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
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 H₂
• 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 (AlH₃)
- 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, MgH₂, LiBH₄ & others and also to assess their aging durability during extended cycling

- **Accomplishments:**
  - MAS-NMR determined phase formation and reversibility in LiBH₄/MgH₂ (SNL):
    - ⁷Li, ¹¹B and ¹H 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.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Code</th>
<th>Treatment</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiH+MgB₂</td>
<td>LCS-55</td>
<td>As ball milled</td>
<td>From J. Vajo [HRL]</td>
</tr>
<tr>
<td>LiBHₓ+MgH₂</td>
<td>LCS-55: RX-1</td>
<td>Absorbed H²</td>
<td>Saturated hydrides</td>
</tr>
<tr>
<td>LiH+MgB₂</td>
<td>LCS-55: RX-2</td>
<td>Desorbed H²</td>
<td>very metallic, max spinning = 6 kHz</td>
</tr>
<tr>
<td>MgB₂ + LiH + LiBHₓ</td>
<td>LCS-55: RX-2 + SiO₂ Powder</td>
<td>Desorbed H²: diluted for better MAS-NMR</td>
<td>Incomplete desorb reaction noted</td>
</tr>
</tbody>
</table>

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1H MAS NMR Spectra
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7Li MAS NMR
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11B NMR Spectra
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LiH+MgB₂ LCS-55 As ball milled From J. Vajo [HRL]
LiBHₓ+MgH₂ LCS-55: RX-1 Absorbed H² Saturated hydrides
LiH+MgB₂ LCS-55: RX-2 Desorbed H² very metallic, max spinning = 6 kHz
MgB₂ + LiH + LiBHₓ LCS-55: RX-2 + SiO₂ Powder Desorbed H²: 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$_x$Si$_y$H$_z$ 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$_y$Si$_z$H$_x$) phases that limits of complete reversibility – an issue to be looked for with other combinations.

MAS-NMR confirm the LiSiH phase [Li$_y$Si$_z$H$_x$] and some c-Si phase, **but no LiH!**
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)

• 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


- Ti roles in alanates (i.e., NaAlH₄) 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 ⁴⁵Sc is excellent candidate & is also good catalyst!
- Obtained initial MAS-NMR spectra [¹H, ²³Na, ²⁷Al, & ⁴⁵Sc] on Sc-doped NaAlH₄ samples.

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)

- 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 AlH₃.

- Accomplishments:
  - Obtained MAS-NMR results on AlH₃ samples with α-, β- and γ-phases and monitored Al metal & H₂ gas formation during spontaneous decomposition (BNL)

Conclusions:
- Two types of Al atoms in γ-AlH₃ but only one site in α & β phases – will help solve these structures from PND & PXRD
- ²⁷Al NMR shifts consistent with AlH₆ sites will assess differences in bonding to relate to decomposition of these AlH₃ 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. [Destabilized 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(BH₄)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 AlH₃ phases and decomposition processes (BNL, U. Hawaii, IFE-Norway)
Summary JPL Tasks in MHCoE

**FY 2006 Milestones**

- Complete an initial phase cycling tests on at least one destabilized hydride system (e.g. LiBH₄/MgH₂ or Li-Mg-N-H)  
  **Due**: August, 2006
- Provide a top-level estimate of mass, volume, & thermal parameters for a prototype destabilized/complex hydride storage vessel  
  **Due**: 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 2\textsuperscript{nd} phase NMR studies on Li-Mg-N-H samples (SNL)
- Complete 2\textsuperscript{nd} phase NMR studies on AlH₃ samples (BNL)
- Perform NMR studies on alanates, borohydrides, etc. from MHCoE team
### A. Destabilized Hydrides

<table>
<thead>
<tr>
<th>Organization</th>
<th>Task #</th>
<th>Task Description</th>
<th>FY05</th>
<th>FY06</th>
<th>FY07</th>
<th>FY08</th>
<th>FY09</th>
<th>FY10</th>
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<tr>
<td>JPL</td>
<td>1.1.1</td>
<td>Conduct cycling studies on Li-Mg-Ni-H and Li-B-Mg-H systems</td>
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<tr>
<td>JPL</td>
<td>1.1.2</td>
<td>Use MAS-NMR to measure phases in mixtures of LiBH, with various hydrides (e.g., MgH₂, LiNH₂); extend to other candidate materials</td>
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### B. Complex Anionic Materials (Borohydrides & Alanates)

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<th>Description</th>
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<th>FY06</th>
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<td>JPL</td>
<td>2.2.1</td>
<td>NMR analysis of samples in the Na-Si-H system provided by SNL</td>
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### C. Amide/Imides (M-N-H Systems)

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<td>JPL</td>
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<td>NMR study the nature of N-H bond</td>
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### D. Alanes (AlH₃)

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<tr>
<td>JPL</td>
<td>2.4.1</td>
<td>Complete nuclear magnetic resonance (NMR) characterization on selected alanes</td>
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### E. Engineering Analysis & Design

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<td>Vessel Modeling (Detailed Component Fidelity)</td>
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<td>JPL</td>
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<td>Materials Compatibility</td>
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Back-up Slides (Not presented)
Responses to Previous Year Reviewers’ Comments

• NA – This Project was new in FY-05 and was not reviewed.
• **Published Papers**

• **Papers Submitted for Publication**

• **Manuscripts in Preparation or Planned**
•Presentations made in 2005/2006


•Presentations planned for remainder FY-06