Development of Magnesium Boride Etherates as Hydrogen Storage Materials

Dr. G. Severa (PI) and Prof. C. M. Jensen (Co-PI)

University of Hawaii at Manoa

DOE Annual Merit Review June 5-9, 2017
Overview

Timeline and Budget

- Project Start Date: 10/01/2016
- Project End Date: 09/31/2019
- Percent Completion: 16%

Barriers

<table>
<thead>
<tr>
<th>Barrier</th>
<th>Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low System Gravimetric capacity</td>
<td>&gt; 7 wt% H₂ system</td>
</tr>
<tr>
<td>Low System volumetric capacity</td>
<td>&gt; 40 g/L system</td>
</tr>
<tr>
<td>Low System fill times</td>
<td>1.5 kg hydrogen/minute</td>
</tr>
</tbody>
</table>

Partners

- HyMARC Consortium
  - SNL: High Pressure Hydrogenation
  - SNL: Surface Characterizations
  - LLBL & LLNL: Theoretical Modelling

Timeline and Budget

- Total Project Budget FY17-FY19: $1,204,366
- Total Project Budget FY 17: $270,878
- Total Recipient Share FY 17: $27,086
- Total Federal Share FY17: $243,792
- Expended DOE Funds FY: $49,761.59 as of 3/31/17
Objective: Synthesize and Characterize Magnesium Boride Etherates Hydrogen Storage Materials Capable of Meeting DOE 2020 Targets.

- Demonstrate ≥ 7.0 wt % hydrogen uptake by a MgB₂ etherate at ≤ 300 °C, 700 bars 48 hrs and reversible release of ≥ 2 wt% H₂ by at least one MgB₂ etherate.

### RELEVANCE

<table>
<thead>
<tr>
<th>Storage Parameter</th>
<th>Units</th>
<th>2020 Target</th>
<th>Ultimate Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low System Gravimetric capacity</td>
<td>kg H₂/kg system</td>
<td>0.055</td>
<td>0.075</td>
</tr>
<tr>
<td>System volumetric capacity</td>
<td>kg H₂/L system</td>
<td>0.040</td>
<td>0.070</td>
</tr>
<tr>
<td>System fill times (5 kg)</td>
<td>kg H₂/min</td>
<td>1.5</td>
<td>2.0</td>
</tr>
<tr>
<td>Min Delivery Pressure</td>
<td>bar</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>Operational cycle (1/4 tank to full)</td>
<td>cycles</td>
<td>1500</td>
<td>1500</td>
</tr>
</tbody>
</table>

RELEVANCE: Recent Advances in Mg(BH$_4$)$_2$ Research

- Recent improvements in magnesium borohydride research.

<table>
<thead>
<tr>
<th>Hydrogenation Product</th>
<th>Dehydrogenation Product</th>
<th>Hydrogenation</th>
<th>Dehydrogenation</th>
<th>Cycling wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temp °C</td>
<td>P atm</td>
<td>time h</td>
<td>Temp °C</td>
</tr>
<tr>
<td>MgB$_2$ (HP)</td>
<td>&gt;400</td>
<td>&gt;900</td>
<td>108</td>
<td>530</td>
</tr>
<tr>
<td>MgB$_2$ (reactive ball milling/HT-HP)</td>
<td>/400</td>
<td>10/400</td>
<td>10/24</td>
<td>390</td>
</tr>
<tr>
<td>Mg$<em>{0.75}$Mn$</em>{0.25}$B$_2$</td>
<td>380</td>
<td>150</td>
<td>38</td>
<td>225-400</td>
</tr>
<tr>
<td>Mg(B$_3$H$_8$)$_2$(THF)$_x$/2MgH$_2$</td>
<td>200</td>
<td>50</td>
<td>2</td>
<td>180</td>
</tr>
<tr>
<td>Mg(B$_3$H$_8$)$_2$/2MgH$_2$</td>
<td>250</td>
<td>120</td>
<td>48</td>
<td>250</td>
</tr>
<tr>
<td>Mg(B$<em>{10}$H$</em>{10}$)$_2$(THF)$_x$/4MgH$_2$/X</td>
<td>200</td>
<td>50</td>
<td>2</td>
<td>200</td>
</tr>
</tbody>
</table>

Mg(BH$_4$)$_2$ ammoniates
- Improved kinetics on dehydrogenation even though, NH$_3$, very stable BN products formed.

