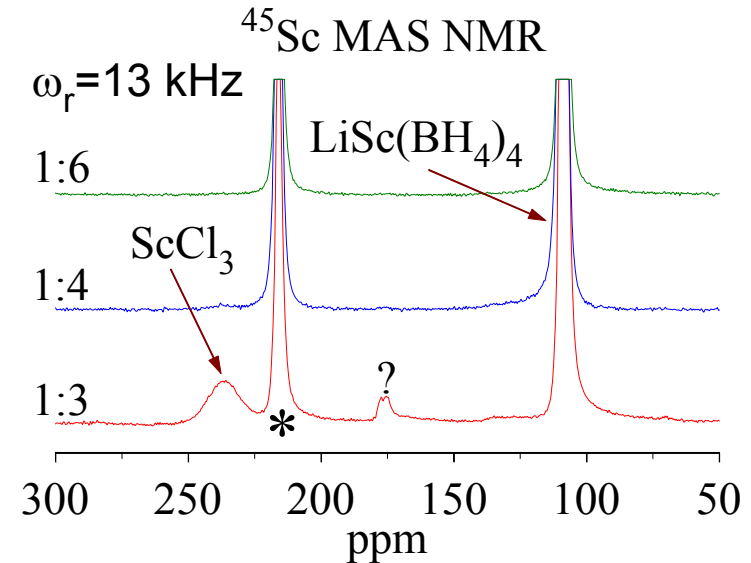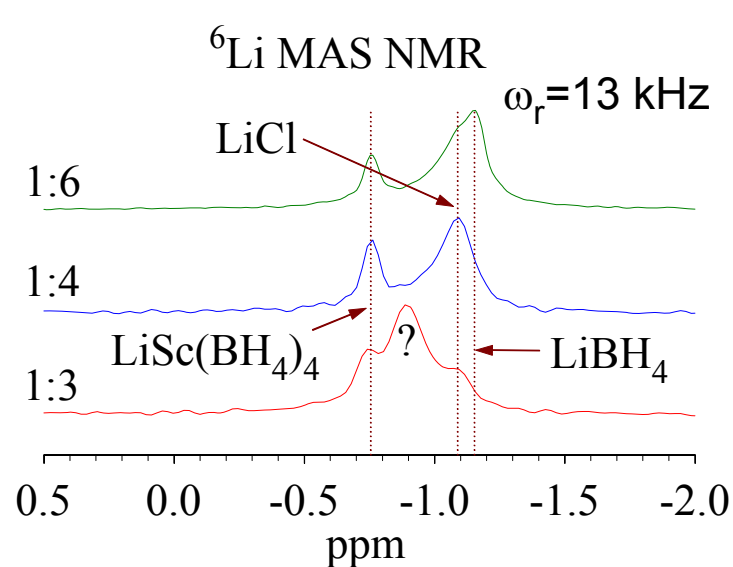
Metathesis Synthesis of Borohydrides by Ball Milling (BM) Method

- Approach used by Y. Nakamori & S. Orimo to make $M(BH_4)_n$ & $M'M(BH_4)_n$
- Caltech: Anhydrous $ScCl_3$ and $LiBH_4$ (Aldrich, $\geq 90\%$) mixed with five 0.5" diameter SS balls in a Fritsch-pulverisette 6 planetary mill at 500 rpm for 3 hours

