Development and Evaluation of Advanced Hydride Systems for Reversible Hydrogen Storage

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– A Participant in the DOE Metal Hydride Center of Excellence –

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This presentation does not contain any proprietary or confidential information

Project ID
ST-17

Overview

Timeline

- Project start date: FY05
- Project end date: FY09
- 25 % complete

Budget

- Expected total project funding:
  - $1.78M (DOE)
- Funding received in FY05
  - $150K (DOE)
- Funding received for FY06:
  - $261K (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 five sub-group Tasks [primarily with Caltech, HRL, NIST, BNL, SNL, LLNL in FY-06]
- Washington U. and Caltech to support a new [FY-06] BES Project on solid state NMR of light element hydrides
- International: IFE (Norway), Philips (Netherlands), CNRS (France), and AIST (Japan)

Objectives of JPL within MHCoE

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

(1) Validation of initial storage properties and reversibility in light element metal hydrides and assess their aging durability during extended cycling
- Nanophase, destabilized hydrides based upon LiH, MgH_2, & $LiBH_4$ produced at HRL, Caltech, & other MHCoE partners.
- Complex hydrides (e.g., amides/imides, borohydrides, & AlH_3-hydrides) provided by SNL, NIST, BNL. & other MHCoE partners

(2) Support developing lighter weight and thermally efficient hydride storage vessels and experimentally demonstrating their compatibility with appropriate complex and destabilized nanophase hydrides.

FY05/FY06 Objectives:

- **Determine reversibility of the destabilized LiH/Si & LiH/Ge systems**
- **Evaluate behavior of destabilized MgH_2/$LiBH_4$ & MgH_2/Si systems to assess reversibility, kinetics, & H_2 storage parameters against targets**
- **Characterize phases & chemical bonding via MAS-NMR for Li amides/imides, AlH_3, & selected other hydrides provided by MHCoE partners to better understand basic chemisorption processes**
- **Start extended cycling tests on at least one destabilized hydride (i.e., Li-Mg-N-H) to assess lifetime potential & durability.**

Approach of JPL in MHCoE

Perform Analysis and Characterization of Selected Hydrides:

- Volumetric measurements hydrogen storage capacities and pressures on destabilized nanophase and complex metal hydrides.
- Magic Angle Spinning - Nuclear Magnetic Resonance (MAS-NMR) measurements performed at Caltech Solid State NMR Facility to assess the phase compositions and chemical bonding parameters.
- Examinations by neutron scattering and diffraction, etc. in collaboration with MHCoE partners NIST and Caltech.

Prototype Hydride Beds Development and Life Testing:

- Evaluate the performance and robustness of candidate hydrides using well-characterized experimental test-beds during many cycles of hydrogen absorption and desorption.
- Support development of more efficient hydride storage vessels to reduce storage system mass and demonstrate their compatibility with appropriate complex and destabilized nanophase hydrides.
- Support system design and analyses using methods established at JPL for sorption cryocooler hydride compressor beds.

JPL Supporting All MHCoE Groups

DOE/EERE

Metal Hydride Center of Excellence (MHCoE)
MHCoE Coordinating Council ('06)
Sandia National Laboratory (SNL) - Lead

Project Groups

A

Destabilized Hydrides

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

B

Complex Anionic Materials

- **SNL(POC)**
- **U. Hawaii**
- **UIUC**
- JPL
- ORNL
- NIST
- U. Pitt
- UNR

C

Amides/ Imides (M-N-H System)

- **SNL(POC)**
- **GE**
- **U. Utah**
- **UNR**
- **ORNL**
- **Intematix**
- U. Hawaii
- JPL

D

Alanes (AlH_3)

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

E

Engineering Analysis & Design

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

F

Novel or Cross Cutting Concepts

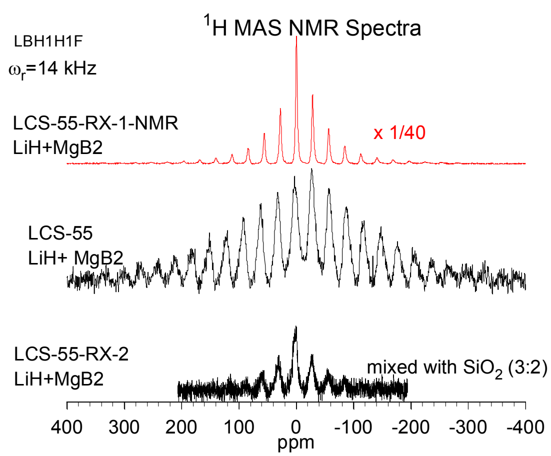
To be Determined Later.

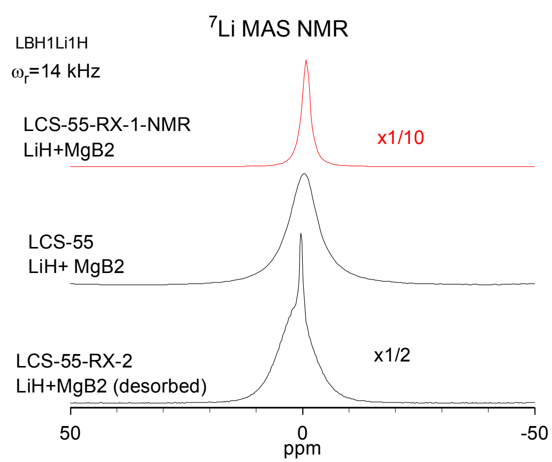
Task 1 - Destabilized Hydride Systems (POC = HRL)

