Jet Propulsion Laboratory
California Institute of Technology

DOE Hydrogen Program

METAL HYDRIDE CENTER OF EXCELLENCE

Development and Evaluation of Advanced Hydride Systems for Reversible Hydrogen Storage

Robert C. Bowman
& Joseph W. Reiter

Jet Propulsion Laboratory
California Institute of Technology
Pasadena, CA 91109-8099

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

May 16, 2007

This presentation does not contain any proprietary or confidential information

Project ID
STP32

Jet Propulsion Laboratory
California Institute of Technology

Overview

METAL HYDRIDE CENTER OF EXCELLENCE

Timeline

- Project start date: FY05
- Project end date: FY09
- 50 % complete

Budget

- Expected total project funding:
  - $1.859M (DOE)
- Funding received in FY06
  - $311K (DOE)
- Funding received for FY07:
  - $400K (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, HRL, NIST, GE Global, U. Hawaii, BNL, SNL, U. Utah in FY-06 & FY-07]
- Washington U. and Caltech in support a BES H_2 Storage Project on solid state NMR studies of light element hydrides
- International: IFE (Norway), Philips (Netherlands), CNRS (France), and AIST (Japan)

Jet Propulsion Laboratory
California Institute of Technology

Objectives of JPL within MHCoE

METAL HYDRIDE CENTER OF EXCELLENCE

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 Caltech, U. Hawaii, NIST, & other MHCoE partners.
- Complex hydrides (e.g., amides/imides, borohydrides, & AlH_3-hydrides) provided by GE, U. Utah, U. Hawaii & 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.

FY06/FY07 Objectives:

- **Evaluate behavior of destabilized MgH_2/$LiBH_4$ systems to assess reversibility, kinetics, & H_2 storage parameters against targets.**
- **Characterize phases & chemical bonding via MAS-NMR for Li amides/imides, AlH_3, borohydrides, & selected other hydrides provided by MHCoE partners to better understand basic chemisorption processes.**
- **Start extended cycling tests on at least one destabilized & catalyzed hydride to assess lifetime potential & durability – however, this system needs to have viable kinetics and reversibility to justify commitment.**

Jet Propulsion Laboratory
California Institute of Technology

Approach of JPL in MHCoE – Materials Development

METAL HYDRIDE CENTER OF EXCELLENCE

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 partner NIST.

Jet Propulsion Laboratory
California Institute of Technology

Approach of JPL - Engineering

METAL HYDRIDE CENTER OF EXCELLENCE

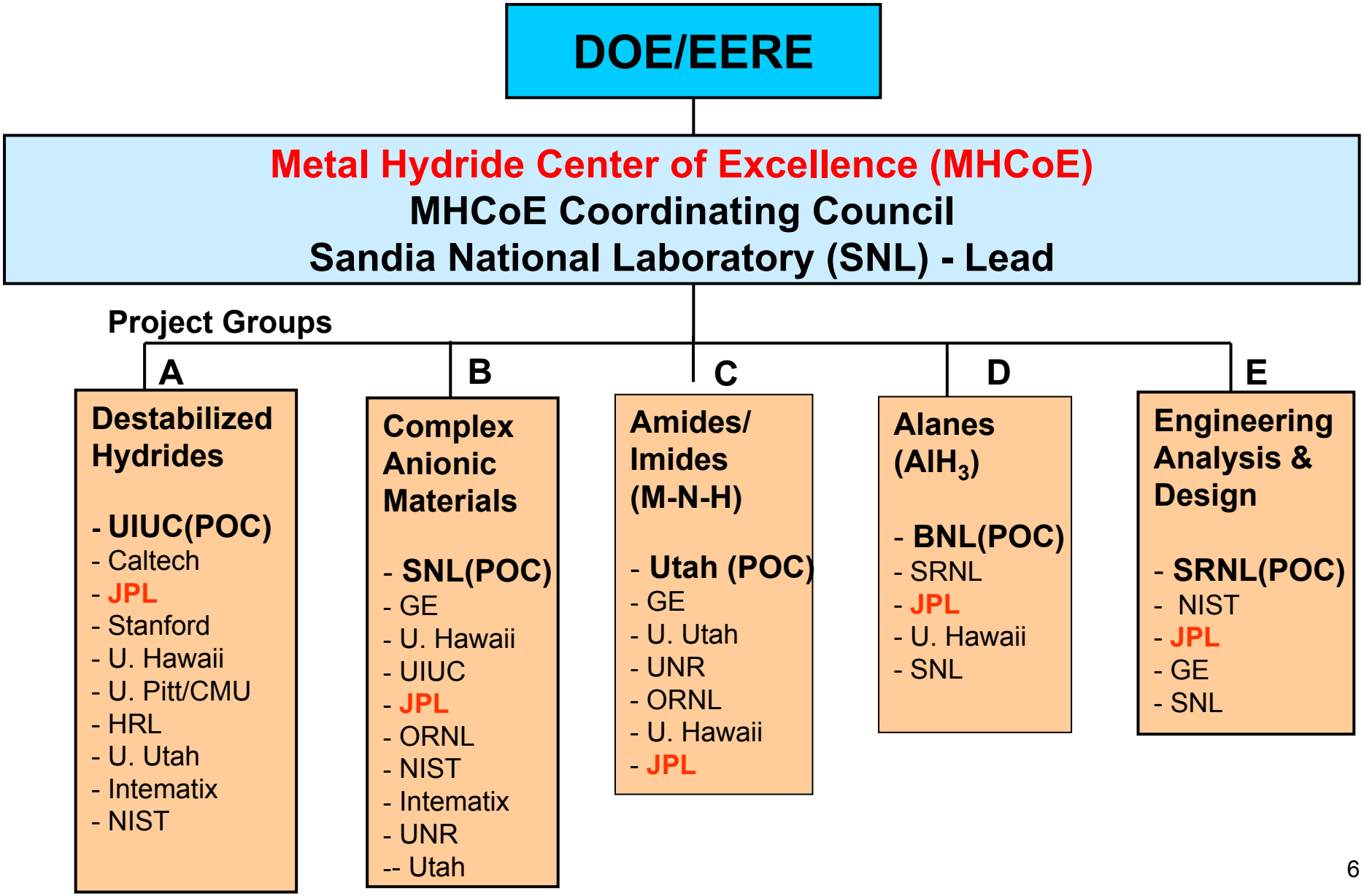
Prototype Hydride Beds Development and Life Testing:

- 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.
- Evaluate the performance and robustness of candidate hydrides using well-characterized experimental test-beds during many cycles of hydrogen absorption and desorption.