ratio ($ScCl_3 + xLiBH_4$)	non-ionic route	ionic route
1:3	$ScCl_3 + 3LiBH_4 = Sc(BH_4)_3 + 3LiCl.$	$ScCl_3 + 3LiBH_4 = \frac{3}{4} LiSc(BH_4)_4 + 9/4 LiCl + \frac{1}{4} ScCl_3.$
1:4	$ScCl_3 + 4LiBH_4 = Sc(BH_4)_3 + 3 LiCl.+ LiBH_4$	$ScCl_3 + 4LiBH_4 = LiSc(BH_4)_4 + 3 LiCl.$
1:6	$ScCl_3 + 6LiBH_4 = Sc(BH_4)_3 + 3 LiCl. + 3LiBH_4$	$ScCl_3 + 6LiBH_4 = LiSc(BH_4)_4 + 3 LiCl + 2LiBH_4.$
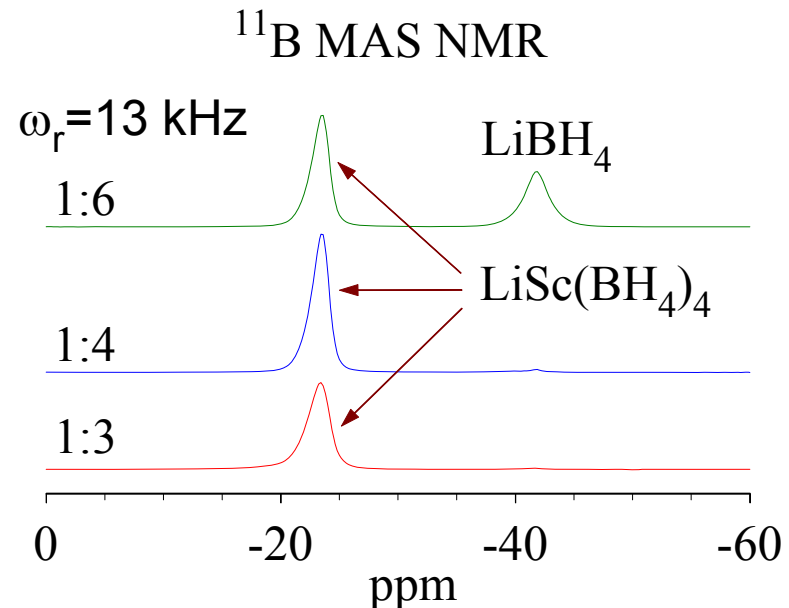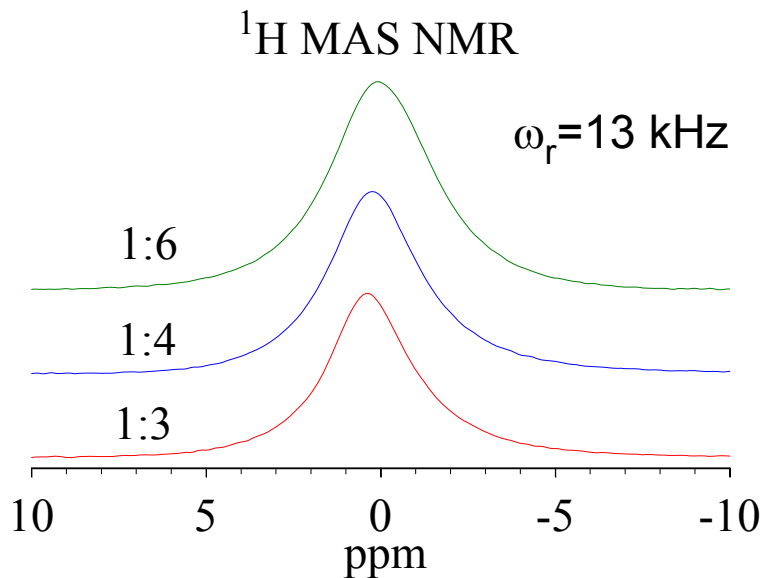
MAS proton & [11]B spectra for ball milled mixtures of $ScCl_3/LiBH_4$ in the ratios 1:3, 1:4, and 1:6. Peak assignments were obtained from combined analyses of spectra for all nuclei.

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MAS and CPMAS spectra of ^{6}Li and ^{45}Sc nuclei (also ^{11}B) for ScCl$_3$/LiBH$_4$ in the ratios 1:3, 1:4, and 1:6 show only LiSc(BH$_4$)$_4$ phase is formed. The "?" in ^{6}Li and ^{45}Sc spectra are from a species without protons (i.e., probably Li$_3$ScCl$_6$).

