Development and Evaluation of Advanced Hydride Systems for Reversible Hydrogen Storage

Joseph W. Reiter, Jason A. Zan, Robert C. Bowman, Jr., & Son-Jong Hwang (Caltech)

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

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Overview: Project Details

Timeline
• Project start date: April, 2005
• Project end date: Dec., 2009
• 80 % 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 FY08:
  – $487.2K (DOE)
• Funding received for FY09:
  – $500.0K (DOE)

Partners
• Participant in DOE MHCoE – collaborations with partners in all four sub-group Projects, primarily with Caltech, SNL, ORNL, U. Utah, HRL, NIST, Ohio State, U. Hawaii in FY08-09
• Limited collaboration on inter-Center activities with Hydrogen Storage Engineering Center of Excellence (HSECoE)
• International: IFE (Norway), Tohoku U. (Japan), and AIST (Japan)
Relevance: Objectives

Overall Goal/Primary Objective

**Develop and demonstrate light-metal hydride systems that meet or exceed the 2010/2015 DOE goals for on-board hydrogen storage through the validation of storage properties and reversibility in light element hydrides**

- Nanophase, destabilized hydrides based upon LiH, MgH₂, & LiBH₄
- Complex hydrides (e.g., amides/imides, borohydrides, & AlH₃-based hydrides)
- Samples provided by numerous MHCoE partners, as opportunities are presented

Tasks

1. **Phase Identification:**
   Perform NMR characterizations of phase relations for Li-Mg-Al-N-H, Li-B-Mg-H, and Li-Sc-B-H systems, with attention to suitability for cycling, as per:
   - Reversibility
   - Kinetics, towards meeting DOE delivery and refueling targets
   - H₂ storage parameters, with attention to approaching the 2010/2015 goals

2. **Reaction Pathways:**
   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

3. **Cycling Stability:**
   Extended cycling tests had been postponed through early FY2008 since no primary candidate was identified; progress has been made to accomplish this investigation with Ca(BH₄)₂ in FY2009.

4. **Hydride Bed Design:**
   This engineering sub-task was postponed and then shifted out of MHCoE into the new Hydrogen Storage Engineering Center of Excellence (HSECoE) for FY2009.
Relevance: Milestones

- Milestones (excerpted from 2008 Annual Operating Plan where appropriate)

<table>
<thead>
<tr>
<th>Milestone</th>
<th>Date</th>
<th>Status</th>
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<tbody>
<tr>
<td>Perform NMR characterization study of reaction pathways and bonding in the M-B-H (M=Ca, Mg, Li) system (Task 2)</td>
<td>3/08</td>
<td>40%: milestone added late in FY2008; work will continue into FY2009</td>
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<tr>
<td>Complete NMR characterization studies of phase relations for Li-Mg-Al-N-H system, Li-B-Mg-H, and Li-Sc-B-H phases (Task 1)</td>
<td>6/08</td>
<td>90%: Li-Sc-B-H paper submitted, Li-Mg-Al-N-H work continues (U. Utah), focusing on Li-B-Mg-H in early FY2009</td>
</tr>
<tr>
<td>Complete initial degradation study on either a destabilized system (i.e., Li-Mg-Al-N-H) or a more promising TBD complex hydride (Task 3)</td>
<td>9/08</td>
<td>15%: Task shifted to FY2009; planning for extended cycling of Ca(BH₄)₂</td>
</tr>
<tr>
<td>Generate a Review Report on the state-of-art metal hydride storage vessels from literature sources including assessment of models that can analyze and predict hydride bed behavior (Task 4)</td>
<td>9/08</td>
<td>25%: (MHCoE Project E discontinued during FY2008)</td>
</tr>
<tr>
<td>Perform detailed 2-phase system engineering and thermal performance modeling studies on metal hydride demonstrator beds (Task 4)</td>
<td>9/08</td>
<td>50%: (MHCoE Project E discontinued during FY2008)</td>
</tr>
</tbody>
</table>

- Engineering (Project E) work has shifted to the new Hydrogen Storage Engineering Center of Excellence (HSECoE) in FY2009
Overview: JPL’s Role in MHCoE

