Lightweight Intermetallics for Hydrogen Storage

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GE Global Research

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– A Member of the DOE Metal Hydride Center of Excellence –
Program Overview

Timeline
• Project start date: FY05
• Project end date: FY09
• Percent complete: 60%

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

Budget
• Total Project Funding: $3.47M
  – DOE Share: $2.78M
  – GE & OSU Share: $0.69M
• Funding Received for FY07
  $430K (DOE), $115K (GE)

Partners/Collaborations
• Member of DOE MHCoE
## Objectives

<table>
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<th>Overall</th>
<th>Discover and develop a high capacity (&gt; 6 wt.%%) lightweight hydride capable of meeting or exceeding the 2010 DOE/FreedomCAR targets.</th>
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</table>
| FY05    | • Develop a combinatorial synthesis and high-throughput screening methodology for metal hydride discovery  
          • Identify hydrides from combinatorial samples and validate them through gram-quantity sample tests |
| FY06    | • Identify the crystal structures of Mg(BH$_4$)$_2$ using XRD, neutron diffraction and computer modeling  
          • Perform combinatorial and computational screening of catalysts and dopants for Mg(BH$_4$)$_2$ |
| FY07    | • Perform combinatorial and computational screening of catalysts, dopants and complexes for Mg(BH$_4$)$_2$  
          • Explore ways to make the materials reversible |
| FY08    | • Study the desorption mechanism and explore ways to make the Mg(BH$_4$)$_2$ reversible  
          • Explore new hydride materials |
Approach

• Study the crystal structures and the decomposition mechanisms using multiple techniques such as in-situ XRD, interrupted PCT tests, boron NMR, IR, DSC, and residual gas analysis;
• Develop reversibility strategy from detailed mechanistic understanding of the complex desorption processes;
• Synthesize new hydrides and complexes.
Mechanistic Understanding: Combined In-situ XRD and gas analysis

Sample holder
- Gas inlet
- Sapphire capillary
- Heating coils
- Thermocouple
- Gas outlet to RGA
- Slide to open

max T: 450 °C  max P: 2000 psi

Image plate readout

Integrated diffraction pattern (phases & crystal structure)

Time resolved patterns (reaction pathway)

Diffraction setup
- 2D Image Plate
- Sample cell

RGA (gas analysis)

nsLS
IR UV X

Brookhaven National Laboratory
Mg(BH$_4$)$_2$ – Hydrogen Desorption (XRD)

**Complex hydrogen desorption pathway**

- **Mg + B$^*$**
- **MgH$_2$ + B$^*$**
- **Amorphous$^*$ + B$^*$**

**Reaction Stages**
- **HT Mg(BH$_4$)$_2$**
- **LT Mg(BH$_4$)$_2$**

**Temperature (°C)**
- 180 °C
- 290 °C
- 350 °C
- 380 °C

**Heat flow (W/g)**

**2θ angle (°)**
Mg(BH$_4$)$_2$ – Hydrogen Desorption (MS)
Mg(BH$_4$)$_2$ Desorption (NMR)

Mg(BH$_4$)$_2$ $\rightarrow$ Intermediate $\rightarrow$ MgH$_2$ + 2B + 3H$_2$

Released hydrogen (wt %; TPD)

MgH$_2$ $\leftrightarrow$ Mg + H$_2$

Mg(BH$_4$)$_2$ $\rightarrow$ “amorphous phase” + H$_2$

$\rightarrow$ crystalline MgH$_2$ + “amorphous boron”

$\rightarrow$ Mg + “amorphous boron” + H$_2$

Mg(BH$_4$)$_2$ Desorption

Much clearer understanding of the complex desorption process achieved.
NH₃ Complexes of Metal Borohydrides

- NH₃ complexes of several metal borohydrides synthesized.
- Aluminum and zinc borohydrides have low H₂ desorption T.
- Reversibility unexplored yet.

\[
\text{MCl}_n + 2+n \text{ LiBH}_4 \xrightarrow{\text{Et}_2\text{O}} \text{Li}_2\text{Mg(BH}_4)_2 \xrightarrow{\text{NH}_3\text{}} \text{M(BH}_4)_n\cdot6\text{NH}_3 + 2 \text{ LiBH}_4
\]

\[
\begin{align*}
\text{M(BH}_4)_n\cdot2\text{NH}_3 & \quad \text{wt % H}_2 \\
\text{Mg(BH}_4)_2\cdot2\text{NH}_3 & \quad 16.0 \\
\text{Zn(BH}_4)_2\cdot2\text{NH}_3 & \quad 10.9 \\
\text{Al(BH}_4)_3\cdot2\text{NH}_3 & \quad 17.1 \\
\text{Ti(BH}_4)_3\cdot2\text{NH}_3 & \quad 14.3
\end{align*}
\]

- Al B.001—
- Al A.001–
- Zn A.001—
- Zn B.001–

Exo Up Universal V4.1D TA Instruments

160 °C

150 °C
NH₃ Complexes of Metal Borohydrides

• NH₃ complexes may be a very effective way to fine-tune the thermodynamics of borohydrides:
  • Reduction of desorption temperature ($T_{\text{des}}$) when the borohydride $T_{\text{des}}$ is high, e.g. reduce the $T_{\text{des}}$ of Mg(BH₄)₂ from 290°C to ~ 100°C in Mg(BH₄)₂(NH₃)₂.
  • Increase $T_{\text{des}}$ of several borohydrides when their $T_{\text{des}}$ is low (too unstable), e.g. increase the $T_{\text{des}}$ of Al(BH₄)₃ and Zn(BH₄)₂ to ~ 150-160°C
• Need to understand the mechanism to take full advantage of this tunability.
• Ammonia formation may be a concern.
• Need more work to explore reversibility of such complexes.
Summary

• Gained significant better understanding of the desorption process of Mg(BH$_4$)$_2$ in collaboration with JPL/Caltech using five independent techniques.
• Discovered the formation of an amorphous MgB$_{12}$H$_{12}$ intermediate phase.
• Discovered reversible behavior at about 300°C and 100 bar H$_2$ pressure from Mg(BH$_4$)$_2$ to Mg(BH$_4$)$_{2-x}$ during the initial decomposition process of Mg(BH$_4$)$_2$.
• Synthesized NH$_3$ complexes of several borohydrides and found favorable tunability of their desorption temperatures,
• Recommend to explore reversible hydrogen storage via (Li,Na,Mg,K,Ca)$_x$B$_{12}$H$_{12}$ $\leftrightarrow$ (Li,Na,Mg,K,Ca)(BH$_4$)$_x$. 
Future Work

**FY08**

- Borane & high P reversibility experiments
- Synthesis of single-phase $\text{MB}_{12}\text{H}_{12}$ phase for mechanism and structure study ($M = \text{Li, Mg, and Ca}$)
- Synthesize other complexes of $(\text{Mg,Ca})(\text{BH}_4)_2$

**FY09**

- Synthesize $\text{Mg(BH}_4)(\text{AlH}_4)$ & other $\text{Mg(BH}_4)_2$ complexes to improve desorption temperature, reversibility & kinetics
- Explore new classes of materials in collaboration with ORNL, Sandia, U. Utah, and JPL/Caltech
- Continue mechanistic work for improving reversibility