^{6}Li MAS NMR, ω_r=13 kHz

^{45}Sc MAS NMR, ω_r=13 kHz

$$LiSc(BH_4)_4 \longrightarrow LiBH_4 + Sc(BH_4)_3$$

$$LiSc(BH_4)_4 \longrightarrow LiH + B + Sc(BH_4)_3 + \frac{3}{2}H_2$$

$$LiSc(BH_4)_4 \longrightarrow LiH + ScH_2 + 4B + \frac{13}{2}H_2$$

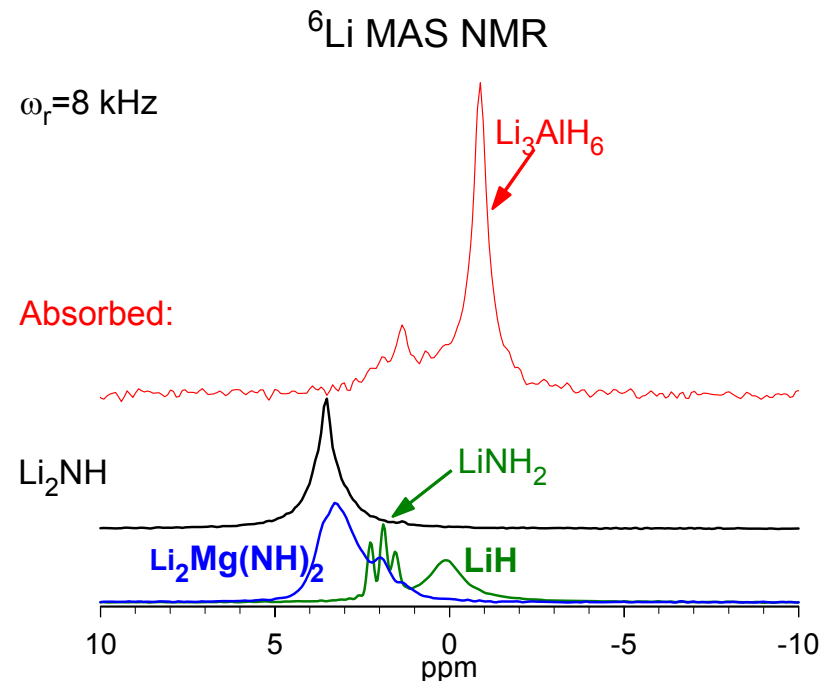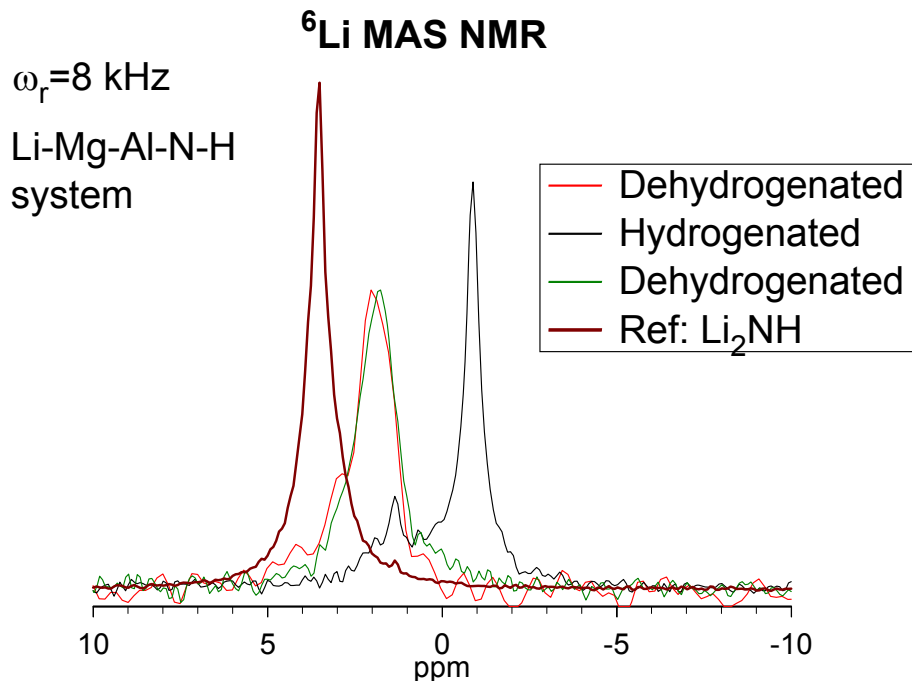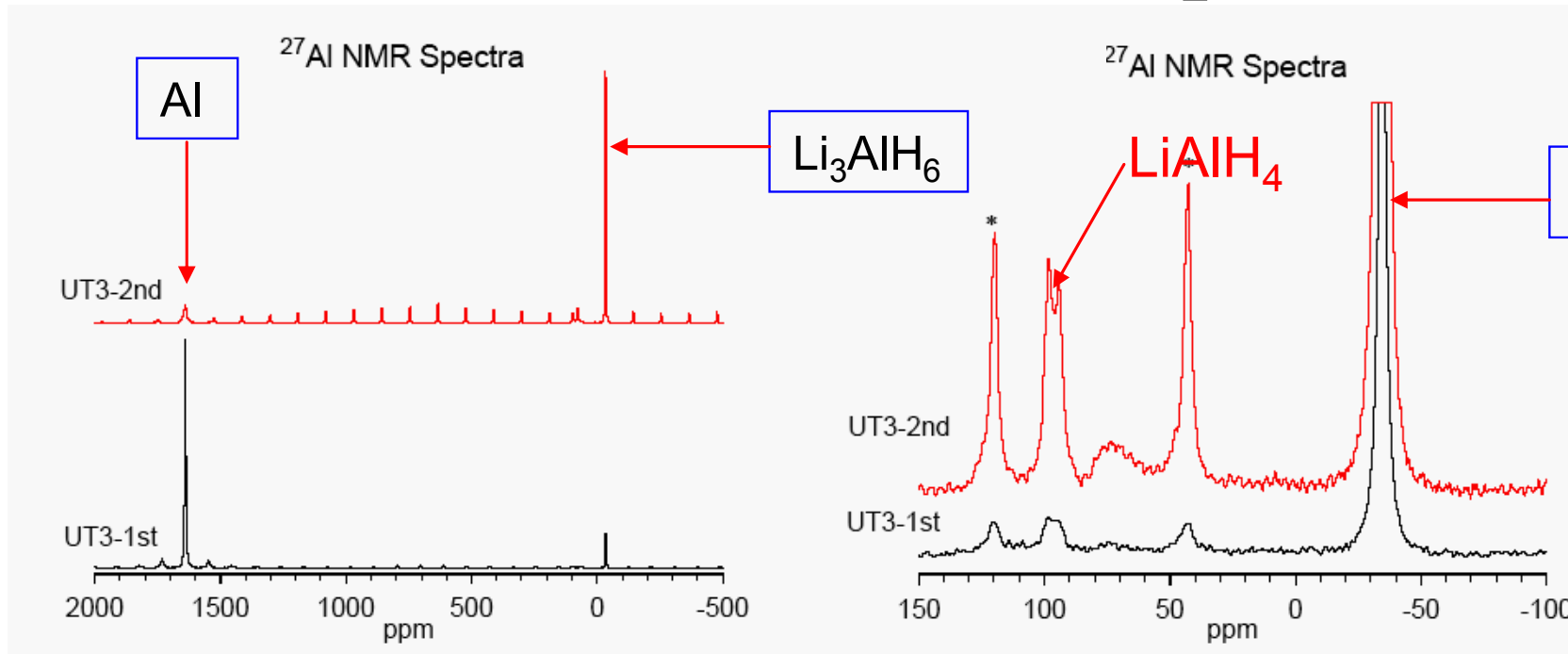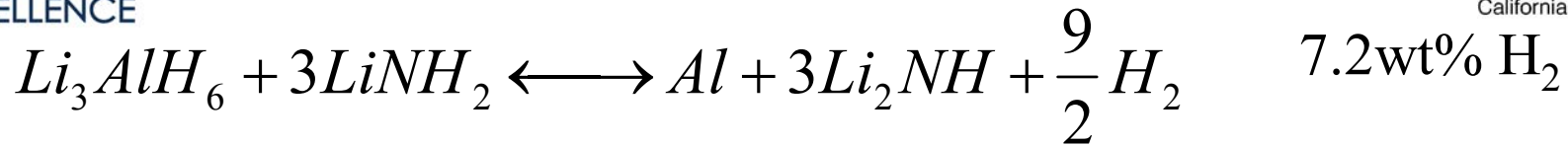$$LiSc(BH_4)_4 \longrightarrow LiBH_4 + ScH_2 + 3B + 5H_2$$