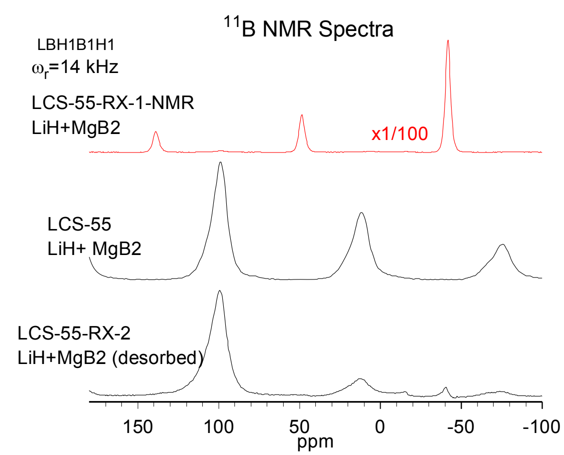
- ## JPL Objectives in FY05/FY06:
  - Validation of initial storage properties and reversibility in nanophase, destabilized hydrides based upon LiH, MgH_2, $LiBH_4$ & others and also to assess their aging durability during extended cycling

- ## Accomplishments:
  - MAS-NMR determined phase formation and reversibility in $LiBH_4/MgH_2$ (SNL):
    - ^{7}Li, ^{11}B and ^{1}H MAS-NMR spectra showed expected different phases with variation in hydrogen contents – foundation for more systematic studies of phase conversion, reversibility, catalytic effects, & degradation behavior.

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
LiH+MgB_2	LCS-55: RX-2	Desorbed H_2	very metallic, max spinning = 6 kHz
MgB_2 + LiH + $LiBH_x$	LCS-55: RX-2 + SiO_2 Powder	Desorbed H_2: diluted for better MAS-NMR	Incomplete desorb reaction noted

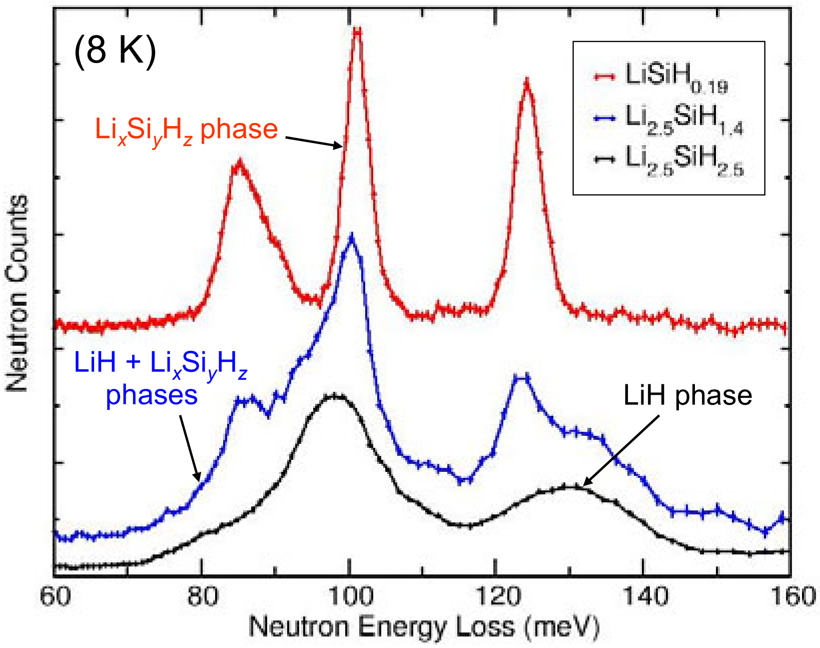






Task 1 Accomplishments - Continued

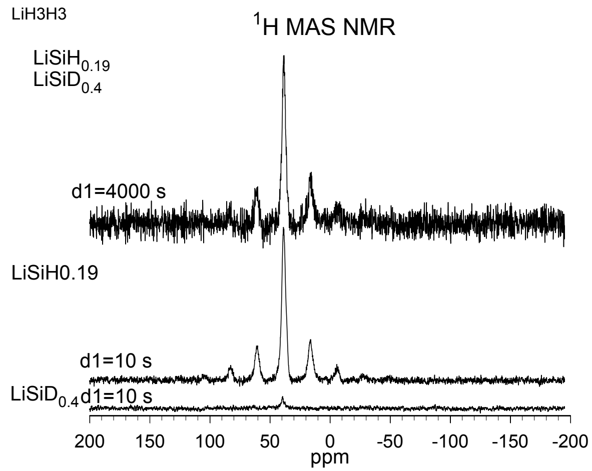
LiH/Si samples – neutron vibrational spectra (NIST), XRD & neutron diffraction patterns, & proton contents verify formation of a ternary Li-Si-H phase initially detected as impurity component by NMR and x-ray diffraction in cycled $Li_{2.5}SiH_x$

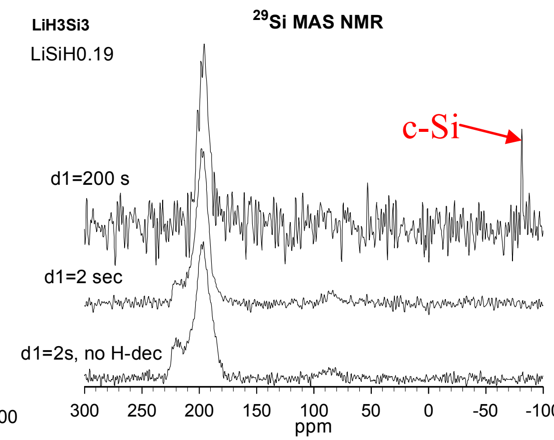


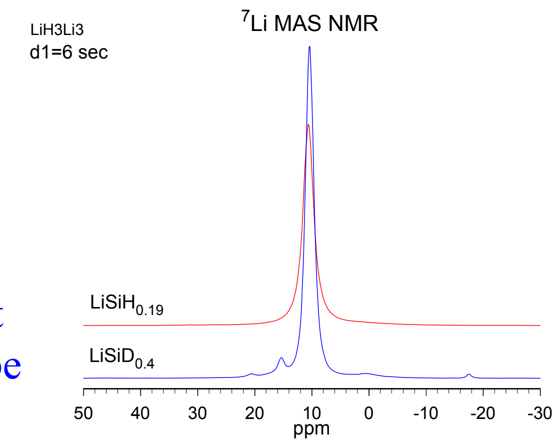
Neutron Vibrational Spectrum of Unknown $Li_xSi_yH_z$ Ternary Phase in $Li_{2.5}SiH_{1.4}$ at 8 K.