Jet Propulsion Laboratory
California Institute of Technology

JPL is Supporting All MHCoE Projects

METAL HYDRIDE CENTER OF EXCELLENCE

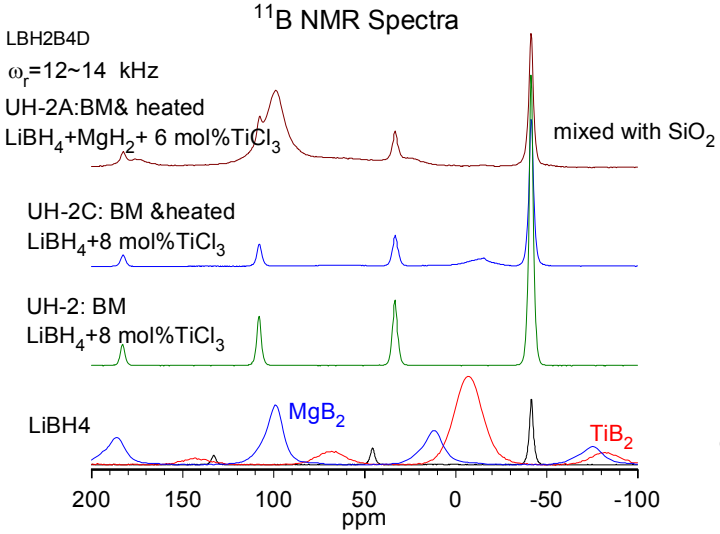


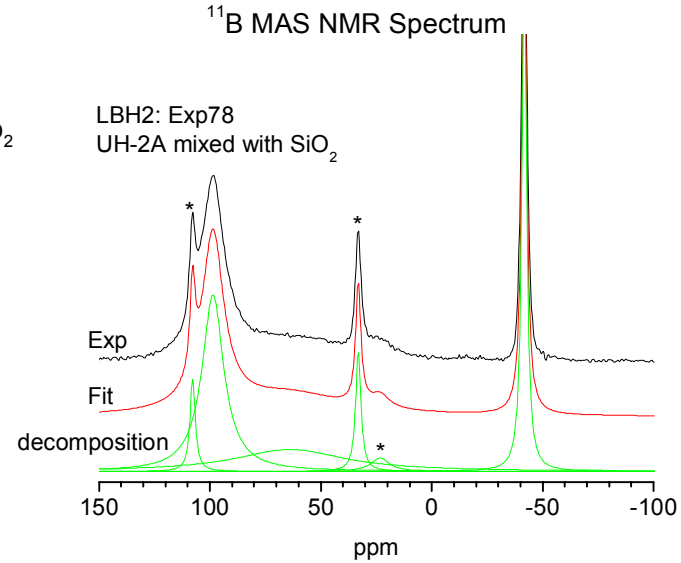
Jet Propulsion Laboratory
California Institute of Technology

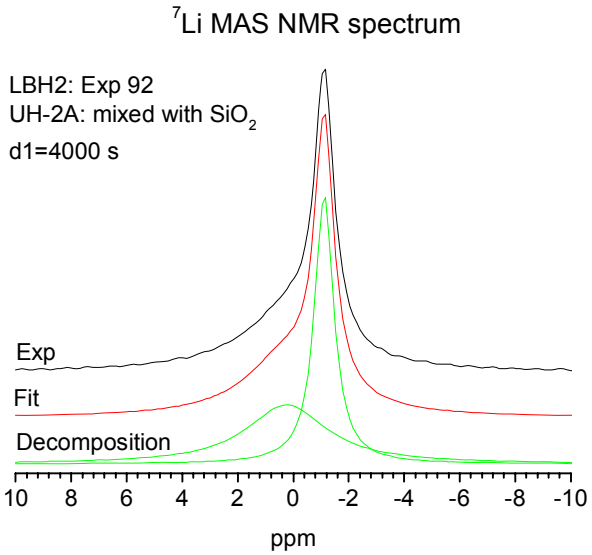
Task A - Destabilized Hydride Systems

METAL HYDRIDE CENTER OF EXCELLENCE

- **JPL Objectives:**
  - 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 for any promising candidates.
- **Accomplishments in FY-06/07:**
  - MAS-NMR determined phase formation and reversibility in $LiBH_4/MgH_2$ (U. Hawaii):
    - ^7Li, ^{11}B and ^1H MAS-NMR spectra showed different phases with variation in hydrogen contents – undergoing more systematic studies of phase conversion, reversibility, catalytic effects, & degradation behavior.







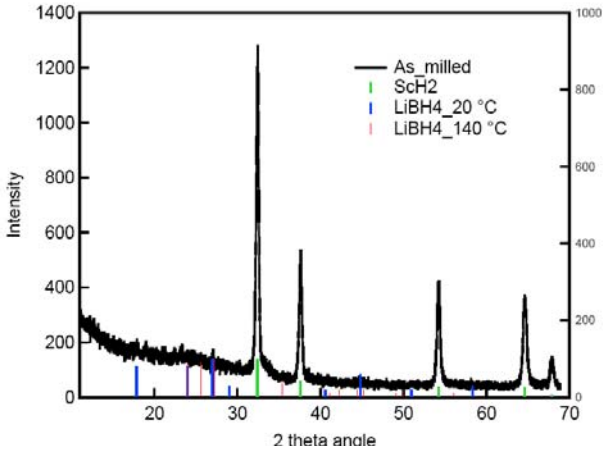
The ^{11}B NMR peaks centered at -41 ppm are from $LiBH_4$ while the peak at 98.4 ppm for sample UH-2A is from MgB_2 with a content of about 45 % (see center spectra deconvolution). ^{11}B CPMAS NMR and ^1H decoupling experiments indicate that the broad peaks at ~ 100 ppm don't couple with ^1H, consistent with the assignment MgB_2 phase. The ^7Li NMR peaks show formation of LIH phase for sample UH-2A.