- Static DFT calculations (no phonons) T=0K
- All reaction equations +67 kJ/mol f.u. or greater (Consistent with NMR!)
- BM method does **NOT** yield the less stable covalent Sc(BH$_4$)$_3$ phase

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- Improve basic understanding of these materials
- Provide info on local chemical bonding during reaction
- Critically test and complement theoretical modeling of reaction mechanisms
- Assess reactions of amides/imides with alanates and borohydrides.

Example: $\frac{2}{3} Li_3 AlH_6 + Mg(NH_2)_2 \longleftrightarrow \frac{2}{3} Al + Li_2 Mg(NH)_2 + 3H_2$ 6.5wt% H_2
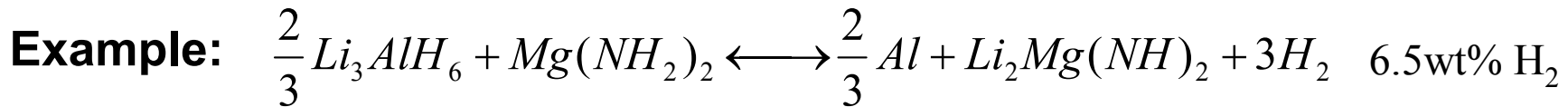
^{6}Li and ^{27}Al spectra indicated reversibility of the Li-Mg-Al-N-H samples from U. Utah.