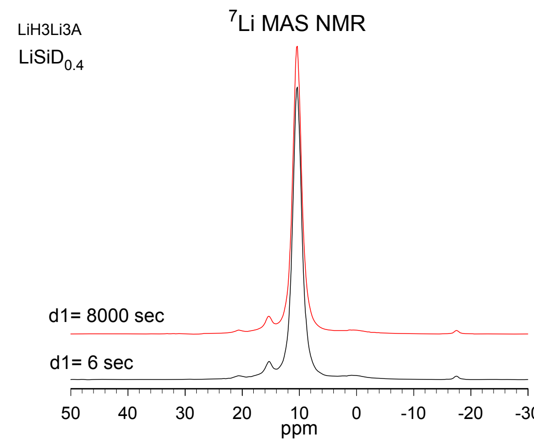
Conclusion: LiH/Si system illustrates both destabilizing and formation of previously unexpected ternary (i.e., $Li_ySi_zH_x$) phases that limits of complete reversibility – an issue to be looked for with other combinations.

MAS-NMR confirm the LiSiH phase [Li_ySiH_x] and some c-Si phase, **but no LiH**!



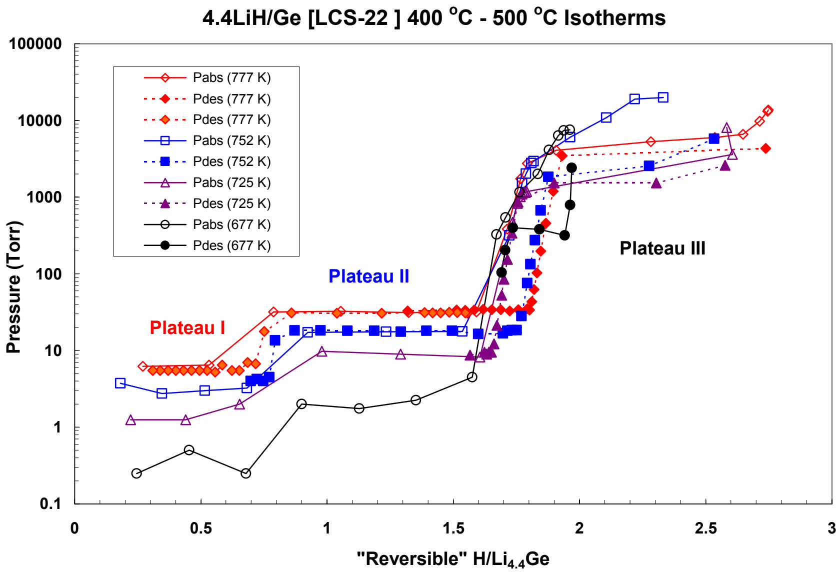


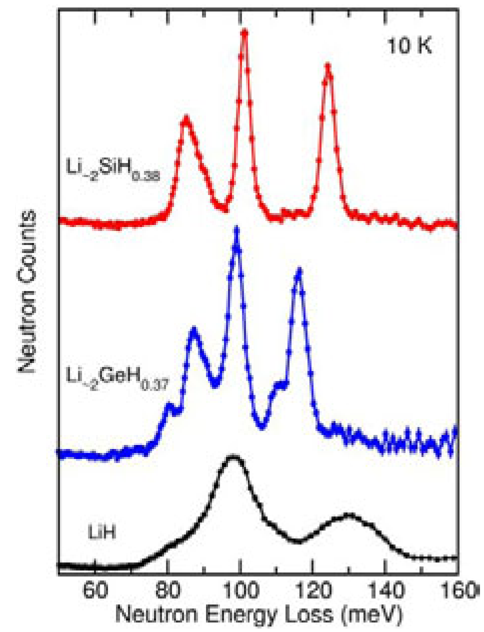




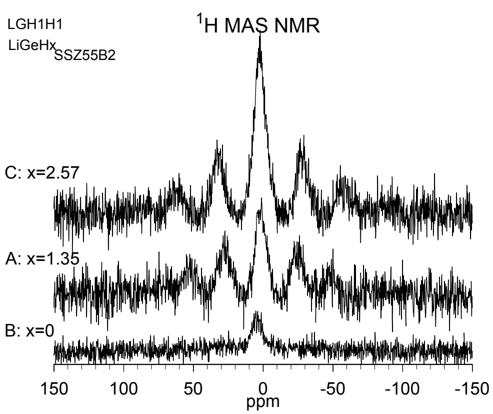
Task 1 Accomplishments - Continued

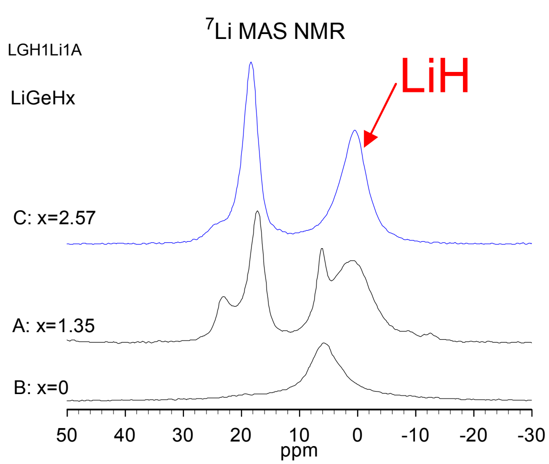
LiH/Ge samples – Similar destabilization behavior to LiH/Si system without a ternary phase a higher LiH/Ge ratio but a $Li_yGe_zH_x$ phase @ LiH/Ge ~ 2 (NIST)





NMR & XRD sees only mixture of LiH & Li_yGe_z phases for LiH/Ge ≥ 4





- NPD and NVS measurements indicate that the new $Li_xGe_yH_z$ ternary phase is similar in structure to the previously discovered $Li_xSi_yH_z$ ternary phase.
- NPD, NVS, and Prompt-Gamma Activation Analysis (PGAA) suggest that the Li/Ge and Li/Si ratios for the ternary phases are equal to or slightly greater than 2.
- The ternary-phase structures for both ternary phases are still unknown.