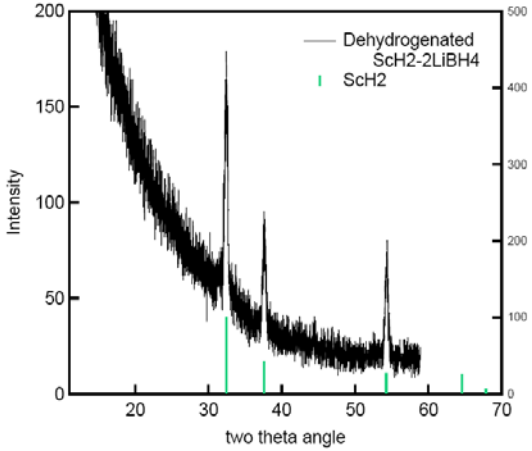
Investigation of the "$ScH_2 + 2LiBH_4 = 2LiH + ScB_2 + 4H_2$" Destabilization Reaction

Jet Propulsion Laboratory
California Institute of Technology

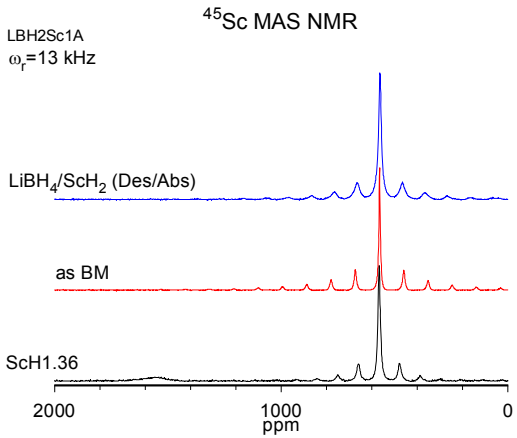
METAL HYDRIDE CENTER OF EXCELLENCE

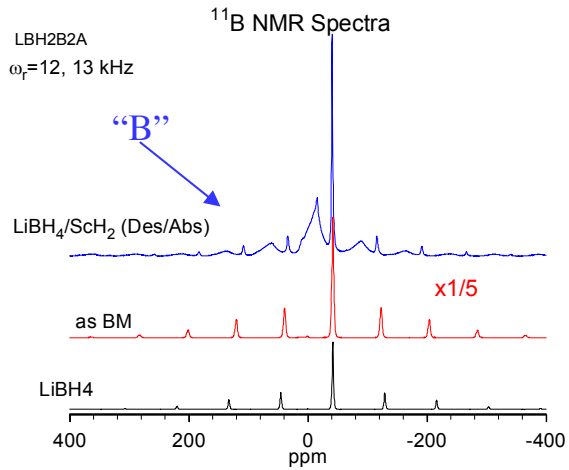
X-ray Diffraction [Not Very Helpful]



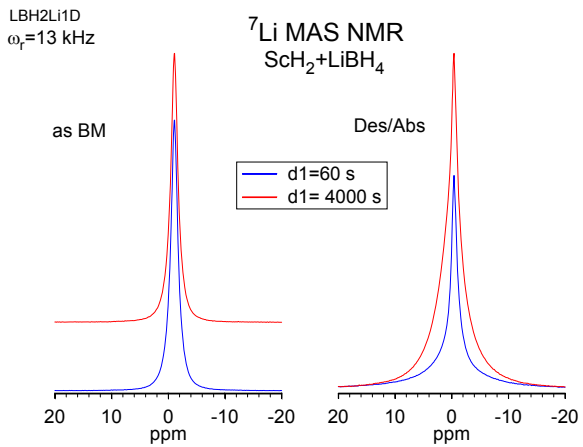


MAS-NMR Spectra: As Milled & Reacted





Detected only ScH_2



Some $LiBH_4$ converted into elemental boron (not ScB_2)

Only $LiBH_4$ in "as BM", but also LiH (seen in d1=4000s scan) in "Des/Abs" sample

Summary: Desorption did **Not** follow the destabilized process of forming ScB_2. Had only partial decomposition of $LiBH_4$ into LiH + B with little reversibility indicated during absorption.

Group B - Complex Anionic Materials

Jet Propulsion Laboratory
California Institute of Technology

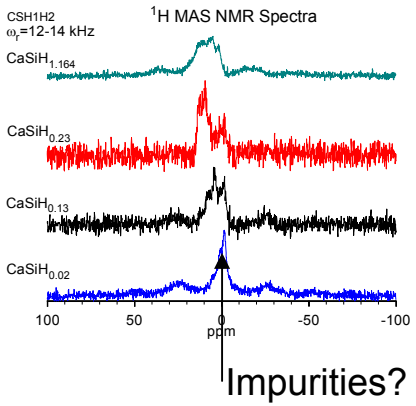
METAL HYDRIDE CENTER OF EXCELLENCE

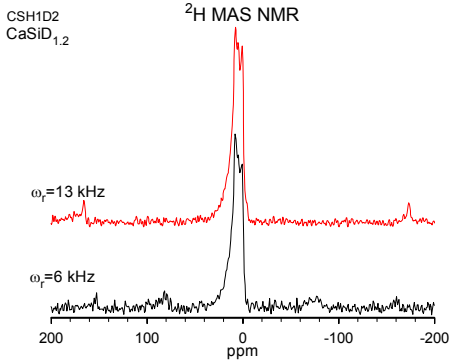
JPL Objectives:

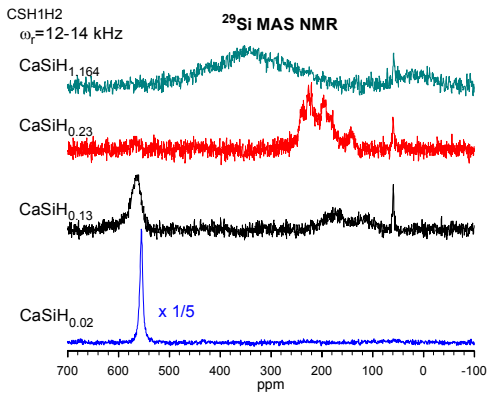
Support phase characterizations and structure & bonding properties for new borohydrides [i.e., $Mg(BH_4)_2$, $Ca(BH_4)_2$] and silicide hydrides [i.e., Ca-Si-H] with NMR measurements in collaboration with SNL, GE Global, NIST, Caltech, & LLNL