Current state-of-the-art:
- Better H$_2$ cycling kinetics (lower pressures and temperatures).
- Lower gravimetric H$_2$ storage capacity.

Mg(BH$_4$)$_2$ and Mg borane etherates
- Improved H$_2$ cycling kinetics on ether coordination, lower H$_2$ capacity.
- Strong coordination of ethers to magnesium at high temp.

Efforts show plausibility of greatly enhancing kinetics of Mg borohydride materials.

Relevance: Potential for Practical Hydrogen Storage Properties

\[
\text{MgB}_2(\text{ether})_x \rightarrow \text{Mg(BH}_4\text{)}_2(\text{ether})_x
\]

<table>
<thead>
<tr>
<th>Mols ether/ Mol MgB₂ (x)</th>
<th>0.70</th>
<th>0.40</th>
<th>0.20</th>
<th>0.10</th>
<th>0.05</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt % Hydrogen</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgB₂(OMe₂)x</td>
<td>9.4</td>
<td>11.1</td>
<td>12.8</td>
<td>13.8</td>
<td>14.3</td>
</tr>
<tr>
<td>MgB₂(THF)x</td>
<td>7.7</td>
<td>9.7</td>
<td>11.8</td>
<td>13.2</td>
<td>14.0</td>
</tr>
<tr>
<td>MgB₂(OCH₂Me₂)x</td>
<td>7.6</td>
<td>9.6</td>
<td>11.7</td>
<td>13.1</td>
<td>14.0</td>
</tr>
<tr>
<td>MgB₂(Dioxane)x</td>
<td>7.0</td>
<td>9.0</td>
<td>11.3</td>
<td>12.8</td>
<td>13.8</td>
</tr>
<tr>
<td>MgB₂(polyether)x</td>
<td>&gt;12</td>
<td>&gt;12</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Lower hydrogenation temperature.
- Lower hydrogenation pressure.
- Increase hydrogen sorption rates.
- Increase amount of cyclable H₂ at moderate temp and pressure.

Potential to improve practical hydrogen storage properties of MgB₂/Mg(BH₄)₂ system.
APPROACH: Synthesize, Characterize and Hydrogenate MgB₂ Etherate Materials

A. Synthesis of MgB₂ etherates by reactive ball milling and heat treatments from:
   1. Mg borane etherates
   2. MgB₂, in presence of ethers.

B. Hydrogenation reactions:
   UH: ≤ 150 bars, ≤ 300 °C and HyMARC-SNL: ≤1000 bars, ≤ 400 °C, ≤ 72 hrs.

C. Characterizations:
   FTIR, TGA-DSC, XRD, ¹¹B and ¹H NMR, TPD-Mass Spec, X-Ray Scattering, TEM, SEM.

D. Theoretical Studies:
   HyMARC: LLBL and LLNL

<table>
<thead>
<tr>
<th>Milestone #</th>
<th>Project Milestones</th>
<th>Quarter</th>
<th>Accomplished</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Development of synthesis for MgB₂ etherates</td>
<td>1</td>
<td>95%</td>
</tr>
<tr>
<td>3.1</td>
<td>Characterize MgB₂ etherate by FTIR, ¹¹B and ¹H NMR, XRD.</td>
<td>2</td>
<td>65%</td>
</tr>
<tr>
<td>4.1</td>
<td>Demonstrate hydrogenation MgB₂ etherate to Mg(BH₄)₂ etherate.</td>
<td>3</td>
<td>50%</td>
</tr>
<tr>
<td>5.1</td>
<td>Demonstrate uptake of ≥7 wt H₂ by a MgB₂ etherate at 300°C.</td>
<td>4</td>
<td>20%</td>
</tr>
<tr>
<td>6.1</td>
<td>Dehydrogenation of one hydrogenated MgB₂ etherate</td>
<td>4</td>
<td>10%</td>
</tr>
</tbody>
</table>