Task 2. Complex Anionic Materials (POC = SNL)

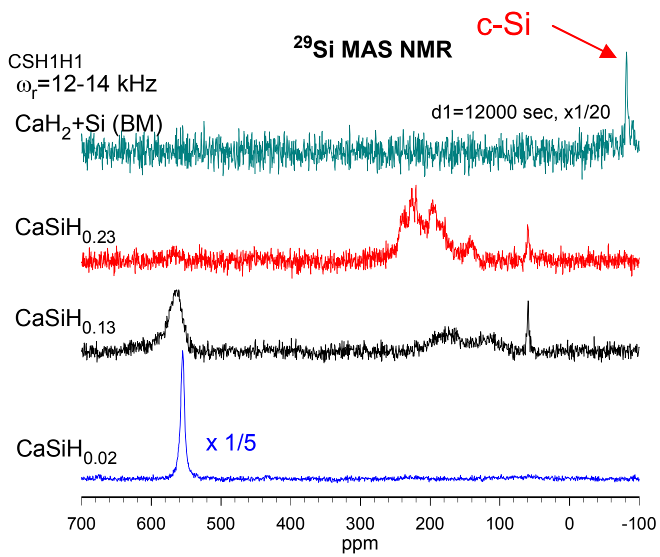
METAL HYDRIDE CENTER OF EXCELLENCE

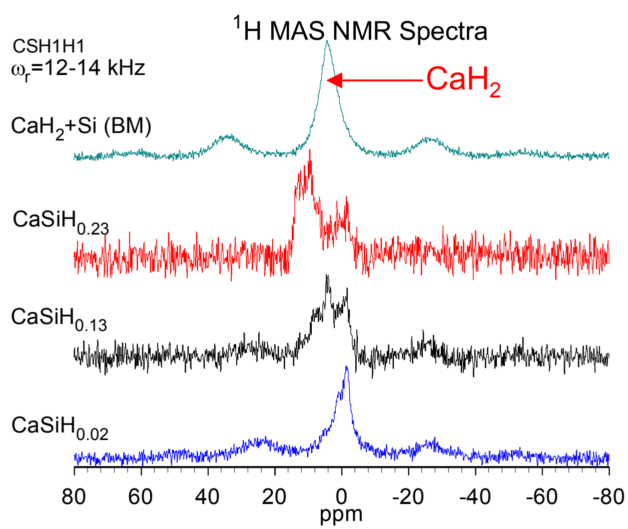
•JPL Objectives:

– Support phase characterizations (i.e., structure & bonding properties) for new borohydrides [i.e., $Ca(BH_4)_2$] and silicide hydrides [i.e., Na-Si-H and Ca-Si-H] with NMR in collaboration with SNL, NIST, Caltech, & LLNL
– Improve understanding of catalysts, dopants, and processing on alanates, borohydrides, and other hydrides.
– Provide novel insights on the phase compositions and local chemical bonding parameters for crystalline and highly disordered (i.e., amorphous) phases at various stages of reactions.
– NMR results will test and complement theoretical modeling of nanophase formation and transitions

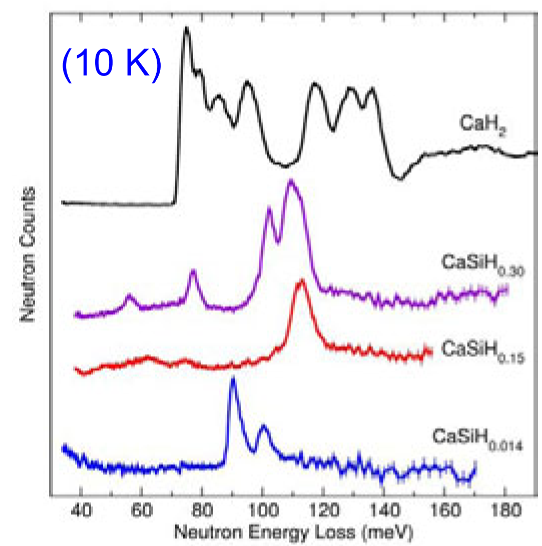
•Accomplishments:

– Obtained MAS-NMR results on samples from MHCoE partners:
  - ➢ Ca-Si-H (NIST) – ^{29}Si and ^{1}H MAS-NMR spectra showed changes with different hydrogen contents similar to hydrogen vibration spectra from NIST due to site occupancy and local structures
  - ➢ Supporting analyses of NMR data from LLNL on Ca-B-H and Na-Si-H samples





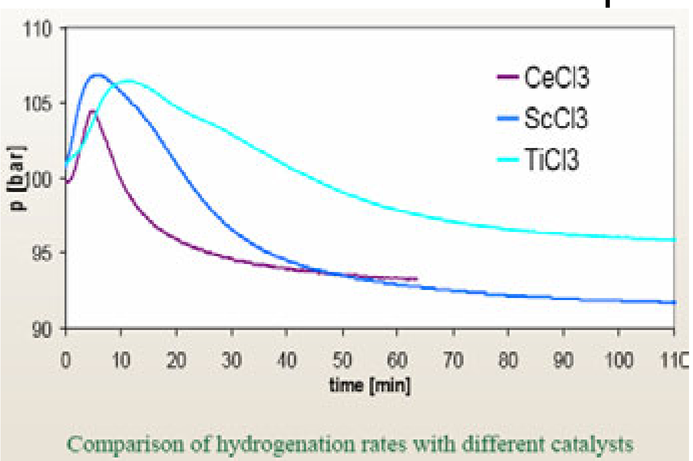
Neutron vibrational spectra of CaH_2 as well as $CaSiH_x$ after various hydrogen treatments (NIST Data)