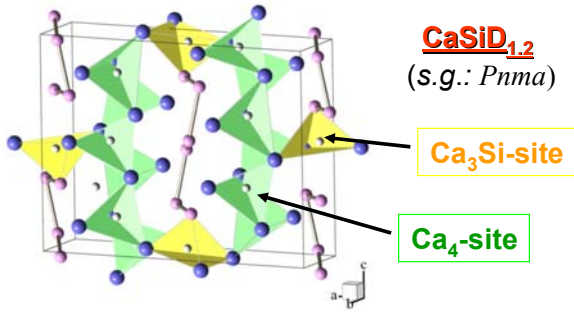
Accomplishments in FY-06/07:

- **MAS-NMR measurements at Caltech Solid State NMR Facility on various complex hydrides.**
- **Supporting analyses of NMR data from LLNL on Ca-B-H and Na-Si-H samples**
- **Performing MAS-NMR on $Mg(BH_4)_2$ and $Sc(BH_4)_2$ phases to assess compositions and transformations as well as look at diffusion processes to understand & improve kinetics**









NIST structure - NPD

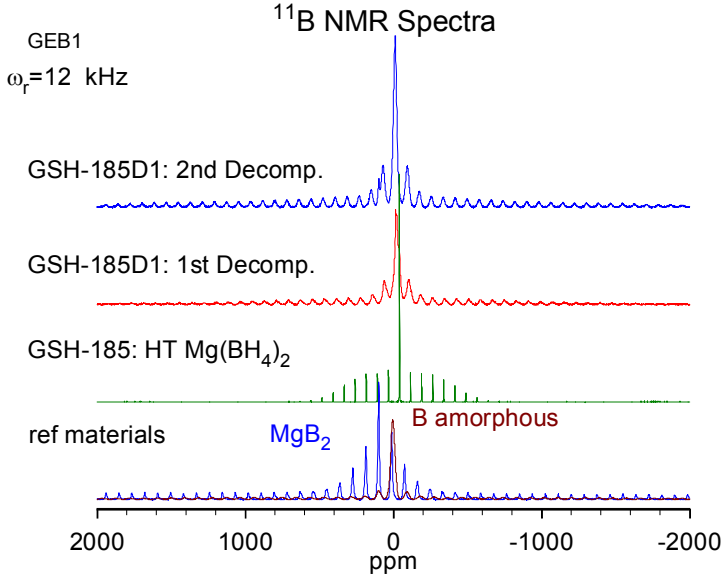
- $CaSiH_x$ (NIST) –^{29}Si, ^1H, & ^2H MAS-NMR spectra showed changes with hydrogen contents, but couldn't confirm 2-site occupancy in $CaSiH_{1.2}$ sample from proton or deuteron spectra.

First MAS-NMR Results for $Mg(BH_4)_2$ System

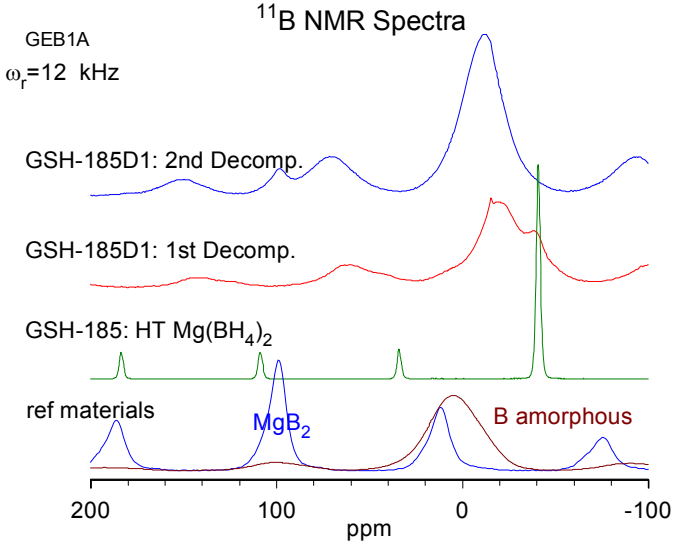
Jet Propulsion Laboratory
California Institute of Technology

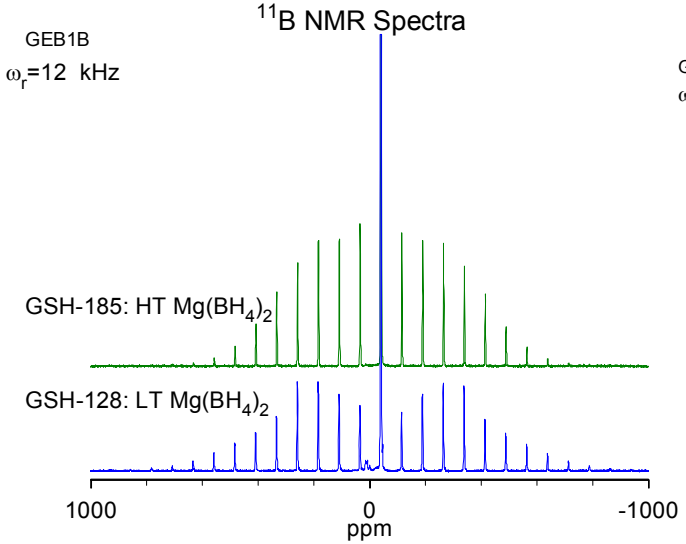
METAL HYDRIDE CENTER OF EXCELLENCE

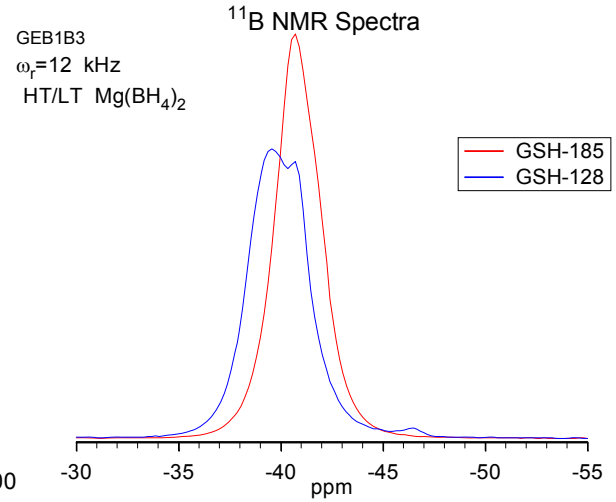
$Mg(BH_4)_2$ Samples from GE



1. GSH-185 as synthesized high temperature (HT) modification of $Mg(BH_4)_2$
2. GSH-185D1 decomposed through the first step (MgH_2 + amorphous B by XRD)
3. GSH-185D2 decomposed through the second step (Mg + amorphous B by XRD)
4. GSH-128 $Mg(BH_4)_2$ as prepared low temperature (LT) phase







NMR data still being analyzed to evaluate phases & local structures.