Go/No-Go Decision: Demonstrate ≥7.0 wt % hydrogen uptake by a MgB₂ etherate at ≤300 °C, 700 bars 48 hrs and reversible release of ≥ 2 wt% H₂ by at least one MgB₂ etherate.
Synthesis Approach 1: Synthesis from Mg Borane Etherate

1. Syntheses of MgB$_2$ Etherates from Dehydrogenation of Mg Borane Etherates

- Synthesis from Mg borane etherates and MgH$_2$
  \[ \text{Mg(B}_x\text{H}_y\text{)}_z\text{X}_g + \text{MgH}_2 \quad (X = \text{Ether}) \]

- Synthesis from Mg borane etherates and other metal hydrides
  \[ \text{Mg(B}_x\text{H}_y\text{)}_g\text{X}_z + \text{MH}_2 \quad (M= \text{LiH, NaH}) \]

<table>
<thead>
<tr>
<th>Dehydrogenation in presence or absence of free ether</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Heat Treatment Under Pressure</td>
</tr>
<tr>
<td>• Ball Milling Pretreatment followed by Heat Treatment Under pressure</td>
</tr>
<tr>
<td>• Ball Milling Pretreatment in ether followed by Heat Treatment Under pressure</td>
</tr>
</tbody>
</table>

Confirm ether coordination by: FTIR, TGA-DSC, XRD, $^{11}$B and $^1$H NMR, TPD-Mass Spec.

Multiple approaches to MgB$_2$ etherates Syntheses
2. Syntheses of MgB₂ Etherates from MgB₂ or its Precursors and Ethers.

a. Synthesis from MgB₂
   - MgB₂ + Ether
   - MgB₂₋ₓYₓ/Mg₁₋ₓB₂Yₓ + Ether; Y=LiH, NaH, Al or transition metal.

b. Synthesis from other MgB₂ precursors
   - MgH₂/Mg + 2B, in presence of ethers

<table>
<thead>
<tr>
<th>Synthesis Approach (in presence of ether)</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Heat Treatment Under Pressure</td>
</tr>
<tr>
<td>• Ball Milling Pretreatment followed by Heat Treatment Under Pressure</td>
</tr>
<tr>
<td>• Ball Milling Pretreatment in Ether followed by Heat Treatment Under Pressure</td>
</tr>
<tr>
<td>• Ball Milling Pretreatment followed by Ultra sonication</td>
</tr>
</tbody>
</table>

Characterization: Confirm ether incorporation by: FTIR, TGA-DSC, XRD, NMR, Mass Spec.

Multiple approaches to MgB₂ etherates Synthesis
Approach: Molecular Dynamic Simulations

**Ab initio** molecular dynamics for chemistry and coordination analysis

Direct simulation of solute-solvent interactions, investigation of formation and/or dissociation of chemical bonds, charge transfer

**Classical + Quantum mechanics** for environment-dependent thermodynamics

Recipes for integrating different levels of theory for the solid/solvent interfaces, Analysis of materials stability depending on particle size and solvent environment

Reactive Quantum Molecular Dynamics Simulations of MgB$_x$H$_y$ in Etherate Liquid

IR Simulations to identify coordinating species.
Stability and reactivity of MgB₂ surfaces in THF

MgB₂-THF interface simulated in classical + quantum mechanics and ab initio molecular dynamics

Change in MgB₂ surface energies by contacting with THF

\[ \Delta \gamma = \gamma_{\text{THF}} - \gamma_{\text{vacuum}} \]