J. Lu, Z. Z. Fang, H. Y. Sohn, R. C. Bowman Jr., and S-J. Hwang, J. Phys. Chem. C **111** (2007) 16686-16692.

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Study of the Reaction Pathways using NMR

$$Li_3AlH_6 + 3LiNH_2 \longleftrightarrow Al + 3Li_2NH + \frac{9}{2}H_2 \qquad 7.2wt\% \ H_2$$

^{27}Al NMR Spectra

Al

Li$_3$AlH$_6$

UT3-2nd

UT3-1st

2000 1500 1000 500 0 -500
ppm

^{27}Al NMR Spectra

LiAlH$_4$

Li$_3$AlH$_6$

UT3-2nd

UT3-1st

150 100 50 0 -50 -100
ppm

Phase composition of UT3-2nd Sample

Components	Chemical shift (ppm)	Rel. Quantity (%)
Al(M)	1640	5.2
AlH$_4^-$	98.8	8.1
Al$_2$O$_3$	74.1	3.8
AlH$_6^{-3}$	-34.6	82.9

➢ Conversion to Li$_3$AlH$_6$ is more than 80% based from NMR results, which also indicate LiAlH$_4$ forming when pressure is 2500 psi.

➢Subsequent studies showing impact of reaction conditions on product yield & formation of AlN phase @ heating rates < 5 K/min.

UT3-1st: Sample UT2 after rehydrogenation at 300 °C and 2000 psi
UT3-2nd: Sample UT2 after rehydrogenation at 300 °C and 2500 psi

Prototype Hydride Beds Development and Life Testing

Objectives:

- **Support development of more efficient hydride storage vessels to reduce storage system mass while retaining viable thermal management during H_2 absorption & desorption.**

- **Support system design and analyses using methods and analytical models established at JPL for sorption cryocooler hydride compressor beds.**

- **Evaluate the performance and robustness of candidate hydrides during many cycles of hydrogen absorption and desorption.**

  Deferred conducting cycling tests in FY-07/08 as $LiBH_4/MgH_2$ and other borohydride systems are not attractive due to slow kinetics & poor reversibility – will start cycling tests only if a viable candidate is identified from current screening assessments.

Accomplishments during FY07/08

• **Completing Metal Hydride Storage Survey Report on status of the vessel design configurations and thermal analyses methodologies**
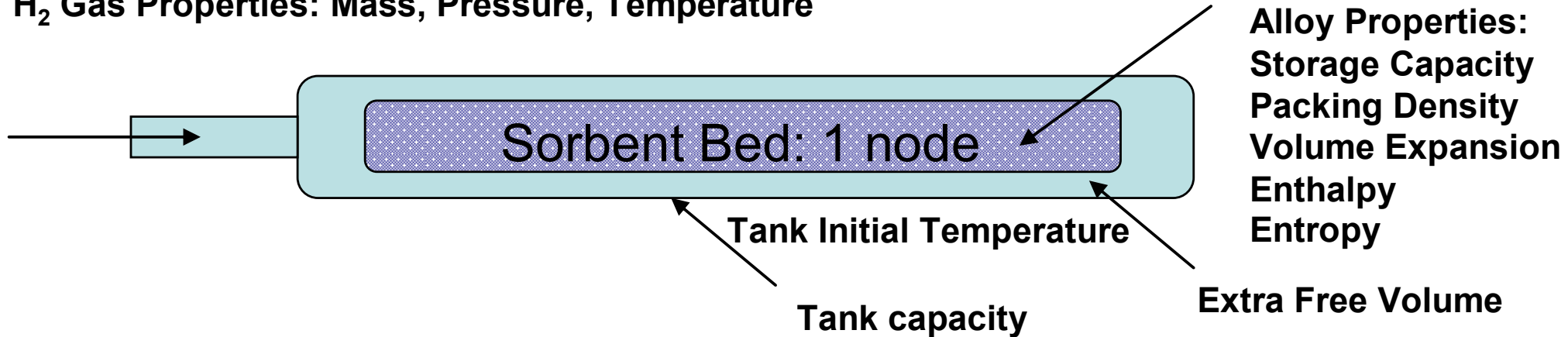
  ➢ Compiled from literature sources:
  ➢ Teaming with SRNL, UTRC, SNL, & DOE/EERE
  ➢ Progress reported at MS&T'07 Meeting, Detroit, MI (September 2007) and at DOE SSAWG Meeting, Washington DC (December 2007).
  ➢ Draft Report is planned to be completed in June 2008.

• **Evaluate MH System thermal performance with analysis codes adapted from models previously developed for JPL sorption cryocoolers:**

  ➢ Comparisons using generic bed design configurations:
    ▪ Known hydrides (e.g., $LaNi_{4.8}Sn_{0.2}$, AB_2, and bcc-type alloys)
    ▪ Light complex hydrides (e.g., alanates, etc.)
  ➢ Assess feasibility of rapid absorption filling of "Hybrid HP-LT Hydride Vessels"
    ▪ Materials limited by heat transfer processes rather than reaction kinetics
    ▪ Compare behavior of various AB_5 and AB_2 alloys.