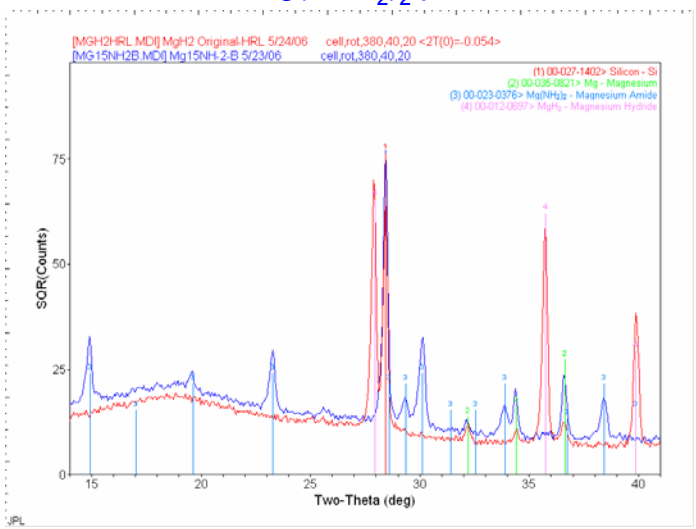
Task C: Evaluations of Amides/Imides

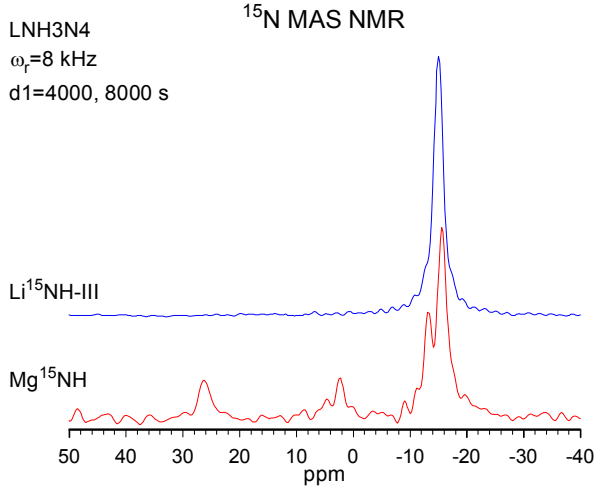
Jet Propulsion Laboratory
California Institute of Technology

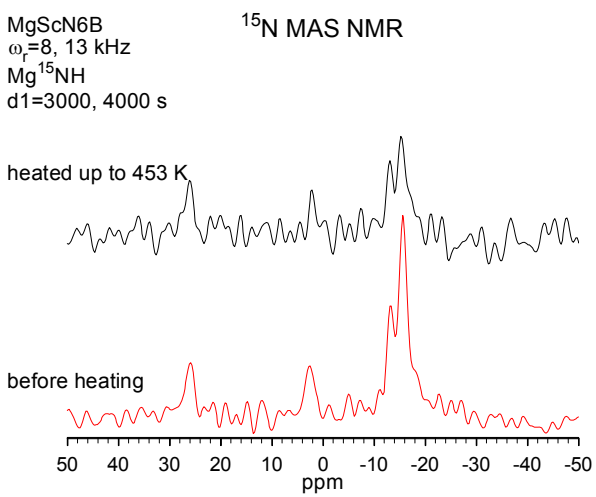
METAL HYDRIDE CENTER OF EXCELLENCE

- **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 critically test and complement theoretical modeling of mechanisms for phase transformation including assessing role of ammonia on reaction & degradation
- **Accomplishments in FY-06/07:**
  - Prepared ^{15}N enriched $Mg(^{15}NH_2)_2$ with characterization by XRD and ^{15}N MAS-NMR

XRD patterns for original MgH_2 and amide. The MgH_2 pattern is in red & $Mg(^{15}NH_2)_2$ pattern is in blue.







- Synthesis of $Mg(^{15}NH_2)_2$ was much more difficult than anticipated from literature.
- See differences in ^{15}N NMR spectra between Li amide (1 peak) & Mg amide (~4 peaks) – not quantitatively interpreted yet!
- Use this $Mg(^{15}NH_2)_2$ material to prepare Mg imide/nitride & Li-Mg-N-H phases to evaluate $-NH_2$ & -NH bonding and dynamics using ^{15}N NMR spectra

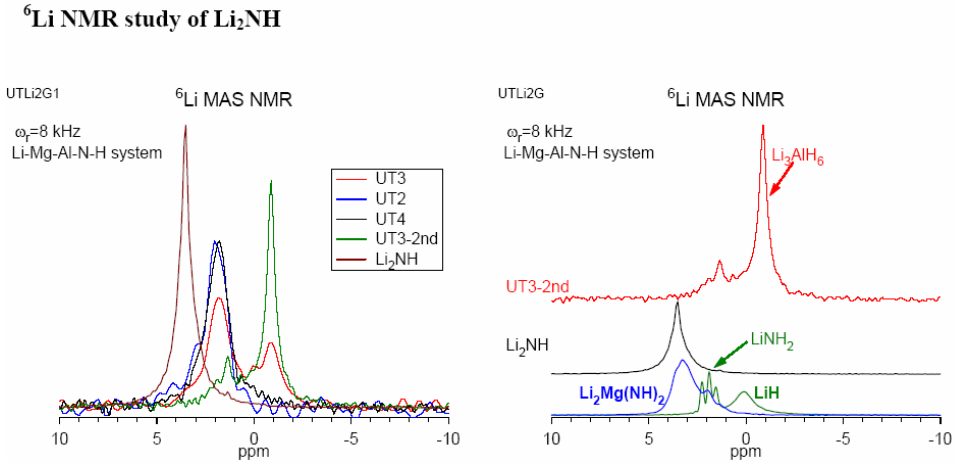
Task C: Evaluations of Amides/Imides (Continued)