Coordinating Council (2008-2009)

Bruce Clemens (Stanford, POC A), Craig Jensen (UH, POC B), Zak Fang (Utah, POC C), Jim Wegrzyn (BNL, POC D), Don Anton (SRNL), J.-C. Zhao (OSU), Jay Keller (SNL) and Lennie Klebanoff (SNL)

Project Groups

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

B
- Complex Anionic Materials
  - UH (POC)
  - SNL
  - OSU
  - UIUC
  - JPL
  - ORNL
  - NIST
  - UNR
  - Utah
  - UTRC

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

D
- Alane (AlH₃)
  - BNL (POC)
  - SRNL
  - U. Hawaii
  - SNL
  - UIUC
  - UNB
  - JPL

Note: Original Project E (eng.) discontinued with HSECoE
Approach

- Multi-disciplinary Analysis and Characterization of Selected Hydrides to Elucidate Fundamental Processes

- Thermo-volumetric measurements
  - Determinations of fundamental hydrogen storage capacities and equilibrium pressures on destabilized nanophase and complex metal hydrides

- “Magic Angle” Spinning Nuclear Magnetic Resonance (MAS-NMR)
  - Measurements are performed at Caltech Solid State NMR Facility (CSNF, Dr. Son-Jong Hwang, lead) to assess the phase compositions and chemical bonding parameters
  - NMR analysis is identifying the character of B-H bonding and reaction pathways in the metal-borohydride systems; this technique can distinguish amorphous/nanophase species that are not otherwise sensible via x-ray diffraction or vibrational spectroscopy methods

- Neutron scattering spectroscopy
  - Examinations of structures by neutron scattering and diffraction, etc. in collaboration with MHCoE partner NIST

- Raman spectroscopy
  - Measurements made at Caltech to determine mechanisms of desorption processes

- Theoretical collaborations
  - Interactions with MHCoE theory teams (i.e., UCLA/UMSL, etc.) on phases and destabilization behavior
Technical Accomplishments

**Ca(BH₄)₂ Reaction Mechanism Study - 1**

- NMR shows the crystalline phase Ca(BH₄)₂ after absorption via the powder pattern from the spinning sidebands and chemical shift position.

- Following hydrogenation at 330 °C, about 57% of boron is now present as α-Ca(BH₄)₂: the Intermediate ~ 30%, CaB₆ ~ 13%.

- The use of catalyst (samples provided by SNL) showed change of crystalline polymorphs of the recovered powder (α → β). This interesting result shows various additional transformations among different polymorphs around the reaction temperature.
Technical Accomplishments

**Ca(BH\textsubscript{4})\textsubscript{2} Reaction Mechanism Study - 2**

MHCoE Project B: *Complex Anionic Materials*

- NMR identifies Desorption/Absorption of Ca(BH\textsubscript{4})\textsubscript{2} at low temperatures (<350 °C) typically show residual Ca(BH\textsubscript{4})\textsubscript{2}, Ca-B-H intermediate (-20 ppm), and CaB\textsubscript{6}.

- The Ca-B-H intermediate is not yet fully characterized while its chemical shift is very close to CaB\textsubscript{12}H\textsubscript{12} (sample provided from SNL). Dissolution of the desorbed material in water did not show the presence of [B\textsubscript{12}H\textsubscript{12}]\textsuperscript{2-} phase, unlike LiBH\textsubscript{4} or MgBH\textsubscript{4} cases\textsuperscript{1}.

