Lightweight Metal Hydrides for Hydrogen Storage

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Program Overview

Timeline

- Project start date: March 2005
- Project end date: August 2011
- Percent complete: 90%

Barriers

- Right heat of formation (J)
- Absorption / desorption kinetics (E)
- Reversibility for borohydrides (D, P)

Budget

- Total Project Funding: $4.5M
  - DOE Share: $3.6M
  - OSU Share: $0.9M
- Funding Received for FY10
  - $700K (DOE), $175K (OSU-Cost)
- Funding for FY11: $212K

Partners/Collaborations

- Members of DOE MHCoE
- Collaborations with ORNL, NIST, Caltech, UTRC, SNL, and Univ. of Utah, Univ. of Washington, and Ford.
## Objectives & Relevance

<table>
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<tr>
<th>Overall</th>
<th>Discover and develop a high capacity (&gt; 6 wt.%) lightweight hydride capable of meeting or exceeding the 2015 DOE/FreedomCAR targets.</th>
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<tbody>
<tr>
<td>FY10</td>
<td>• Study the <strong>structure</strong> and hydrogen storage properties of AlB₄H₁₁;</td>
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<td>• Synthesize and study AlB₅H₁₂ and AlB₆H₁₃ for hydrogen storage property measurements;</td>
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<td>• Synthesize and study other borane compounds.</td>
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<td>FY11</td>
<td>• Complete structure analysis for AlB₄H₁₁</td>
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<td>• Perform study on the absorption &amp; desorption kinetics and catalytic effects to improve the reversibility of AlB₄H₁₁;</td>
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<td>• Complete a final report.</td>
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This project is directly exploring materials to meet the DOE 2015 hydrogen storage targets.
Approach

- Study aluminoborane compounds such as AlB$_4$H$_{11}$ for hydrogen storage;
- Study the crystal structures and the decomposition mechanisms using multiple techniques such as interrupted PCT tests, NMR, IR, DSC, and residual gas analysis;
- Develop reversibility strategy from detailed mechanistic understanding of the complex desorption processes (such understanding is crucial for reversibility of all borohydrides);
- Synthesize new hydrides and complexes in collaboration with ORNL, NIST, Northwestern, JPL, Caltech, and Sandia.
Background on $\text{AlB}_4\text{H}_{11}$

- Low desorption temperature (starts $\sim120^\circ\text{C}$), 13.5 wt.% $\text{H}_2$ with small amounts of $\text{B}_2\text{H}_6$ ($\sim1$ vol.% gas).
- DSC shows endothermic desorption: thermodynamically reversible.
- Clearly demonstrated partial reversibility using PCT, IR and NMR at mild conditions.
- Amorphous structure with polymerization.

Temperature: 200 °C
Pressure 100 bar (1st), 97 bar (2nd)

Des/Reabs $[\text{AlB}_4\text{H}_{11} + \text{catalyst}]$

Low desorption temperature (starts $\sim120^\circ\text{C}$), 13.5 wt.% $\text{H}_2$ with small amounts of $\text{B}_2\text{H}_6$ ($\sim1$ vol.% gas).

DSC shows endothermic desorption: thermodynamically reversible.

Clearly demonstrated partial reversibility using PCT, IR and NMR at mild conditions.

Amorphous structure with polymerization.
amorphous and polymeric...there is nothing like it known...

Structure of AlB₄H₁₁

- Solution NMR
- IR
- Reactivity
- Mechanism

Prototype electrostatic ground state (PEGS) + DFT simulations

Solid-state NMR

Valence bond theory

Mass spec

Neutron vibration spectroscopy

Neutron total scattering spectroscopy (NOVA) analysis

Technical Accomplishments
Structure of $\text{AlB}_4\text{H}_{11}$

$\text{BH}_4$

$^{11}\text{B}$ NMR of $\text{AlB}_4\text{D}_{11}$ residual solution

- $\text{AlB}_4\text{H}_{11}$ not soluble in most of the solvents.
- We analyzed the residual reaction solution for structure information.
- The $^{11}\text{B}$ NMR from $\text{AlB}_4\text{D}_{11}$ shows at least two different boron units.
- The $^{11}\text{B}$ NMR chemical shifts consistent with solid state NMR.
• The $^{27}\text{Al}$ NMR shows additional peaks in addition to that of $\text{Al(BD}_4\text{)}_3$.
• Some peaks consistent with solid-state NMR, but other peaks couldn’t be explained at this point.
The $^2$H NMR also shows additional peaks in addition to that of Al(BD$_4$)$_3$.

