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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Project ID
# STP32
Overview

Timeline

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

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 H₂
• P. Lack of Understanding of Hydrogen Physisorption and Chemisorption

Budget

• Expected total project funding:
  – $1.859M (DOE)
• Funding received in FY06
  – $311K (DOE)
• Funding received for FY07:
  – $400K (DOE)

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 H₂ Storage Project on solid state NMR studies of light element hydrides
• International: IFE (Norway), Philips (Netherlands), CNRS (France), and AIST (Japan)
Develop and demonstrate light-metal hydride systems that meets or exceeds the 2010/2015 DOE goals for on-board hydrogen storage

**Objectives of JPL within MHCoE**

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.
Approach of JPL in MHCoE – Materials Development

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.
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.
JPL is Supporting All MHCoE Projects

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

Project Groups

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

B
Complex Anionic Materials
- SNL (POC)
- GE
- U. Hawaii
- UIUC
- JPL
- ORNL
- NIST
- Intematix
- UNR
- Utah

C
Amides/Imides (M-N-H)
- Utah (POC)
- GE
- U. Utah
- UNR
- ORNL
- U. Hawaii
- JPL

D
Alanes (AlH₃)
- BNL (POC)
- SRNL
- JPL
- U. Hawaii
- SNL

E
Engineering Analysis & Design
- SRNL (POC)
- NIST
- JPL
- GE
- SNL
Task A - Destabilized Hydride Systems

- **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):
    - $^7$Li, $^{11}$B and $^1$H MAS-NMR spectra showed different phases with variation in hydrogen contents – undergoing more systematic studies of phase conversion, reversibility, catalytic effects, & degradation behavior.

  ![11B NMR Spectra](image1)
  ![11B MAS NMR Spectrum](image2)
  ![7Li MAS NMR spectrum](image3)

  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 $^1$H decoupling experiments indicate that the broad peaks at ~ 100 ppm don’t couple with $^1$H, consistent with the assignment MgB$_2$ phase. The $^7$Li NMR peaks show formation of LiH phase for sample UH-2A.
Investigation of the “$\text{ScH}_2 + 2\text{LiBH}_4 = 2\text{LiH} + \text{ScB}_2 + 4\text{H}_2$” Destabilization Reaction

X-ray Diffraction [Not Very Helpful]

MAS-NMR Spectra: As Milled & Reacted

Detected only $\text{ScH}_2$

Some $\text{LiBH}_4$ converted into elemental boron (not $\text{ScB}_2$)

Only $\text{LiBH}_4$ in “as BM”, but also $\text{LiH}$ (seen in $d_1=4000$s scan) in “Des/Abs” sample

**Summary:** Desorption did **Not** follow the destabilized process of forming $\text{ScB}_2$. Had only partial decomposition of $\text{LiBH}_4$ into $\text{LiH} + \text{B}$ with little reversibility indicated during absorption.
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

• CaSiH$_x$ (NIST) —$^{29}$Si, $^1$H, & $^2$H 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

**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

**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)

- 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

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\text{\textbf{Li NMR study of Li$_2$NH}}
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$^{27}$Al NMR Spectra

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\text{\textbf{Li$_3$AlH$_6$}}
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- NMR confirmed that Li$_3$AlH$_6$ is in the hydrogenated product – meaning the reaction is reversible!
- NMR verified the basic reaction hypothesis – Li$_2$Mg(NH)$_2$ and Al metal are confirmed as the dehydrogenated products.
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 AlH₃.

Accomplishments in FY-06/07:

- MAS-NMR measurements on various AlH₃/AlD₃ 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-AlH₃ from different sources [Only BNL-Dow has trapped H₂ gas]
Task D: Evaluations of Alanes (Continued)

Plot of fraction ($\phi$) of $\gamma$-AlH$_3$, Al(M), and $\alpha$-AlH$_3$ during the room temperature decomposition of the $\gamma$-AlH$_3$ sample, and plot of [-ln(1-$\alpha$)] vs t, where $\alpha$ is the fractional decomposition of $\gamma$-AlH$_3$.

$\alpha$-phase has only a single $^{27}$Al peak

$\gamma$-phase has two $^{27}$Al peaks in MAS-NMR
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

• **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)

**Task A. [Destabilized 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(BH₄)₂ (GE), Ca(BH₄)₂ (SNL), catalyzed borohydrides and alanates (U. Hawaii and IFE), and NaMgH₃ (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.

**Task C. [Evaluations of Amides/Imides]**
• Continued systematic ¹⁵N, 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 AlH₃ 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.
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 parameters), & reversibility assessments via NMR in numerous systems (i.e., Li-Mg-B-H, Li-Sc-B-H, Li-B-Ca-Al-H, AlH₃, 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.