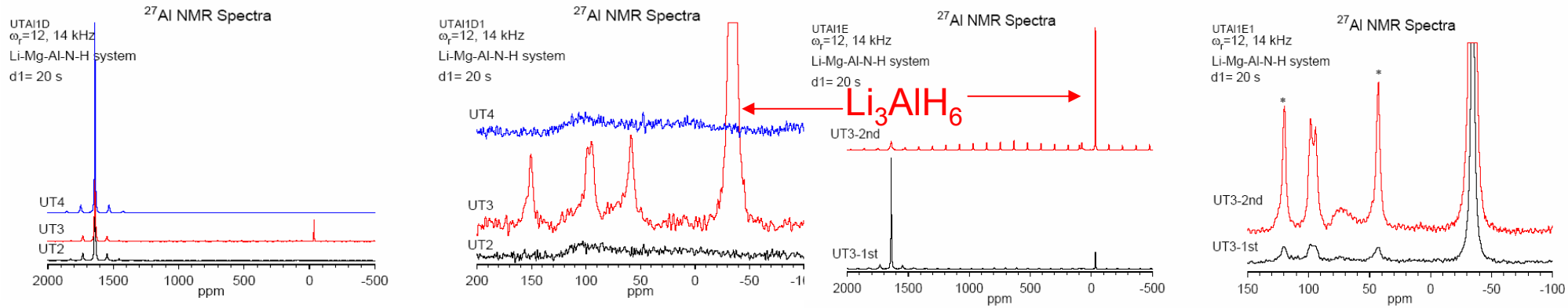
Jet Propulsion Laboratory
California Institute of Technology

METAL HYDRIDE CENTER OF EXCELLENCE

- Demonstrated the reversible reactions in Li-Mg-Al-N-H samples from U. Utah using ^{6}Li and ^{27}Al MAS-NMR spectra.

UT1: Raw material: Al, $LiNH_2$, MgH_2, catalyst
UT2: Sample UT1 after dehydrogenation
UT3: Sample UT2 after rehydrogenation
UT3-2: Another UT2 sample after rehydrogenation
UT4: Sample UT3 after dehydrogenation





- NMR confirmed that Li_3AlH_6 is in the hydrogenated product – meaning the reaction is reversible!
- NMR verified the basic reaction hypothesis – $Li_2Mg(NH)_2$ and Al metal are confirmed as the dehydrogenated products.

Jet Propulsion Laboratory
California Institute of Technology

Task D: Evaluations of Alanes

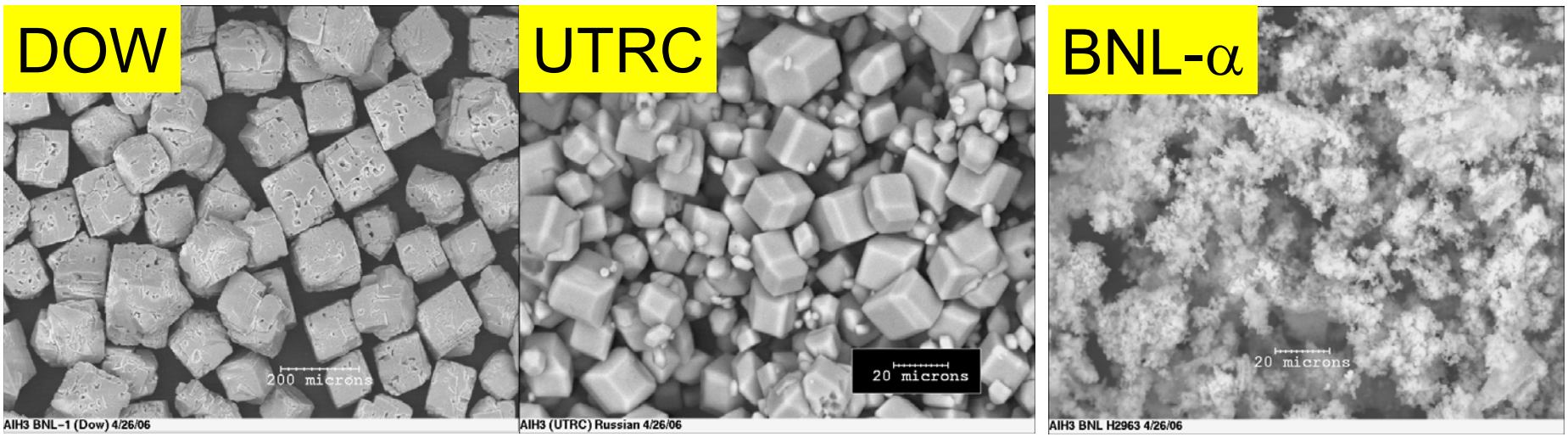
METAL HYDRIDE CENTER OF EXCELLENCE

JPL Objectives:

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

Accomplishments in FY-06/07:

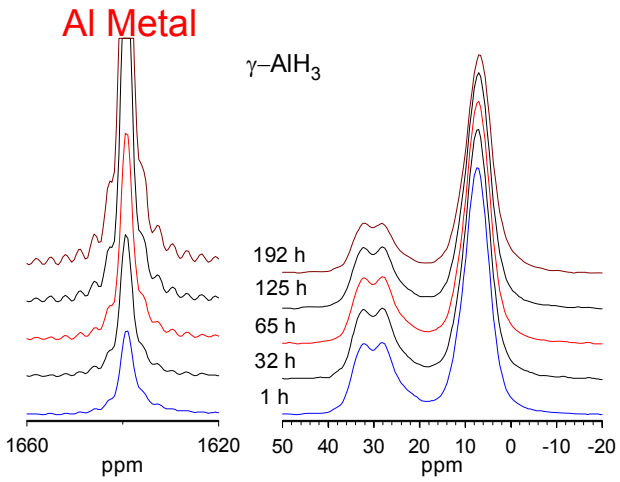
- MAS-NMR measurements on various AlH_3/ AlD_3 samples.
- Samples with α-, β- and γ-phases from BNL, UTRC, and U. Hawaii measured
- Monitored Al metal formation during spontaneous decomposition and in-situ heating
- SEM Images from JPL of α-AlH_3 from different sources [Only BNL-Dow has trapped H_2 gas]