- More refined details about $^2$H signals revealed by solution NMR.
Prototype electrostatic ground state: PEGS


- PEGS
  - Hamiltonian
    \[ E_{\text{tot}} = \sum_{i>j} \frac{Q_i Q_j}{R_{ij}} + \sum_{i>j} \frac{\varepsilon_{ss}}{R_{ij}^{1/2}} \]
    - Coulomb Soft-sphere
  - Annealing Monte-Carlo

- PEGS+DFT procedure
  - Cation Anion group
  - PEGS
  - Ordered crystal structure
  - DFT select
  - Winner with the lowest energy !!!
Structure of AlB$_4$H$_{11}$

Lowest energy structures from PEGS + DFT

Chain: [BH$_4$] + 2[BH$_3$] + [BH] Cluster: [AlH] + 2[BH$_3$] + [BH$_2$] + [BH]

2[BH$_3$] + [BH] forms a B-B circle

$-68.347 \text{ eV}$

[BH$_3$] + [BH$_2$] + [BH] forms a B-B circle

$-68.166 \text{ eV}$

[BH$_3$] + 2[BH$_2$] forms a B-B circle

$-68.584 \text{ eV}$

Yongsheng Zhang, Yongli Wang, Chris Wolverton
Structure of AlB$_4$H$_{11}$

Expt. IR

Computed phonon density of state for structure 6

Yongsheng Zhang
Yongli Wang
Chris Wolverton
Structure of AlB$_4$H$_{11}$

Neutron vibration spectra: experiment vs. calculation

Benchmark:
Even for well-determined single-crystal structures, the theoretical neutron vibration spectra from DFT calculations still show appreciable deviations from experimental ones.

Wei Zhou & Terry Udovic
Structure of $\text{AlB}_4\text{H}_{11}$

Neutron vibration spectra: experiment vs. calculation

- Good overall agreement between experimental and calculated NVS of structure 6.
- We are very close to the right structure.
Structure of AlB$_4$H$_{11}$

AlB$_4$H$_{11}$(s) + NH$_3$(l) → B$_3$H$_8^-$ + BH$_4^-$

$^{11}$B NMR spectra of AlB$_4$H$_{11}$ in liquid ammonia

- The existence of B$_3$ unit was confirmed.
- Two different boron environments – consistent with structure 6
Structure of AlB₄H₁₁

Two Al signals/environments are inconsistent with structure 6
Structure of AlB$_4$H$_{11}$

AlB$_4$D$_{11}$(s) + NH$_3$(l) → B$_3$D$_8^-$ + BD$_4^-$

$^{11}$B NMR

B$_3$D$_8$

BD$_4$

$^{27}$Al NMR

$^2$H NMR

11B-11B  2D NMR

• 2D NMR indicates that the two boron units/groups are not correlated.
• Consistent with structure 6

The total valence electron number in each unsymmetrical unit:
\[3 \text{ (Al)} + 4 \times 3 \text{ (B)} + 11 \times 1 \text{(H)} = 26\]

The bond numbers in each unsymmetrical unit:
- 7 normal bonds (2x B3-Hₜ, Al-B2, B2-Hₜ, B1-Hₜ, 2 x B4-Hₜ)
- 7 three center-two electron bonds (2x Al-H_b-B3, Al-B4-B1, Al-H_b-B1, Al-H_b-B2, B2-H_b-B4, B1-B2-B4).

So 14 bonds need 28 electrons but only 26 electrons are available.