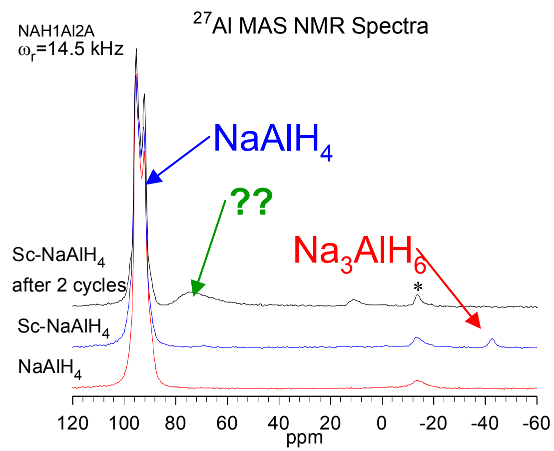
Task 2. Accomplishments - Continued

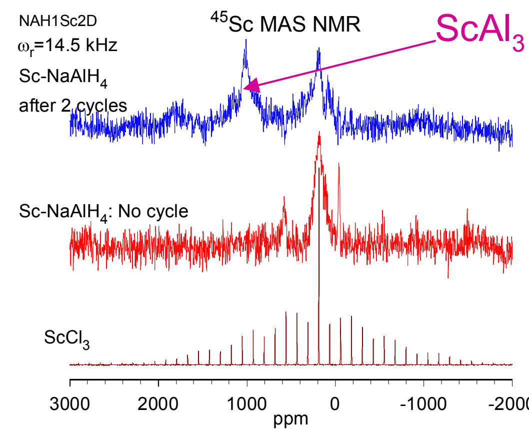
Investigating catalyst mechanisms in alanates & borohydrides – combined study with Washington U./Caltech [Joint effort with BES funding] & IFE [Norway].

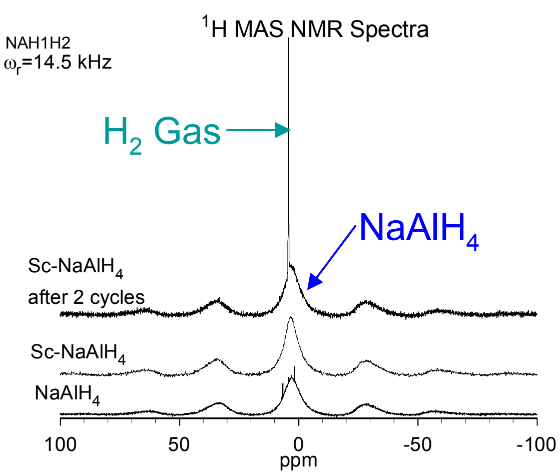
- Ti roles in alanates (i.e., $NaAlH_4$) remains unresolved in spite of extensive studies.
- *In-Situ* NMR measurements of diffusion & phase transformation at Wash.U. are starting.
- Ti is extremely difficult nuclei for NMR, but ^{45}Sc is excellent candidate & is also good catalyst!
- Obtained initial MAS-NMR spectra [^{1}H, ^{23}Na, ^{27}Al, & ^{45}Sc] on Sc-doped $NaAlH_4$ samples.

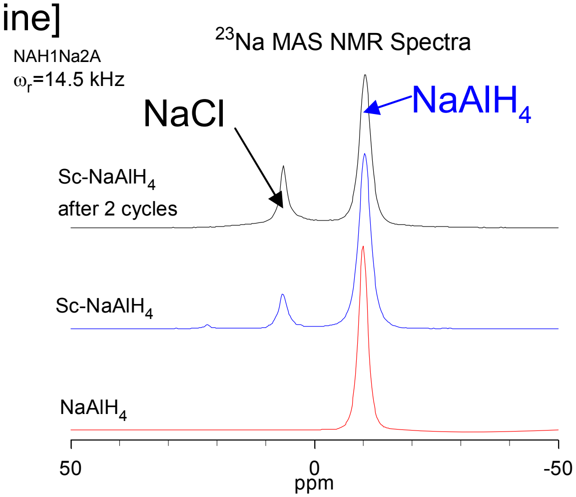


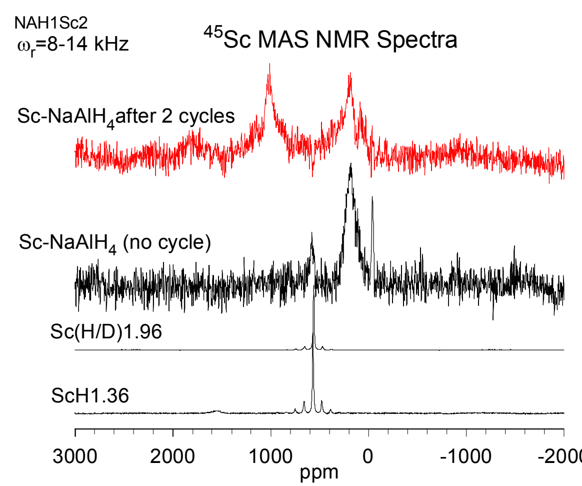
B. Bogdanovic, Adv. Mater. [2006 on-line]