Excel Hydride Model to Determine Cooling For Hydride Bed Charging

H$_2$ Gas Properties: Mass, Pressure, Temperature

Alloy Properties:
Storage Capacity
Packing Density
Volume Expansion
Enthalpy
Entropy

Sorbent Bed: 1 node

Tank Initial Temperature

Extra Free Volume

Tank capacity

$$\text{Cooling Required} = \frac{Q_{charging} - Q_{absorbed\_by\_hydrogen} - Q_{absorbed\_by\_alloy}}{\text{Fueling Time}}$$

- ## Model Features:
  - 1 node model
  - 0 order comparison of hydrides

- Heat from bed charging is dependant on alloy enthalpy and hydrogen mass absorbed by the alloy
- Heat Absorbed by Alloy & Hydrogen depend on equilibrium temperature
  - Van't Hoff Equation: P-C-T Curves not included
  - Does not account for the sloped plateaus

Hybrid Tank Cooling Estimates

Abilities:

- Fast back of the envelope approach to calculating required cooling for charging a hydride bed at low pressures
- Calculates hydrogen charged into the alloy
- Calculates an equilibrium temperature
- Can do a 0-order comparison of alloys without taking specific geometry into account
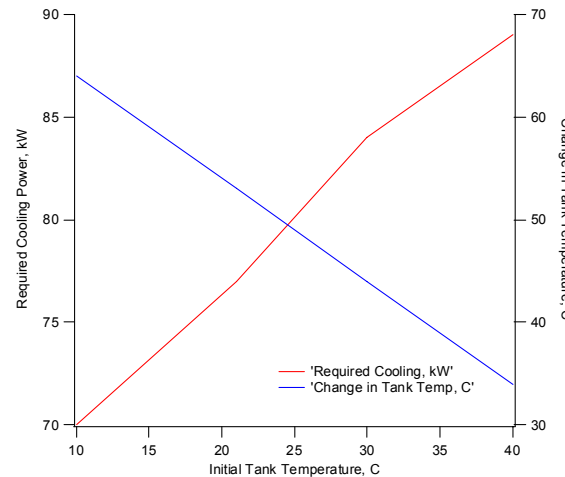
Limitations:

- Does not include Pressure, Temperature, Concentration Curves
- Model code predicts hydrogen always absorbed by the alloy even at high temperatures (not realistic)
- Comparison between two alloys can be difficult due to limitations on pressure, temperature, and hydrogen concentration relationship
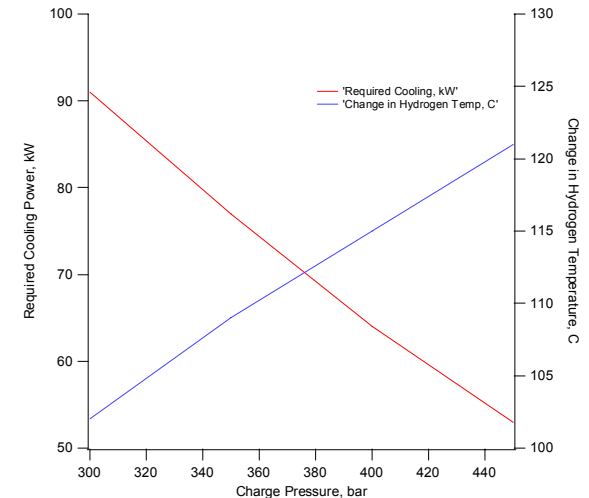
Some Parametric Results for a Ti-Based AB$_2$ Alloy
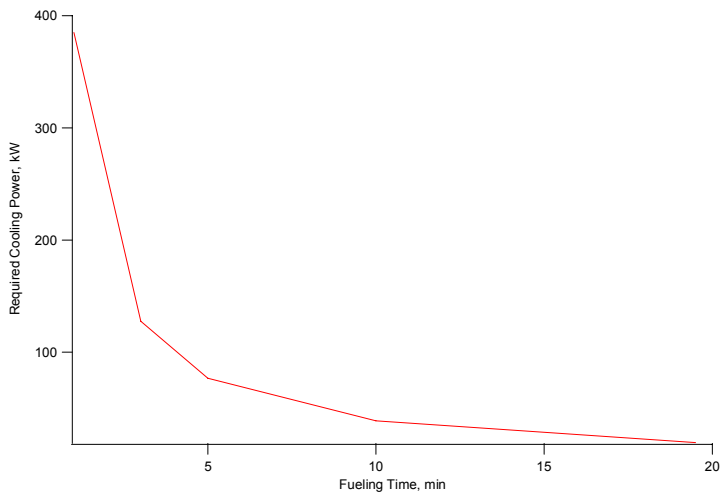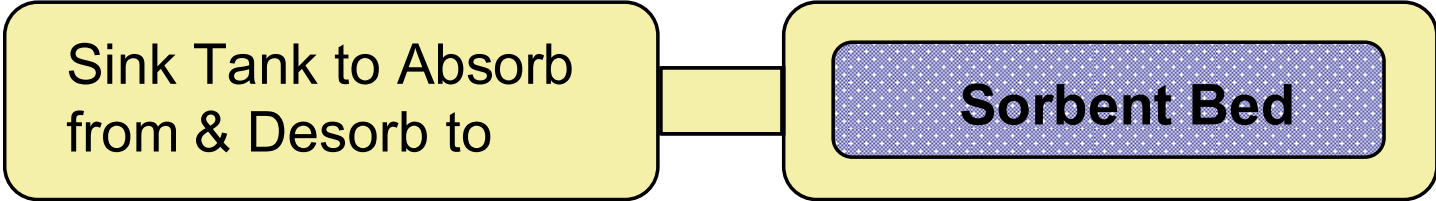

