Program Overview

Timeline

• Project start date: FY05
• Project end date: FY09
• Percent complete: 40%

Budget

• Total Project Funding: $3.47M
  – DOE Share: $2.78M
  – GE Share: $0.69M
• Funding Received for FY06
  $450K (DOE), $112K (GE)
• Funding Received for FY07
  $375K (DOE), $100K (GE)

Barriers

• Right heat of formation
• Absorption / desorption kinetics
• Reversibility for borohydrides

Partners/Collaborations

• Member of DOE MHCoE
• Collaborations with ORNL, JPL, Caltech, UIUC, CMU, U. Pitt, SNL, Univ. Nevada
### Objectives

<table>
<thead>
<tr>
<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(BH₄)₂ using XRD, neutron diffraction and computer modeling  
          • Perform combinatorial and computational screening of catalysts and dopants for Mg(BH₄)₂ |
| FY07    | • Perform combinatorial and computational screening of catalysts, dopants and complexes for Mg(BH₄)₂  
          • Explore ways to make the materials reversible |
Approach

High-throughput screening (HTS) & mechanistic understanding are important parts of GE’s methodology.

GE downselected Mg(BH₄)₂ family borohydrides for further exploration.
Mg(BH$_4$)$_2$ Desorption

Mg(BH$_4$)$_2$ (14.8 wt.% H theoretical)

**Mg(BH$_4$)$_2$**

- **Released hydrogen (wt %; TPD)**
- **Temperature (°C)**
- **2θ angle (°)**
- **RGA Signal (mTorr)**

- **380°C**
  - Crystalline MgH$_2$

- **350°C**
  - “Amorphous” MgH$_2$

- **295°C**
  - Mg

- **HT Mg(BH$_4$)$_2$**

**Pattern Number**

- **0**
- **2**
- **4**
- **6**
- **8**
- **10**
- **12**

**Temperature (°C)**

- **0**
- **100**
- **200**
- **300**
- **400**
- **500**

**2θ angle (°)**

- **0**
- **5**
- **10**
- **15**
- **20**
- **25**
- **30**

**RGA Signal (mTorr)**

- **0**
- **1x10^-8**
- **1x10^-7**
- **1x10^-6**
- **1x10^-5**
- **1x10^-4**

- **Mg**
- **B$_2$H$_6$ & N$_2$$^\uparrow$
- **BH$_3$ & N$$^\uparrow$
- **O$_2$$^\uparrow$
- **H$$^\uparrow$
- **H$_2$$^\uparrow$
- **He$$^\uparrow$
Mg(BH$_4$)$_2$ Desorption

\[ \text{Mg}\]  

Complimentary data from 4 types of experiments

\[ \text{Mg(BH}_4\text{)}_2 \rightarrow \text{“amorphous MgH}_2\text{” + “amorphous boron” + H}_2 \]
\[ \rightarrow \text{crystalline MgH}_2 + \text{“amorphous boron”} \]
\[ \rightarrow \text{Mg + “amorphous boron” + H}_2 \]
Mg(BH$_4$)$_2$: Initial NMR Measurements

Samples: GE-103: Mg(BH$_4$)$_2$  GE103D: desorbed Mg(BH$_4$)$_2$

- Certainly remarkable structural change around boron elements is observed via $^{11}$B MAS NMR.
- The $^{11}$B peak for Mg(BH$_4$)$_2$ is very close to that for LiBH$_4$ (i.e., with similar BH$_4^-$ ion environments).
- The desorbed sample shows the formation of “amorphous” boron & some MgB$_2$ (peak at ~100 ppm).
- The quantity of MgB$_2$ is minor in GE-103D & seems to be absent in GE-103, which is only Mg(BH$_4$)$_2$.
- $^{11}$B CPMAS NMR with protons on GE-103D indicated that the main peak at ~ 0 ppm is protonated, suggesting formation of amorphous boron with some H attachment. More study underway.
- The full widths of the $^{11}$B for GE-103 and GE-103D are very different & also different from reference amorphous boron. This reflects significant differences in the quadrupolar interactions for this nucleus - giving us another tool to extract information on the local structure and bonding parameters.