Valence bond analysis shows that Structure 6 needs improvement.
Structure of AlB$_4$H$_{11}$

- Two types of boron environments (BH$_4$ and a triangular B-B-B unit) are clearly identified from both solution NMR and solid state NMR as well as PEGS+DFT calculations.
- We are very confident that the boron units in AlB$_4$H$_{11}$ are already clearly identified.
- Structure 6 needs modification to incorporate two Al environments.
- Bond valence analysis also suggests that structure 6 needs modification.
- A new set of PEGS + DFT calculations was performed at Northwestern based on the above information and produced a new two formula unit structure (denoted as 2fu_structure, ~ 400 meV lower energy than structure 6)
Structure of AlB$_4$H$_{11}$

Expt. IR

Computational phonon density of state for the 2fu_structure

Yongsheng Zhang
Yongli Wang
Chris Wolverton
Structure of AlB$_4$H$_{11}$

Neutron vibration spectra: experiment vs. calculation

- Good overall agreement between experimental and calculated NVS of 2fu_structure.
Structure of AlB$_4$H$_{11}$

Xiaoguang Bao

Technical Accomplishments

Good overall agreement between experimental and calculated $^{11}$B NMR (±5 ppm is considered good agreement).

Computed $^{11}$B NMR peak positions using 2fu_structure

Yongsheng Zhang
Yongli Wang
Chris Wolverton
Brief Summary of AlB$_4$H$_{11}$ Structure Analysis:

- We are very confident that the two boron units (BH$_4$ and a triangular B-B-B unit) in AlB$_4$H$_{11}$ are already clearly identified.
- The new 2fu_structure has two Al environments.
- AlB$_4$D$_{11}$ made for NOVA analysis which will provide radial atom distribution information for structure refinement.
- We probably got the right structure or are very close the right structure.
3 LiBH₄ + AlCl₃ → AlBH₆H₁₃ + ½ B₂H₆ + 2 H₂

Al(BH₄)₃ + 2 B₄H₁₀ → (BH₄)Al(B₃H₈)₂ + 2 H₂

(n-C₄H₉)₄NB₃H₈ + BBr₃

THFBBH₃ + KBH₄

IR consistent with values reported by Himpsl & Bond
AlB$_6$H$_{13}$

Technical Accomplishments

First weight loss @ 190 °C.

Large amount of B$_2$H$_6$ formation during desorption makes AlB$_6$H$_{13}$ unsuitable for hydrogen storage
NaB$_3$H$_8$ – 12.6 wt.% H

Technical Accomplishments

- Safe (B$_2$H$_6$ and BF$_3$ free) synthesis developed for unsolvated NaB$_3$H$_8$.
- Thermal decomposition gives a significant amount of borane species.
- Uns suited for reversible onboard hydrogen storage.
- Structure identified ($Pmmm$).
**NaB₃H₈ – 12.6 wt.% H**

11B NMR spectra of water solution

- > 50 % NaBH₄ hydrolysed over a day
- < 10 % NaB₃H₈ hydrolysed over a week.

**Technical Accomplishments**

- Hydrolysis produces high (10.5) wt.% pure H₂.
- High solubility and good stability in H₂O.
- Cobalt-based catalyst effective for hydrolysis.
- Better than NaBH₄ (7.5 wt.% H) and NH₃BH₃ (5.1 wt.% H) for hydrolysis (solubility in water considered).
\( \text{NH}_4\text{B}_3\text{H}_8 - 20.5 \text{ wt.\% H} \)

\[
\text{NH}_4\text{Cl} + \text{NaB}_3\text{H}_8 \rightarrow \text{NH}_4\text{B}_3\text{H}_8 + \text{NaCl}
\]

- Thermal decomposition exothermic – not suited for onboard reversible storage.
- Thermal decomposition gives of a significant amount of borane species.
NH₄B₃H₈(s) + 6H₂O(l) $\xrightarrow{\text{cat.}}$ NH₄⁺(aq) + 3BO₂⁻(aq) + 2H⁺(aq) + 9H₂(g)

7.5 wt.% H (including H₂O weight)

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Technical Accomplishments

- Hydrolysis produces high (7.5 wt.%) pure H₂.
- High solubility and good stability in H₂O.
- Cobalt-based catalyst effective for hydrolysis.
- Better than NaBH₄ and NH₃BH₃ for hydrolysis.