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Technical Accomplishments

$M(B_{12}H_{12})_n$ Characterization

- Various dodecaborane samples were characterized by NMR and other spectroscopic tools in collaboration with SNL, S. Jalisatgi (U. Missouri-Columbia), J.-C. Zhao (OSU), T. Udovic (NIST)

- $^{11}$B MAS NMR spectra show characteristic down field shifts for $M =$ alkali metal vs alkali earth metal cations, and quadrupole coupling constants were varied in ~ 100 kHz range; the BH$_4$ icosahedrons becomes highly mobile (sharp center NMR line as for Mg) as water molecules are introduced to the crystalline phases

- Removal of crystalline water becomes a challenging issue for certain metals (e.g. Mg)

- NMR remains an excellent tool for characterizing the details of these complex B-H systems
Technical Accomplishments

Reactivity of $\text{Li}_2\text{B}_{12}\text{H}_{12} \cdot n(\text{H}_2\text{O})$ - 1

MHCoE Project B: Complex Anionic Materials

- Direct dehydrogenation of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ material was attempted in order to elucidate reaction pathways in the M-B-H system (M = Li, Mg, Ca)

- Dehydrogenation to $500 \degree C$ of 525 mg of material yields an initial 3.7% loss, with most activity occurring between $300-400 \degree C$
**Technical Accomplishments**

*Reactivity of Li$_2$B$_{12}$H$_{12}$·n(H$_2$O) - 2*

- Based on several experiments, it appears that in the MB$_{12}$H$_{12}$ system (M = Li, Mg, Ca), high affinity with H$_2$O results in B-OH formation during heating, even as water is being removed.

- The presence of water in these material systems proves a universal difficulty in practice as there are several hydration states in each system.
**Technical Accomplishments**

**Destabilizing Reactions of \(M(B_{12}H_{12})_n\)**

- \(\text{Li}_2\text{B}_{12}\text{H}_{12} + \text{MH}_2\) (\(M=\text{Mg, Ca}\)) which were reported\(^1\) to have favorable \(\Delta H_{\text{react}}\) appear to show high kinetic barrier.

- \(\text{Li}_2\text{B}_{12}\text{H}_{12} + 6\text{MgH}_2\) \(\text{Des} 400 \, ^o\text{C}\)

- \(\text{Li}_2\text{B}_{12}\text{H}_{12} + 6\text{MgH}_2\) \(\text{Reabs} 300 \, ^o\text{C}\)

- \(\text{Li}_2\text{B}_{12}\text{H}_{12} + 2\text{CaH}_2\) \(\text{Des} 400 \, ^o\text{C}\)

\(\text{Li}_2\text{B}_{12}\text{H}_{12} + \text{MH}_2\) (\(M=\text{Mg, Ca}\)) which were reported\(^1\) to have favorable \(\Delta H_{\text{react}}\) appear to show high kinetic barrier.

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Technical Accomplishments

Heating Rate Effects on $\text{Li}_3\text{AlH}_6 + \text{Li}_2\text{NH}$

- System has 7.2 wt% H$_2$ capacity; all samples were prepared by jar-rolling/ball-milling for 80 hours, dehydrogenated at 300°C in vacuum for 6 hours (collaboration with Z. Fang at U. Utah)

- Preferential formation of AlN or $\text{Li}_3\text{AlH}_6$ depends on heating rate$^1$; $\text{Li}_3\text{AlH}_6$ formation needs heating rate of 5 °C/min, and $T_{\text{react}} > 250$ °C

- MAS-NMR proves a good probe of pathways via $^{27}\text{Al}$ spectra


### Sample Description

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
<th>Weight (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UT-37</td>
<td>Hydrogenated at 300 °C at heating rate of 10 °C/min under 2650 psi of H$_2$</td>
<td>53.4</td>
</tr>
<tr>
<td>UT-38</td>
<td>Hydrogenated at 250 °C at heating rate of 10 °C/min under 2650 psi of H$_2$</td>
<td>53.8</td>
</tr>
<tr>
<td>UT-39</td>
<td>Hydrogenated at 300 °C at heating rate of 1 °C/min under 2650 psi of H$_2$</td>
<td>51.4</td>
</tr>
<tr>
<td>UT-40</td>
<td>Hydrogenated at 250 °C at heating rate of 1 °C/min under 2650 psi of H$_2$</td>
<td>61.5</td>
</tr>
</tbody>
</table>
Technical Accomplishments