<table>
<thead>
<tr>
<th>(0001) basal</th>
<th>( \Delta \gamma ) (eV/Å²)</th>
<th>(10-10) edge</th>
<th>( \Delta \gamma ) (eV/Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg-terminated</td>
<td>−0.23</td>
<td>Mg-edges</td>
<td>−0.19</td>
</tr>
<tr>
<td>B-terminated</td>
<td>−0.20</td>
<td>B-edges</td>
<td>−0.15</td>
</tr>
</tbody>
</table>

Interaction with THF stabilizes MgB₂ surfaces, especially for Mg-exposed surfaces

Explicit observation of bond formation between MgB₂ and THF
1. MgB$_2$ Etherate from Mg Borane Etherate: **Synthesis from Mg Triborane THF**

$$2\text{MgB}_3\text{H}_8(\text{THF})_2 + \text{MgH}_2 \xrightarrow{\text{THF}} 3\text{MgB}_2(\text{THF})_x + 9\text{H}_2$$

**Characterization of synthesized product**

- **FT-ATR**: No B-H stretches.
- **Presence of MgO and THF**

**$^{11}$B Solution NMR in D$_2$O** indicates no soluble boron species.

*Confirming absence of Mg borane etherates.*

- **Weight loss at 80-400 °C** indicate release of strongly coordinated species (e.g. THF or H$_2$).

- **Heat treated MgB$_3$H$_8$(THF)$_x$/MgH$_2$**

- **XRD**: Preliminary XRD indicate mostly MgO and broad peak? at $\sim$20°

**Integrity and Mass Spec:**

- **Direct confirmation of strongly coordinated THF** to be performed by TPD Mass Spec.
Accomplishments and Progress

2. MgB₂ Etherates Syntheses from MgB₂

A. Synthesis By Heat Treatment

Characterization of synthesized products

\[
\text{MgB}_2 + xX \xrightarrow{\leq 300 \, ^\circ\text{C}} \xrightarrow{\leq 24 \, \text{h}} \text{MgB}_2(X)_x
\]

X= THF, Tetruglyme (TG), Dioxane

**All Samples:** MgB₂ and some MgO.
**MgB₂-tetraglyme:** Decreased MgB₂ peak intensity and amorphous phase?

XRD and TGA indicates reactivity of ethers with Mg boride.
Accomplishments and Progress

2. MgB$_2$ Etherates Syntheses from MgB$_2$

B. Synthesis By Ball Milling Approach

Characterization of synthesized products.

- MgB$_2$ peaks decrease for THF and Triglyme samples.
  - Ether role in decreasing MgB$_2$ crystallinity.
- Products different from heat treated synthesis.

XRD of pure MgB$_2$ ball milled (BM) 5hrs; MgB$_2$-ether samples BM total of 9 hrs, including 4 hrs with ethers.

NMR, XRD and FTATR inconclusive in directly confirming presence of sub-stoichiometric amounts of ether.
Accomplishments and Progress

Hydriding of MgB₂ Etherates Synthesized by Ball Milling Approach

Currently Ball Milled MgB₂-THF shows greatest promise at 300 oC hydrogenations.

\[
\text{MgB}_2(\text{THF})_x + \text{H}_2 \quad \xrightarrow{1000 \text{ bar}} \quad \xrightarrow{300 \text{ oC, 72 hrs}} \quad \text{Magnesium borohydride species}
\]

Preliminary TGA analysis of hydrogenated ball milled MgB₂-THF indicates significant weight loss (~4.9 wt %) at 300 oC.

No indication of hydrogenation observed with ball milled MgB₂-tetraglyme and MgB₂-triglyme samples at 300 oC from XRD and IR.

Preliminary hydrogenations confirm for the FIRST TIME formation significant amounts of β-Mg(BH₄)₂ at 300 oC!
Accomplishments and Progress

Hydriding of MgB$_2$ Etherates Synthesized by Ball Milling Approach

Currently Ball Milled MgB$_2$-THF shows greatest promise at 300 °C hydrogenations.

\[
\text{MgB}_2(\text{THF})_x + \text{H}_2 \overset{1000 \text{ bar}}{\underset{300 \text{ °C}, 72 \text{ hrs}}{\longrightarrow}} \text{Magnesium borohydride species}
\]

XRD of hydrogenated ball milled samples: MgB$_2$ and MgB$_2$-THF confirming $\beta$-Mg(BH$_4$)$_2$ formation at 300 °C.