Measurements performed by Sonjong Hwang and Bob Bowman
Mg(BH$_4$)$_2$: Crystal Structures & Decomposition

Crystal structure transition at 185°C

MgH$_2$

300 °C

HT Mg(BH$_4$)$_2$

185 °C

LT Mg(BH$_4$)$_2$

80 °C

Partially Solvated Mg(BH$_4$)$_2$

Temperature (°C)

0 100 200 300 400

Pattern Number

0 5 10 15 20 25 30 35

Pattern Number

0 5 10 15 20 25 30 35

2θ angle (°)

100 200 300 400

RGA Signal (mTorr)

1x10$^{-8}$ 1x10$^{-7}$ 1x10$^{-6}$ 1x10$^{-5}$ 1x10$^{-4}$

Metals and Hydrides Center of Excellence

imagination at work

BROOKHAVEN NATIONAL LABORATORY
Mg(BH₄)₂ LT structure

LT Mg(BH₄)₂
- Hexagonal – P6₁
- a = 10 Å, b = 10 Å, c = 37 Å
- V = 3435 Å³;  Z = 30
- Density = 0.785 calc

The fit of experimental and calculated powder diffraction data by Rietveld refinement for the LT Mg(BH₄)₂ phase. The high-angle data are enlarged 5x for clarity.

Hexagonal, corner-shared Mg(BH₄)₄ tetrahedrons (Mg: center, BH₄: vertex).
Tetrahedral BH₄ (B: center, H: vertex). B-H bond length: 1.12 Å. Mg-B bond lengths: 2.34 -2.47 Å. Mg is bonded to 8 H.

Crystal structure ID is essential for computational screening of dopants

In collaboration with J.H. Her and P. Stephens at SUNY Stony Brook
Mg(BH₄)₂ HT structure

HT Mg(BH₄)₂
- Orthorhombic – Fddd
- $a = 37$ Å, $b = 18.5$ Å, $c = 11$ Å
- $V = 7550$ Å³; $Z = 64$
- Density = 0.7 meas.; 0.76 calc

The fit of experimental and calculated powder diffraction data by Rietveld refinement for the HT Mg(BH₄)₂ phase. The high-angle data are enlarged 8x for clarity.

In collaboration with J.H. Her and P. Stephens at SUNY Stony Brook

Orthorhombic, corner-shared Mg(BH₄)₄ tetrahedrons (Mg: center, BH₄: vertex). The BH₄ unit is also tetrahedral (B: center, H: vertex). B-H bond length: 1.14 Å. Mg-B bond lengths: 2.34 - 2.47 Å. Mg is bonded to 8-12 H.
Mg(BH$_4$)$_2$: Catalyst Screening Results

- Catalyst screening performed for many compositions
- The catalyst precursors Ti(BH$_4$)$_3$, CpTi(BH$_4$)$_2$, Cp$_2$TiBH$_4$ and Cp$_2$ZrBH$_4$ reduce Mg(BH$_4$)$_2$ decomposition temperature by up to 50 °C
- No catalyst found yet to enable MgH$_2$ + 2B + 4H$_2$ $\rightarrow$ Mg(BH$_4$)$_2$ reaction
Mg(BH$_4$)$_2$: Vapor Pressure

\[ \text{Mg(BH}_4\text{)}_2(s) \rightarrow \text{Mg(BH}_4\text{)}_2(g) + \text{H}_2 \]

\( \Delta H^\circ = 93.3 \text{ kJ/mol} \)

\[ p_{\text{H}_2} = 0.977 p_{\text{Total}} \]

\[ \ln P_T(Pa)_{\text{Mg(BH}_4\text{)}_2} = \frac{-11.23 \times 10^3}{T(K)} + 18.385 \]

\[ p_{\text{Mg(BH}_4\text{)}_2} = 0.023 p_{\text{Total}} \]

Summary

- No detrimental cations effusing out – stable
- Low Vapor pressures observed up to \(~250^\circ\text{C}\)
- \(~98%\) of Pressure is due hydrogen evolution
- \( P_{\text{H}_2(225^\circ\text{C})} = 8.8 \times 10^{-6} \text{ atm} \) (\(8.8 \times 10^{-1} \text{ Pa}\))
- \( P_{\text{Mg(BH}_4\text{)}_2} = 2.03 \times 10^{-7} \text{ atm} \) (\(225^\circ\text{C}\)) (\(2 \times 10^{-2} \text{ Pa}\))
- Measured Average MW: 2.42 g/mol of effusing gas between 25°C and 250°C

Cleanest borohydride tested for vapor pressure
Mg(BH$_4$)$_2$(NH$_3$)$_2$: orthorhombic ($Pcab$; $a = 17.487\text{Å}$, $b = 9.413\text{Å}$, $c = 8.732\text{Å}$). It consists of isolated tetrahedra of Mg(BH$_4$)$_2$(NH$_3$)$_2$. The tetrahedra are weakly connected via B-H---H-N “hydrogen” bonds to form three-dimensional network.