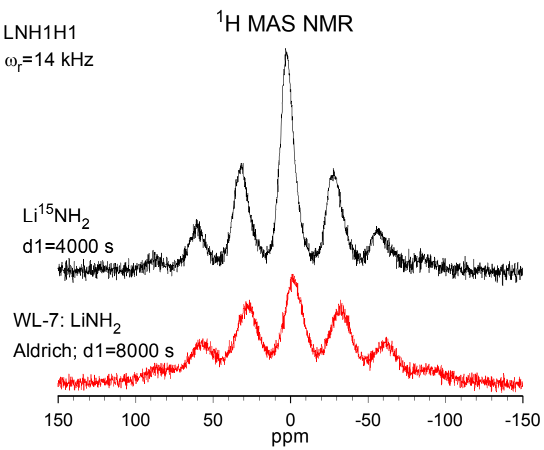


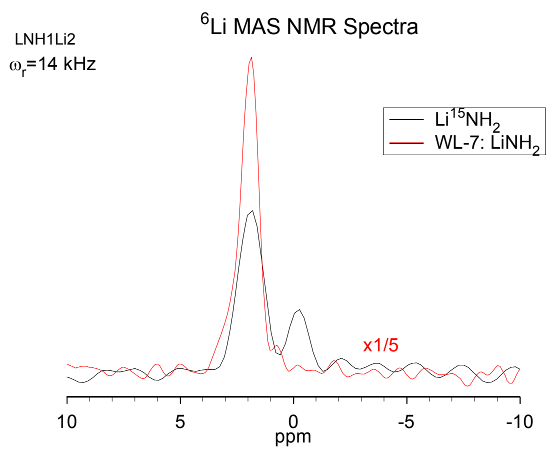


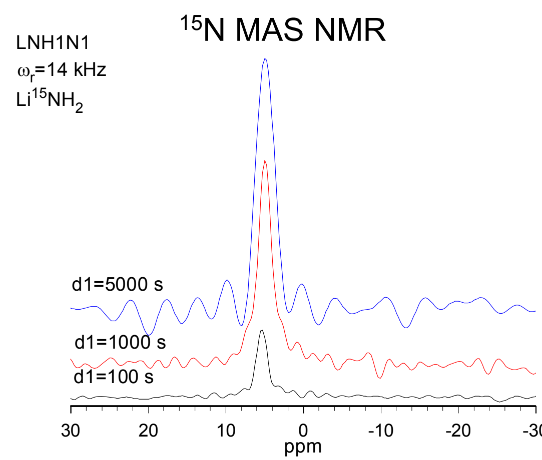


Task 3: Evaluations of Amides/Imides (POC = SNL)

- **JPL Objectives:**
  - Improve understanding on formation, processing, and degradation of amides/imides.
  - Provide novel insights on the phase compositions and local chemical bonding parameters for crystalline and highly disordered (i.e., amorphous) phases at various stages of reactions.
  - NMR results will test and complement theoretical modeling of mechanisms for phase transformation including assessing role of ammonia on reaction & degradation
- **Accomplishments:**
  - Produce the first ^{15}N-enriched sample of $LiNH_2$ (see MAS-NMR spectra) to allow ^{15}N MAS-NMR measurements of chemical bonding in various phases of Li-Mg-N-H.
  - Filled a reactor with Li-Mg-N-H [SNL] for initial volumetric characterization before starting cycling measurements.







Comment: First ^{15}N-enriched amide sample is mixture of LiH & $LiNH_2$

Task 4: Evaluations of Alanes (POC = BNL)

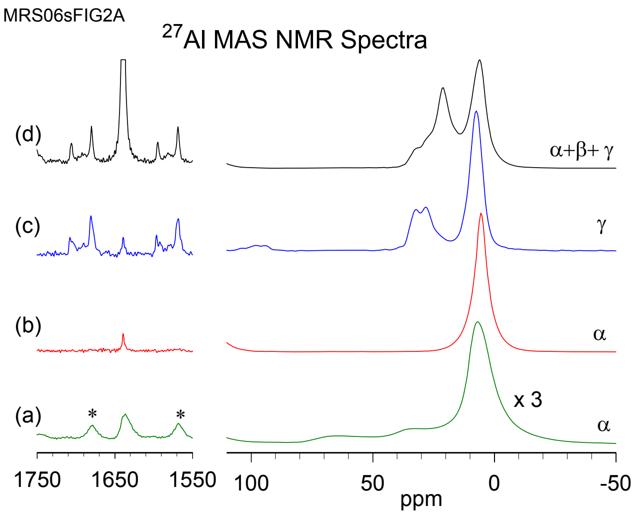
METAL HYDRIDE CENTER OF EXCELLENCE

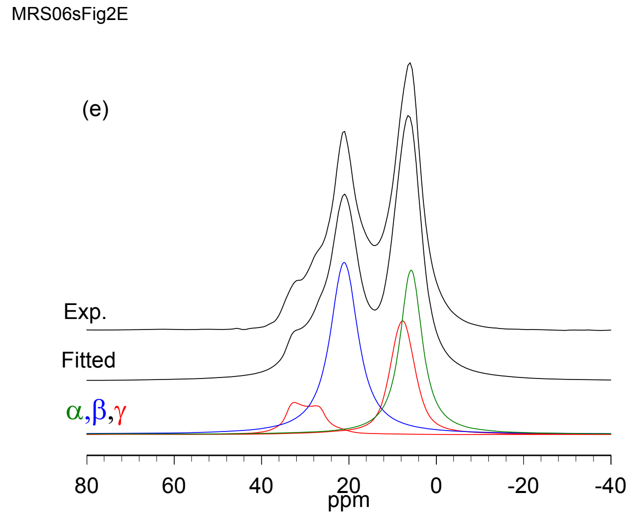
•Objectives:

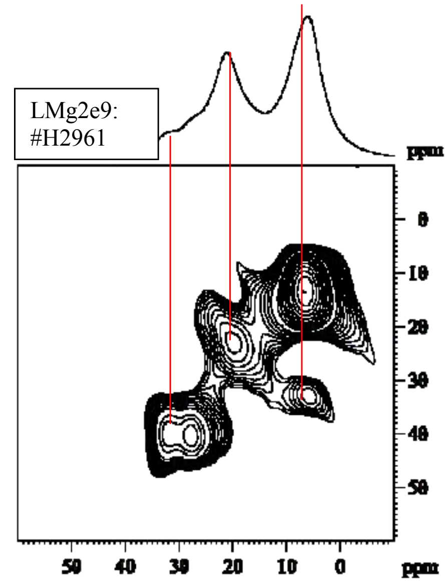
— Use NMR to provide novel insights on the phase compositions, decomposition, and local chemical bonding parameters for crystalline and highly disordered (i.e., amorphous) phases of AlH_3.