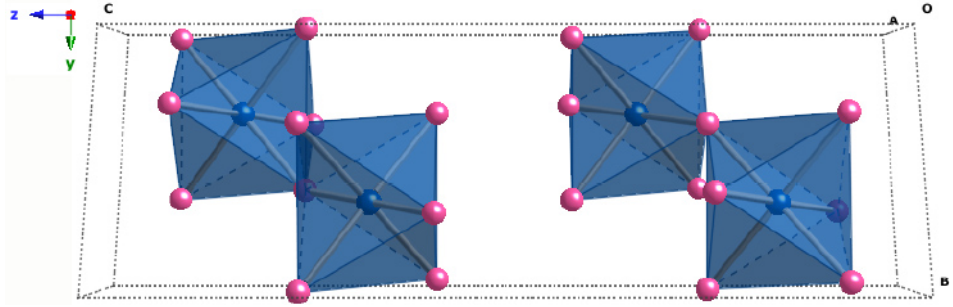


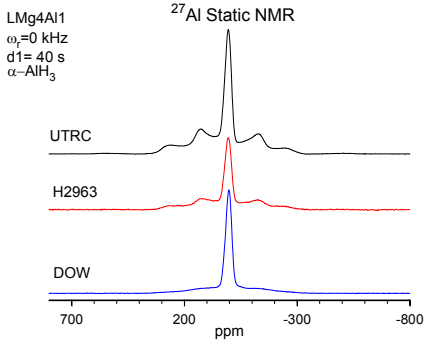
Task D: Evaluations of Alanes (Continued)

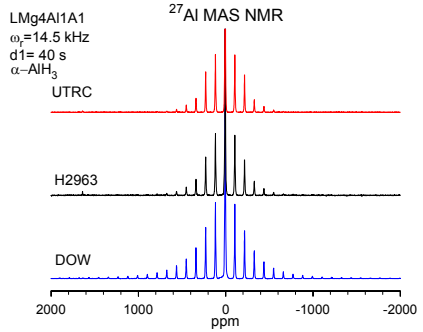
Jet Propulsion Laboratory
California Institute of Technology

METAL HYDRIDE CENTER OF EXCELLENCE

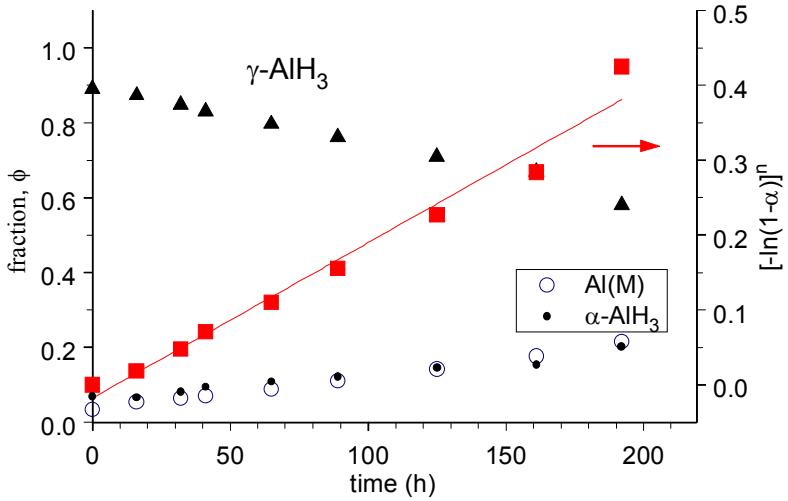


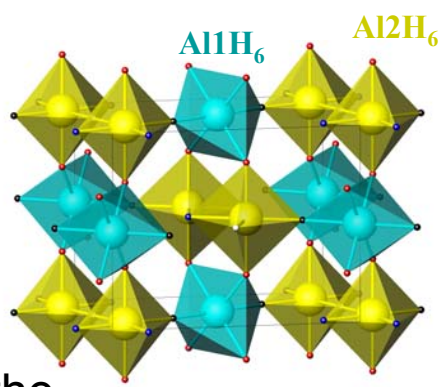


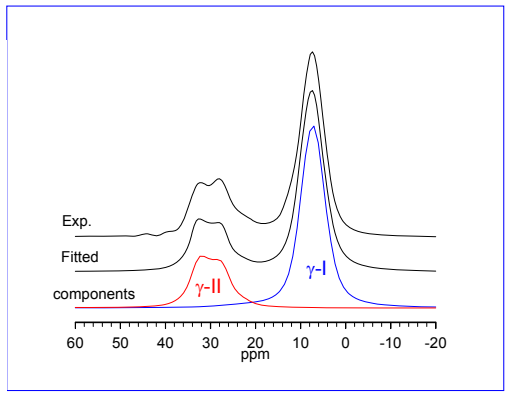




α-phase has only a single ^{27}Al peak







Plot of fraction (ϕ) of γ-AlH_3, Al(M), and α-AlH_3 during the room temperature decomposition of the γ-AlH_3 sample, and plot of [-ln(1-α)] vs t, where α is the fractional decomposition of γ-AlH_3.