- 16 wt% H theoretical
- Complexes to reduce the $T_{des}$
Mg(BH₄)₂(NH₃)₂ Desorption

- Onset @ 80-90 °C

Volumetric measurements

- 10 wt.% H released by 225°C, 13 wt.% total, 16 wt.% theoretical
- Assumes H₂ is only gas released
- Only partially reversible – see slide 16
• Significant NH\textsubscript{3} observed with some BH\textsubscript{3} / B\textsubscript{2}H\textsubscript{6}.
• Decomposition product liquid $\rightarrow$ amorphous $\rightarrow$ Mg.
Mg(BH$_4$)$_2$(NH$_3$)$_2$: partial recharging?

- No change seen in XRD – most phases amorphous
- Recharging beyond Mg to MgH$_2$, but not fully reversible

60 bar initial pressure
Mg(BH₄)(AlH₄): Synthesis & Decomposition

2 MgCl₂ + LiAlH₄ + LiBH₄ $\xrightarrow{\text{Et}_2\text{O}}$ Mg(BH₄)(AlH₄) + Li₂MgCl₄

- Substantial decrease in $T_{\text{des}}$ comparing to Mg(BH₄)₂
- Low wt. % hydrogen due to the presence of Li₂MgCl₄

Assume pure Mg(BH₄)(AlH₄)

Attractive desorption temperature & capacity (11.4 wt.% H theoretical)
Summary: Status vs DOE Targets

- **DOE 2010 Goal**
- **DOE 2015 Goal**

**Hydrogen storage capacity (wt % H)**

- Assume 1/3 for balance of plant

**Temperature (°C)**

- **Mg(BH₄)₂(NH₃)₂** (theoretical)
- **Mg(BH₄)₂**

**Mg(BH₄)(AlH₄) (pure)**

**AIH₃**

**2LiBH₄ + MgH₂**

**Catalyzed Mg(BH₄)₂(NH₃)₂**

**Catalyzed Mg(BH₄)₂**
Summary

• Mg(BH$_4$)$_2$ crystal structure identification accomplished – enable more realistic theoretical predictions of dopants & energistics
• Combinatorial screening found effective catalyst precursors that reduce the $T_{\text{des}}$ of Mg(BH$_4$)$_2$ by 50°C.
• Mg(BH$_4$)$_2$(NH$_3$)$_2$ synthesized & crystal structure identified
• Catalyzed Mg(BH$_4$)$_2$(NH$_3$)$_2$ desorption starts at 80-90°C & can complete at <300°C, giving 13 wt% H (16 wt%H theoretical)
• Mg(BH$_4$)(AlH$_4$) desorption starts at ~100°C & completes at 250°C (11.2 wt%H, theoretical)
• Collaborations ongoing with MHCoE partners to explore mechanisms and ways to reversibility
Future Work

**FY07**

- Combinatorial screening of dopants and catalysts for Mg(BH$_4$)$_2$(NH$_3$)$_2$, Mg(BH$_4$)(AlH$_4$), & Mg(BH$_4$)$_2$
- Computational predictions of dopants for these hydrides
- Borane & high P reversibility experiments
- Mechanistic understanding for reversibility clues
- Go/No-Go for Mg(BH$_4$)$_2$

**FY08**

- Continue on catalyst and doping study of Mg(BH$_4$)$_2$(NH$_3$)$_2$, Mg(BH$_4$)(AlH$_4$), & Mg(BH$_4$)$_2$ to improve reversibility & kinetics
- Perform system-level evaluation of properties such as cycling stability/degradation, thermal conductivity
- Go/No-Go for Mg(BH$_4$)$_2$(NH$_3$)$_2$ & Mg(BH$_4$)(AlH$_4$) reversibility: < 400°C & < 200 bar