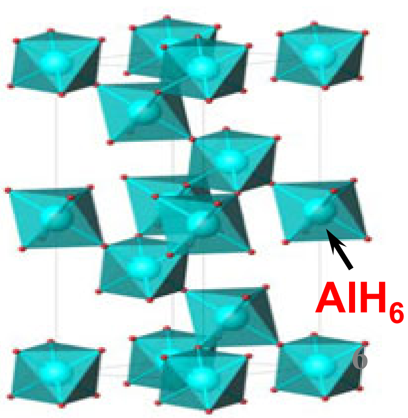
•Accomplishments:

– Obtained MAS-NMR results on AlH_3 samples with α-, β- and γ-phases and monitored Al metal & H_2 gas formation during spontaneous decomposition (BNL)



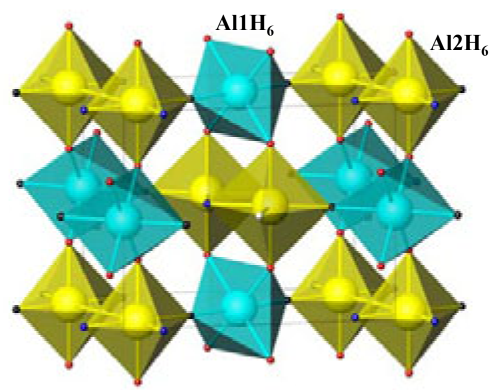






α-AlH_3

γ-AlH_3



Conclusions:

•Two types of Al atoms in γ-AlH_3 but only one site in α & β phases – will help solve these structures from PND & PXRD

•^{27}Al NMR shifts consistent with AlH_6 sites will assess differences in bonding to relate to decomposition of these AlH_3 phases

Models by Y. Yartys (IFE) from a TMS paper [March 2006]

Task 5: Engineering Analysis & Design (POC = SRNL) - Prototype Hydride Storage Bed Analysis, Design and Testing

- **JPL Objectives:**
  - Support developing lighter weight and thermally efficient hydride storage vessels and experimentally demonstrating their compatibility with appropriate complex and destabilized nanophase hydrides.
- **Status:** Just started these activities in FY-06
- **Accomplishments:**
  - Participated in Metal Hydride Systems "kick-off" meeting of the systems working group
  - Participated in Storage System Analysis Working Group Meeting held November 2005 in Palm springs, CA
  - Participated in the first MHCoE ES&D Project kick-off meeting (March 2006)
- **FY-06 Planned Activities:**
  - Evaluate MH System models from ANL "MH-tool" analysis computer model for known hydrides (i.e., $LaNi_{4.8}Sn_{0.2}$) and light complex hydride (e.g., alanates, etc.)
  - Work on storage vessel conceptual designs, etc. with SRNL, SNL & MHCoE partners.

Future Work (FY06/07)

Task 1. [Destablized Hydrides]

• Complete phase formation & reversibility studies on model LiH-Si, LiH-Ge, Li-B-Mg-H, and Mg-Si-H systems (w/HRL, NIST, Caltech).

□ Go/No-Go on viability of LiH-Si & Mg-Si-H systems by end of FY-06

Task 2. [Complex Anionic Materials]

• Continue the characterization of H bonding in the Ca-Si-H system (w/NIST).

• Pursue possibilities of aiding MHCoE partners and others associated with such systems as Na-Si-H (SNL), $Ca(BH_4)_2$ (SNL), catalyzed alanates (IFE), Mg-Ti-H & Mg-Sc-H (Washington U., Philips Research).

Task 3. [Evaluations of Amides/Imides]

• Perform systematic ^{15}N, ^{6}Li, ^{7}Li, and ^{1}H MAS-NMR studies of Li-Mg-N-H phases

• Evaluate accelerated degradation behavior of Li-Mg-N-H samples from SNL.

• Investigate impact of catalysts on reactions kinetics, diffusion, and reversibility for these materials.

Task 4: [Evaluations of Alanes]

• Continue assessments of AlH_3 phases and decomposition processes (BNL, U. Hawaii, IFE-Norway)

Summary JPL Tasks in MHCoE

FY 2006 Milestones	**Due**
• Complete an initial phase cycling tests on at least one destabilized hydride system (e.g. $LiBH_4/MgH_2$ or Li-Mg-N-H)	August, 2006
• Provide a top-level estimate of mass, volume, & thermal parameters for a prototype destabilized/complex hydride storage vessel	September, 2006

FY 2007 Milestones

Milestones for Destabilized Hydride Systems:

- Complete initial degradation study on first destabilized systems (Li-Mg-N-H & Li-B-Mg-H)
- Initiate life cycle testing on best destabilized nanophase candidates

Milestone for Prototype Hydride Storage Bed Design & Testing

- Conceptual design for a prototype complex hydride sorbent bed

Milestones for NMR Evaluations of Advanced Complex Hydrides

- Complete 2nd phase NMR studies on Li-Mg-N-H samples (SNL)
- Complete 2nd phase NMR studies on AlH_3 samples (BNL)
- Perform NMR studies on alanates, borohydrides, etc. from MHCoE team