γ-phase has two ^{27}Al peaks in MAS-NMR

Jet Propulsion Laboratory
California Institute of Technology

Task E: Engineering Analysis & Design

METAL HYDRIDE CENTER OF EXCELLENCE

JPL Objectives:

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

Accomplishments in FY-06/07:

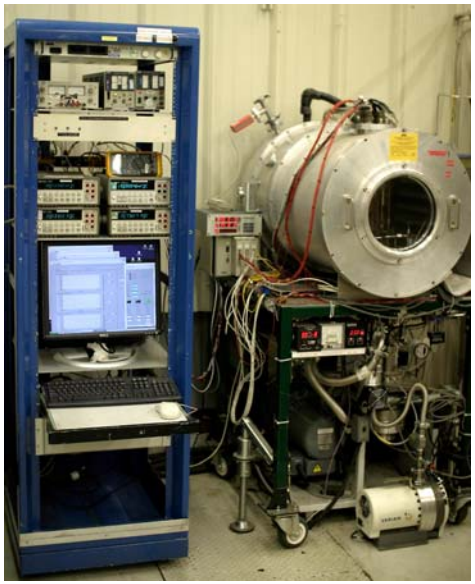
- Participated in several Hydrogen Storage Systems Analysis Working Group (SSAWG) meetings on prospects & limitations of various solid storage methods.
- Leading an EADT sub-team to assess status of previous & current metal hydride storage bed designs and performance models based upon survey of published literature.
- Began surveying approaches within modeling codes & bed design (i.e., "black box" vs detailed configuration) for input requirements and analysis methodology
- Started to specify predictive requirements & capabilities for each modeling approach to reproduce available test results

Deferred conducting any cycling tests in FY-06 as $LiBH_4/MgH_2$ system is not currently attractive for study due to slow kinetics & poor reversibility while the Li-Mg-N-H system was de-emphasized by MHCoE/SNL – plan to start accelerated cycling tests by end of FY-07 if a viable candidate is identified from screening assessments currently in progress.

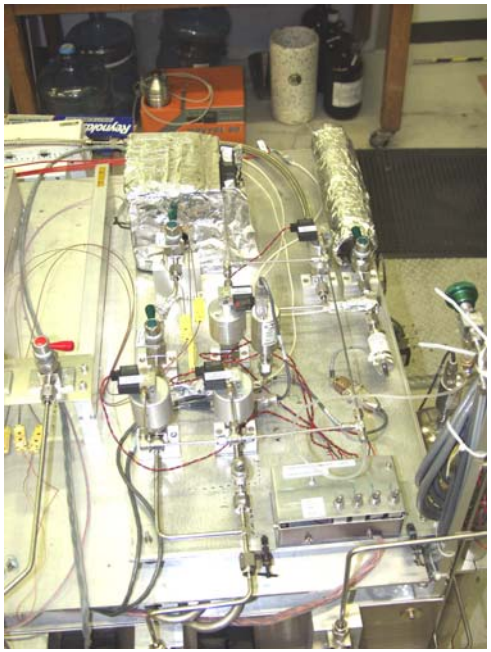
Cycling and Lifetime Testing

Jet Propulsion Laboratory
California Institute of Technology

METAL HYDRIDE CENTER OF EXCELLENCE

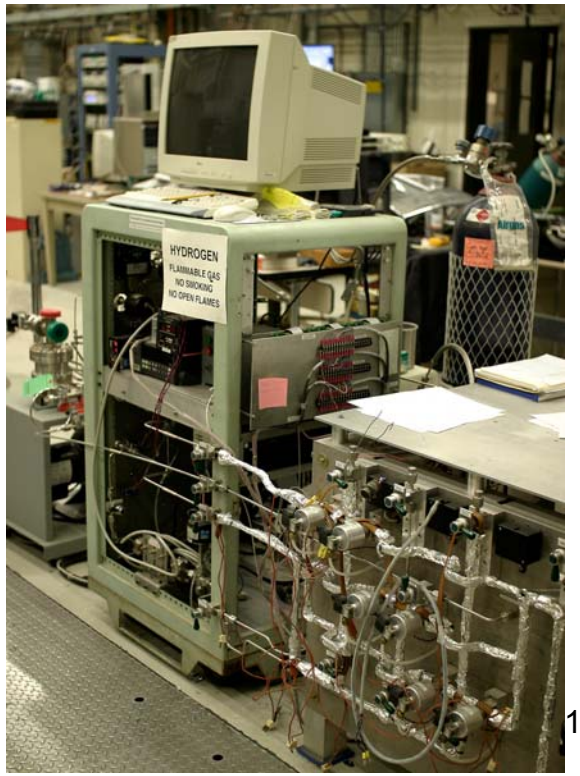


- **Long-term material/component cycling**
  - Automated, PC-controlled cycling station for large (~1 kg mass) hydrogen storage components
  - Originally developed and used for flight-testing of the Planck spacecraft hydride compressor beds
  - Suitable for evaluating advanced hydrides for fuel cell storage materials.



Rapid cycling and characterization

- Automated, PC-controlled station with UHV capability and RGA mass spectrometry
- Capable of performing multiplexed cycling experiments on several parallel samples



Planned Future Work (FY07/08)

Jet Propulsion Laboratory
California Institute of Technology

METAL HYDRIDE CENTER OF EXCELLENCE

Task A. [Destablized Hydrides]

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

Task B. [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 $Mg(BH_4)_2$ (GE), $Ca(BH_4)_2$ (SNL), catalyzed borohydrides and alanates (U. Hawaii and IFE), and $NaMgH_3$ (SRNL and Washington U.)
- Greater effort of using ^2H MAS-NMR on deuteride samples to determine locations and dynamics for hydrogen isotopes in disordered and nanophase hydrides.
- Continue collaboration with Washington U. [Mark Conradi, et al.] on NMR studies of diffusion and phase transformations in complex hydrides – emphasis on roles of catalysts.

Task C. [Evaluations of Amides/Imides]

- Continued systematic ^{15}N, ^6Li, MAS-NMR studies of Li-Mg-Al-N-H phases from U. Utah
- Investigate impact of catalysts on reactions kinetics, diffusion, and reversibility for these materials.

Task D: [Evaluations of Alanes]

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

Task E: [Engineering Analysis & Design]

- Complete literature survey review on state-of-hydride beds designs and performance.
- Develop prototype hydride bed for accelerated performance and cycling tests
- Perform accelerated cycling study on at least one promising hydride material.

Jet Propulsion Laboratory
California Institute of Technology

Summary of JPL in MHCoE

METAL HYDRIDE CENTER OF EXCELLENCE

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 parameters), & 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 MHCoE partners.
- NMR analysis is identifying amorphous/nanophase species that are not distinguishable via x-ray diffraction or vibrational spectroscopy methods.
- Initiated survey review of hydride storage vessels designs, modeling, and performance to assess state-of-art and directions for improvements.

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

Future Research: Continue NMR/volumetric characterizations of promising candidates and increase system engineering efforts on modeling behavior and materials degradation during extended absorption/desorption cycling studies.