FTIR and XRD of hydrogenated material confirm $\beta$-Mg(BH$_4$)$_2$ synthesis at 300 °C!
Accomplishments and Progress

Hydriding of MgB$_2$ Etherates Synthesized by Ball Milling Approach

Currently Ball Milled MgB$_2$-THF shows greatest promise at 300 °C hydrogenations.

\[
\text{MgB}_2(\text{THF})_x + \text{H}_2 \xrightarrow{1000 \text{ bar}} \xrightarrow{300 \text{ °C, 72 hrs}} \text{MgB}_2 - \text{THF hydrided at 300 °C}
\]

$^{11}$B NMR in D$_2$O/THF indicates mostly $\beta$-Mg(BH$_4$)$_2$
Remaining Challenges and Barriers

- Optimization of hydrogenation to 700 bar at 300 °C with ≥7 wt% H₂ uptake.

- Complete characterization of boride etherates.

- Understanding mechanism of hydrogenation enhancement by ethers, especially THF.
**Proposed Future Work**

**FY 2017**
- **Syntheses:**
  - Continue optimizing synthesis of magnesium boride etherates.
  - Emphasis on MgB$_2$-THF system.
- **Characterizations:**
  - Characterizations of synthesized and hydrogenated MgB$_2$ etherates by various techniques e.g. XRD, FTIR, NMR, TGA-DSC, TEM and TPD-Mass spec.
- **Hydrogenation of Mg boride etherates to Mg borohydride etherates:**
  - Variable pressure and variable time studies
    - Demonstrate hydrogen uptake of 7 wt% at 300 °C.
    - Demonstrate H$_2$ uptake at 700 bar and 48 hrs, maintaining 7 wt% H$_2$ at 300 °C.
- **Computational:**
  - Size-dependent stability and morphology of MgB$_2$ clusters + particles
  - Coordination analysis of solutions and solvent-dependence of stability

**FY 2018**
- Hydrogen cycling studies of magnesium boride etherates.
  - Confirm presence of etherates through cycling.
- Understanding mechanism of kinetic enhancement by etherates.
- Determine the factors that limit H$_2$ cycling kinetics.
  - TEM and X-ray scattering for size and morphology effects; integrate with theory.
- Optimize cycling capacity of MgB$_2$ etherates.
  - Demonstrate reversible H$_2$ uptake $\geq$8.0 wt % at $\leq$300 °C and cycling stability of MgB$_2$ etherates.

Any proposed future work is subject to change based on funding levels
Syntheses: Magnesium boride etherates have been synthesized by ball milling and heat treatment techniques.

Characterizations: Synthesis of magnesium boride etherates is being confirmed by a variety of techniques including FT-ATR, XRD, NMR and TGA-DSC.

Hydrogenations: Magnesium boride etherates were hydrided at ≤1000 bar, 300-400 °C and ≤72 hours.

The ball milled Mg boride and THF samples have best performance with significant hydriding to Mg borohydride at 300 °C!

About 4.9 % weight loss observed from the Mg boride THF hydried at 300 °C.

Characterization: Mg(BH$_4$)$_2$ syntheses confirmed by XRD, FTIR and DSC.

Theoretical Modeling: Molecular Dynamic Simulations indicate strong coordination between THF and MgB$_2$. 
## Collaborations