Fueling time (min) **Initial Tank Temperature** **Maximum H$_2$ Charge Pressure (bar)**

**Need to adapt basic model for including Pressure, Temperature, Concentration relationships more completely.**

JPL SINDA/FLUINT Model For Hydride Bed Charging

Sink Tank to Absorb from & Desorb to

Sorbent Bed

- ## Model Features:
  - Over 7000 nodes for the hydride bed
  - Detailed hydride & bed design properties
  - P-C-T curves are calculated for each node

SINDA Model Hydride Bed

28 nodes length

Cooling Fluid Loop

8 diameter layers
280 nodes
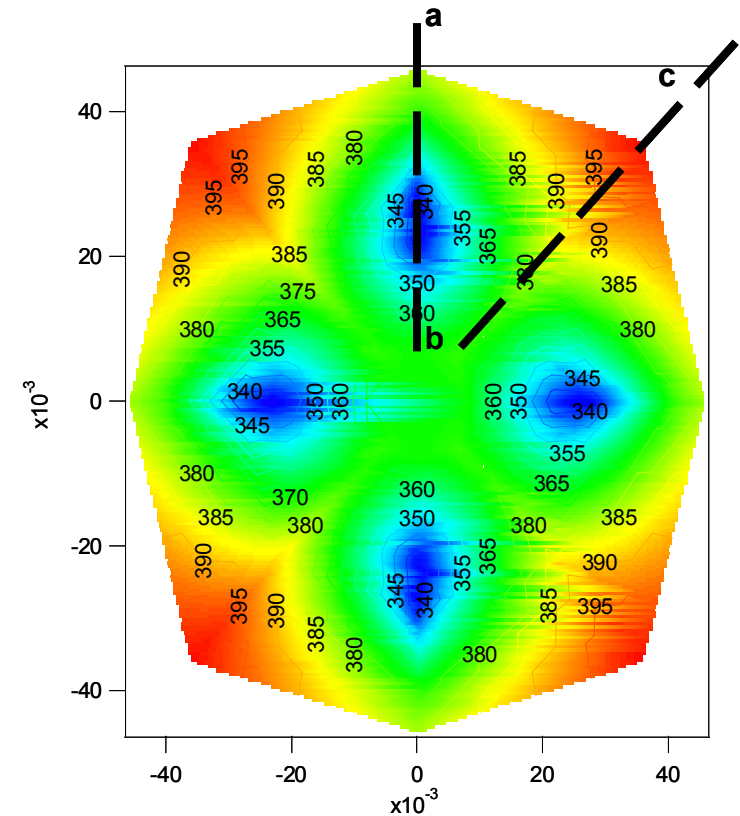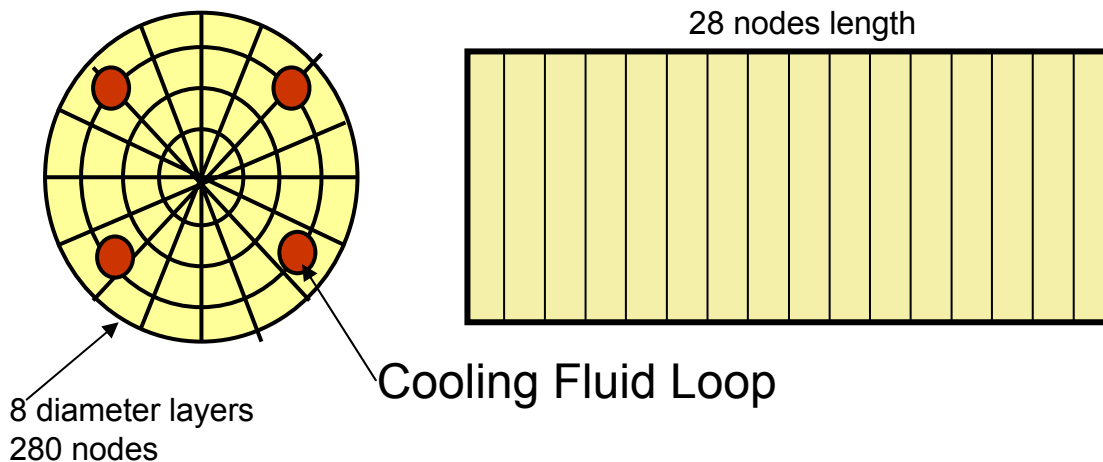
Simulated temperature map shows gradients of ~50 K within bed