MHCoE Master Schedule & Milestones: Summary of JPL Tasks

Organization	Task #	Task Description	10/1 FY05	4/1 FY05	10/1 FY06	4/1 FY06	10/1 FY07	4/1 FY07	10/1 FY08	4/1 FY08	10/1 FY09	4/1 FY09	10/1 FY10
A. Destabilized Hydrides													
	1	Destabilization Strategies and New Systems											
JPL	1.1.1	Conduct cycling studies on Li-Mg-Ni-H and Li-B-Mg-H systems											
JPL	1.1.2	Use MAS-NMR to measure phases in mixtures of $LiBH_4$ with various hydrides (e.g. MgH_2, $LiNH_2$); extend to other candidate materials											
JPL (Lead)	2.2	Phase formation and reversibility studies											
JPL	2.2.1	Complete phase formation and reversibility studies on model LiH-Si, LiH-Ge, Li-B-Mg-H, and Mg-Si-H systems			LiH-Si, LiH-Ge	Li-B-Mg-H		Mg-Si-H					
B. Complex Anionic Materials (Borohydrides & Alanates)													
	2	New Hydrogen Storage Materials											
	2.1	Synthesis of new materials in the ternary Si-system											
	2.2	Characterization of the new materials											
JPL	2.2.1	NMR analysis of samples in the Na-Si-H system provided by SNL											
C. Amide/Imides (M-N-H Systems)													
	1	Improve current system											
	2	Understand reaction mechanism											
JPL	2.2	NMR study the nature of N-H bond											
	5	Cycle stability and contamination test											
JPL, SNL	5.1	Cycle stability test											
D. Alanes (AlH3)													
	1	Aluminum hydride synthesis: Synthesis of alanes that meet 2010 storage targets											
	2	Aluminum hydride properties: Down select alane materials that meet 2010 storage targets											
JPL	2.4	Complete nuclear magnetic resonance (NMR) characterization on selected alanes											
	3	Alane Regeneration: Demonstrate alane regeneration laboratory process											
	4	AlH3 tank study: Complete prototype alane tank system meeting 2010 targets											
E. Engineering Analysis & Design													
	1	Component Design & Testing											
JPL	1.1	Vessel Modeling (Detailed Component Fidelity)											
SNL/JPL	1.2	Materials Compatibility											
JPL	1.3	Vessel Testing (Detailed Component Fidelity)											
	2	Media Engineering Development											
	3	Safety Strategies											
All	3.1	Risk Assessment											
	4	Prototype Vessels											
	5	System Modeling											

Legend:
- ▲ Portfolio Relocation Decision Point (Project bars)
- ◇ Milestone (Subtask bars)
- ⬢ Output (Task bars)

Back-up Slides (Not presented)

Responses to Previous Year Reviewers' Comments

- NA – This Project was new in FY-05 and was not reviewed.

JPL MHCoE Publications

- **Published Papers**
  - R. C. Bowman, Jr., S.-J. Hwang, C. C. Ahn, and J. J. Vajo, “NMR and X-ray Diffraction Studies of Phases in the Destabilized LiH-Si System”, Mater. Res. Soc. Symp. Proc. **837** (2005) paper N3.6.1.
- **Papers Submitted for Publication**
  - S.-J. Hwang, R. C. Bowman, Jr., Jason Graetz, and J. J. Reilly, “Solid State NMR Studies of the Aluminum Hydride Phases” Submitted to Proc. 2006 Spring Meeting, Symposium EE.
- **Manuscripts in Preparation or Planned**
  - R. C. Bowman, Jr., S.-J. Hwang, C. C. Ahn, A. Dailly, and J. J. Vajo, “Studies of Phase Transformations in the Destabilized LiH-Si System”, J. Mater. Res. [Invited to submit].
  - R. C. Bowman, Jr., S-J. Hwang, C. C. Ahn, M. R. Hartman, T. J. Udovic, J. J. Rush, and J. J. Vajo, “Destabilization Behavior and Phase Compositions for LiH-Ge” In Preparation.
  - Son-Jong Hwang, R. C. Bowman, Jr., Jason Graetz and J. J. Reilly, “NMR Studies of the Aluminum Hydride Phases and their Stabilities”, in Preparation.

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- **Presentations made in 2005/2006**
  - R.C. Bowman, Jr., S.-J. Hwang, C. C. Ahn, A. Dailly , J. J. Vajo, T. J. Udovic, M. Hartman, and J. J. Rush, "Studies of Thermodynamics and Phases Produced in the Destabilized LiH-Si System" invited talk at the Nordic Energy Research Meeting, Krusenberg, Sweden, 17-18 June 2005.
  - R. C. Bowman, Jr., "Development of Metal Hydrides for Space Applications and Energy Storage" invited talk at the Materials Science & Technology 2005 Conference, Pittsburgh, PA, 25-28 September 2005.
  - R. C. Bowman, Jr., "Behavior and Properties of Metal Hydrides for Reversible Hydrogen Storage" invited presentation at the WE-Heraeus-Seminar on Hydrogen Storage with Novel Nanomaterials, Bad Honnef, Germany, 24-27 October 2005.
  - M. R. Hartman, T. J. Udovic, J. J. Rush, R. C. Bowman, Jr., J. J. Vajo, and C. C. Ahn, "Neutron Scattering Investigations of a Destabilized LiH:Si System for Hydrogen Storage Applications" 2005 Fall MRS Meeting, Boston, MA, 1 December, 2005.
  - R. C. Bowman, Jr., S-J. Hwang, C. C. Ahn, A. Dailly, M. R. Hartman, T. J. Udovic, J. J. Rush, and J. J. Vajo, "Reversibility and Phase Compositions of Destabilized Hydrides Formed from LiH", invited presentation at the Spring 2006 MRS Meeting, 17-20 April, 2006.
  - Son-Jong Hwang, R. C. Bowman, Jr., Jason Graetz and J. J. Reilly, "NMR Studies of the Aluminum Hydride Phases and their Stabilities", presented at the Spring 2006 MRS Meeting, 17-20 April, 2006.
  - M. R. Hartman, T. J. Udovic, J. J. Rush, R. C. Bowman, Jr., J. J. Vajo, and C. C. Ahn, "Neutron Scattering Investigations of a Destabilized LiH:Si System for Hydrogen Storage Applications" presented at the Spring 2006 MRS Meeting, 17-20 April, 2006.
  - R. C. Bowman, Jr., "Current Status in Developing Advanced Metal Hydrides for Reversible Hydrogen Storage", Invited presentation at 209th Meeting of Electrochemical Society, Denver, CO, May 10, 2006.
- **Presentations planned for remainder FY-06**
  - R. C. Bowman, Jr., J. G. Kulleck, , S.-J. Hwang, M. R. Hartman, T. J. Udovic, and J. J. Rush, "Characterization of Phase Compositions and Structures for Metal Hydrides Used in Hydrogen Storage" invited presentation at Amer. Crystallographic Soc., Honolulu, HI, 22 July, 2006.