<table>
<thead>
<tr>
<th>Partners</th>
<th>Project Roles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sandia National Laboratories (HyMARC)</td>
<td>Collaborating with Dr. Stavila, Dr. White and Dr. Allendorf:</td>
</tr>
<tr>
<td></td>
<td>➢ High pressure hydrogenation experiments.</td>
</tr>
<tr>
<td></td>
<td>➢ Characterization of samples by XRD and TGA-DSC.</td>
</tr>
<tr>
<td>Lawrence Livermore National Laboratory</td>
<td>Collaborating with Dr. Wood and Dr. Kang:</td>
</tr>
<tr>
<td>National Laboratory (HyMARC)</td>
<td>➢ Molecular dynamic simulations of magnesium boride etherates.</td>
</tr>
<tr>
<td>Lawrence Berkeley National Laboratory</td>
<td>Collaborating with Dr. Prendergast’s Group:</td>
</tr>
<tr>
<td>National Laboratory (HyMARC)</td>
<td>➢ Reactive quantum molecular dynamics simulations of MgBₓHᵧ in etherate liquids.</td>
</tr>
<tr>
<td>National Renewable Energy Laboratory</td>
<td>Collaborating with Dr. Gennett:</td>
</tr>
<tr>
<td>National Laboratory (HySCORE)</td>
<td>➢ Temperature programmed desorption.</td>
</tr>
<tr>
<td></td>
<td>➢ Mass spec analyses of desorbed gas.</td>
</tr>
</tbody>
</table>
Acknowledgement

University of Hawaii Team
Prof. C.M. Jensen
Mr. Stephen Kim
Mr. Cody Sugai

HyMARC Consortium: Making facilities and expertise available to the Project.

NREL: Dr. Tom Gennett for assistance with TPD and Mass Spec.

PNNL: Dr. Mark Bowden for XRD of some of the samples.

EERE’s Fuel Cell Technologies Office: Funding.
Technical Back-Up Slides
Kinetic Enhancement in Mg(BH₄)₂/Mg borane System

- Ether coordination decreases hydrogenation pressure, time and temp.

A. None etherated borohydrides

\[
\begin{align*}
2 \text{H}_2 & \quad 2.7 \text{ wt}\% \\
200 ^\circ \text{C} & \\
3 \text{Mg(BH}_4)_2 & \quad \text{Mg(B}_3\text{H}_8)_2 + 2 \text{MgH}_2 \\
250 ^\circ \text{C, 48 hrs} & \quad 120 \text{ atm H}_2
\end{align*}
\]

B. Etherated borohydrides

\[
\begin{align*}
2\text{MgH}_2 + \text{Mg(B}_3\text{H}_8)_2(\text{THF})_2 & \quad 50 \text{ atm H}_2, 200 ^\circ \text{C, 2 hrs} \\
\rightarrow & \quad 3\text{Mg(BH}_4)_2(\text{THF})_x
\end{align*}
\]

- Strong coordination of THF to Mg boranes/borohydrides.
  - Enhanced hydrogen cycling kinetics
  - Lower ΔH of dehydrogenation

Motivation: High Impact of MgB$_2$ Etherates

- No studies on hydrogen storage properties of MgB$_2$, (Mg + 2B), (MgH$_2$ + 2B) coordinated with ethers.
  
  ➢ Strong, stable ether coordination up to 250 °C for THF!

- Complete studies on dehydrogenated forms of magnesium borohydride etherates.

- Towards search of novel ether coordinated MgB$_2$ for practical hydrogen storage?
2. MgB\textsubscript{2} Etherates Syntheses from MgB\textsubscript{2}

A. Synthesis By Heat Treatment

NMR shows minimum changes in $^{11}$B chemical shifts of MgB\textsubscript{2} etherate samples
2. MgB$_2$ Etherates Syntheses from MgB$_2$

**B. Synthesis By Ball Milling Approach**

Characterization of synthesized products.

- Ether stretches observed only in washed and dried glymes (MgB$_2$ triglyme and tetraglyme) samples.
- No ether peaks in THF, Dioxane and Dioxalane BM samples.
Accomplishments and Progress

Comparison of MgB\textsubscript{2}-THF BM 9hr and Pure MgB\textsubscript{2} hydrogenated Samples

![](image1)

- Pure MgB\textsubscript{2} hydrided at 400 °C
- MgB\textsubscript{2} –THF hydrided at 300 °C

11\textsuperscript{B} Solution NMR in D\textsubscript{2}O/THF