1 mol % noble metal
4 mol % transition metal
Summary

- **AlB$_4$H$_{11}$ (13.5 wt.% H):**
  - We mounted a multi-pronged structure analysis of AlB$_4$H$_{11}$ in close collaboration with Northwestern and NIST using solution NMR, solid state NMR, IR, neutron vibration analysis, chemical analysis, bond valence analysis, and PEGS+DFT simulations.
  - Two boron units (BH$_4$ and a triangular B-B-B unit) in AlB$_4$H$_{11}$ are already clearly identified from both solution NMR and solid state NMR as well as PEGS+DFT calculations; and solution $^{27}$Al NMR suggests two Al environments.
  - We think we got the correct structure or we are very close to get the correct structure.
  - AlB$_4$D$_{11}$ is made for NOVA analysis which will provide radial atom distribution information for structure analysis.
Summary (continued)

• **AlB$_4$H$_{11}$ (continued):**
  • We performed catalyst screening for AlB$_4$H$_{11}$, but found no effective catalysts so far.
  • Structure information will provide more insights into hydrogen interaction mechanisms and clues for catalyst exploration.

• **AlB$_6$H$_{13}$:**
  • We finally synthesized this compound for the first time since the 1981 Himpsl and Bond paper.
  • IR consistent with Himpsl and Bond data
  • DSC similar to that of AlB$_4$H$_{11}$.
  • Large amount of B$_2$H$_6$ found by TGA-MS.
  • Probably not a good candidate for reversible hydrogen storage.
Summary (continued)

**NaB₃H₈**:  
- Safe (B₂H₆ and BF₃ free) synthesis developed for NaB₃H₈.  
- Thermal desorption gives of large amount of borane species.  
- Uns suited for reversible onboard hydrogen storage.  
- Hydrolysis produces high wt.% (10.5) pure H₂, Better than NaBH₄ (7.5 wt.% H) and NH₃BH₃ (5.1 wt.% H)  
- High solubility and good stability in H₂O.  
- Cobalt-based catalyst effective for hydrolysis.

**NH₄B₃H₈**:  
- Thermal decomposition exothermic and gives of a significant amount of borane species – not suited for reversible H₂ storage.  
- Hydrolysis produces high wt.% (7.5 wt.%) pure H₂.  
- High solubility and good stability in H₂O.  
- Cobalt-based catalyst effective for hydrolysis.  
- Better than NaBH₄ and NH₃BH₃ for hydrolysis.
Future Work

**FY11**

- Compete the structure identification of AlB$_4$H$_{11}$.
- Based on structural information, study the hydrogen absorption and desorption mechanisms.
- Based on structure and mechanisms, perform screening of catalysts for improved reversibility.
- Provide property data to DOE Hydrogen Storage Engineering Center.
- Write a final report.
Collaborations

• Strong collaborations among OSU, Northwestern and NIST are crucial for the identification of the AlB$_4$H$_{11}$ structure.
• ORNL and OSU collaborate on synthesis and characterization of both AlB$_4$B$_{11}$ and AlB$_6$H$_{13}$. Samples were analyzed at OSU, ORNL, JPL and Caltech for hydrogen desorption and structures (via NMR).
• AlB$_4$H$_{11}$ synthesized at OSU was sent to NIST for neutron analysis.
• Mg(BH$_4$)$_2$ and Li$_2$B$_{12}$H$_{12}$ synthesized at OSU was provided to UTRC and HRL for nano-framework encapsulations.
• Mg(BH$_4$)$_2$ synthesized at OSU was sent to University of Washington for solid state NMR analysis and to NIST for TEM analysis.
• Several compounds synthesized at OSU were sent to Sandia for analysis using STMBS (simultaneous thermogravimetric modulated beam mass spectrometry).
• (NH$_4$)$_2$B$_{12}$H$_{12}$ synthesized at OSU was sent to Ford for further study.
• Initiated collaboration with Kyushu University for NOVA analysis of AlB$_4$D$_{11}$. 
A close collaboration among OSU, Northwestern, NIST and ORNL led to the progress.