Note: Details are in a back-up slide

Planned Future Work (FY08/09)

Destabilized Reactions (Proj. A)

• Continue reaction path investigations using NMR and Raman spectroscopies in the Li-Sc-B-H & $LiBH_4$-$Ca(AlH_4)_2$ systems to understand destabilization and reversibility mechanisms.

• Extend studies of the $LiBH_4$ encapsulated in carbon Aerogel samples to determine chemical bonding of Li and protons with host surfaces via ^{13}C and ^{6}Li MAS-NMR and CP-MAS.

• Apply NMR to identify species in destabilized complex hydride systems that lack definitive crystallographic features or have nanophase structures.

Complex Anionic Materials (Proj. B)

• Continue detailed volumetric & NMR assessments of $Ca(BH_4)_2$ phases (SNL), catalyzed borohydrides and alanates (SNL, U. Hawaii, IFE, and Tohoku U.), and $NaMgH_3$ (SRNL, NIST, and Washington U.)

• Evaluate the desorption and absorption (including potential catalysts) behavior of the polyborane $Li_2B_{12}H_{12}$ via NMR, Raman, and neutron vibrational spectroscopy (Caltech & NIST) then look for methods to enhance reversibility of polyborane reactions.

Amides/Imides (Proj. C)

• Continue systematic ^{27}Al, ^{6}Li, and ^{15}N MAS-NMR studies of Li-Mg-Al-N-H phases (U. Utah).

• Investigate reaction mechanisms, kinetics, diffusion, and reversibility for these materials.

Evaluations of Alanes (Proj. D)

• Assess AlH_3 phases and decomposition processes (U. Hawaii, SRNL, BNL, and IFE)

Engineering Analysis & Design (Proj. E)

• Complete literature survey review on state-of-art hydride bed designs and performance.

• Model optimized H_2 absorption of high-pressure alloy hydride beds for rapid filling rates.

• Perform accelerated cycling study if a promising hydride material can be identified.

Summary of JPL in MHCoE

Approach: JPL supporting MHCoE goals/objectives in two areas
1. Systematic characterizations of phase formation and hydride reversibility using solid state NMR and volumetric measurements (Projects A, B, C, & D)
2. Development of improved hydride storage vessels and system engineering of high performance and long life materials (Project E)

Technical accomplishments and progress:
- Phase characterization, kinetics (i.e., diffusion behavior), & reversibility assessments via NMR in numerous systems (i.e., Li-Mg-B-H, Li-Sc-B-H, Li-B-Ca-Al-H, AlH_3, Li-Mg-Al-N-H) that complement and extend theoretical modeling and empirical discovery studies by other MHCoE partners.
- NMR analysis is identifying amorphous/nanophase species that are not distinguishable via x-ray diffraction or vibrational spectroscopy methods (i.e., established importance of $B_{12}H_{12}$ anions as key intermediates that limit performance of most borohydrides).
- Conducted a survey review of hydride storage vessel configurations and performance to assess state-of-art and provide explicit directions for improvements.

MHCoE Collaborations: Caltech, U. Utah, SNL, GE Global, HRL, NIST, U. Hawaii, SRNL, & UTRC

Future Research: (1) Continue intensive NMR/volumetric characterizations of promising candidates to improve their kinetics and reversibility; (2) Focus system engineering efforts onto modeling behavior during absorption and assessing degradation reactions during extended absorption/desorption cycling.