Characterization of AlB₄H₁₁ - 1

- Material provided by ORNL; effort was a collaboration among JPL, Caltech, ORNL & Ohio State
- Extensive characterization of this new material from ORNL included volumetric work showing 11.4% content (at 400°C); *significant H₂ release occurred in the range 140-200°C*
- Initial NMR spectra revealed a complex boron environment in the products, including both B-H complexes and (possibly) elemental boron with other features, partially avoiding the B₁₂H₁₂ route
Technical Accomplishments

Characterization of AlB₄H₁₁ - 2

- MAS NMR spectra collected during systematic study of the desorption/reabsorption pathways in AlB₄H₁₁¹
  - (a) ¹H NMR suggests partial reversibility of an H₂ bearing phase
  - (b) ¹¹B NMR shows the complexity of the boron environment, as compared to reference AlB₂ and α-B phases
  - (c) ²⁷Al NMR following reabsorption suggests the possibility of reduced Al metal, but this is a topic for further study

JPL Engineering Tasks

• With the transfer of engineering roles out of Project E to the new Hydrogen Storage Engineering Center of Excellence (HSECoE), JPL’s roles in this area were shifted out of MHCoE in FY09

  – Support development of more efficient hydride storage vessels to reduce storage system mass while retaining viable thermal management during H₂ absorption & desorption.
  – Support system design and analyses using methods and analytical models established at JPL for sorption cryocooler hydride compressor beds.
  – Perform literature review on hydride bed design techniques and approaches

• JPL retains engineering functions as a direct partner in HSECoE as well as informal/formal communications via the Engineering Materials Working Group (POC D. Anton, SRNL)

  – See JPL Poster in Engineering session, stp_10_reiter
Proposed Future Work

• Project A - Destabilized Hydride Systems
  – [FY09] Investigate the potential for structured carbon-based materials (aerogels, graphitic carbons, high-surface area materials) as dopants in destabilized hydride systems utilizing volumetric, NMR, and XRD techniques
    • Investigate pore size effects
    • (potential collaborations with Caltech, SRNL, HRL, NIST)

• Project B - Complex Anionic Materials
  – [FY09] Continue phase transformation and reversibility studies of the Ca(BH$_4$)$_2$ system in collaboration with MHCoE partners, lending support with volumetric characterizations as well as MAS-NMR, XRD, and Raman analytical techniques
    • Assess initial cycling data for n~10-100 cycles
    • (SNL, Caltech, U. Hawaii)

  – [FY09-10] Continue studies of possible destabilization routes in material systems containing the [B$_{12}$H$_{12}$]$^{-2}$ anion, especially as it pertains to avoiding the production of this stable intermediate in the Mg-B-H, Li-B-H, Ca-B-H and mixed cation borohydride systems
    • Investigate reaction pathways and bonding
    • Consultation with theory groups
    • (Caltech, SNL, NIST, UCLA, UMSL)

• Project C - Amides/Imides
  – [FY09-10] Perform systematic investigations of $^{15}$N-enriched amine-borohydride materials, leveraging MAS-NMR techniques for the purpose of assessing reaction kinetics, bonding dynamics, and phase transformation effects in the $M$-B-N-H system ($M = Li, Al, Mg$), especially for mixed cation and/or ternary systems
    • (ORNL, Ohio State, U. Utah)
Summary

• **Approach**
  – Systematic characterizations of phase formation and hydride reversibility using solid state NMR and volumetric measurements (Projects A, B, C, & D)

• **Technical Accomplishments**
  – Phase characterization, kinetics (i.e., diffusion behavior), & reversibility assessments via MAS 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)
  – NMR analysis is identifying the character of B-H bonding and reaction pathways in the metal-borohydride systems; this technique can distinguish amorphous/nanophase species that are not otherwise sensible via x-ray diffraction or vibrational spectroscopy methods

• **Collaborations**
  – Caltech, U. Utah, SNL, Ohio State, ORNL, HRL, NIST, U. Hawaii, SRNL, & UTRC

• **Future directions**
  – Continue aggressive investigations of destabilization routes in the MB₁₂H₁₂ system
  – Perform systematic multi-spectroscopic study of results from Ca(BH₄)₂ cycling
  – Utilize NMR methods within ¹⁵N-enriched amide/imide systems