Development of Magnesium Boride Etherates as Hydrogen Storage Materials

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University of Hawaii at Manoa
DOE Hydrogen and Fuel Cells Program Annual Merit Review
April 29 – May 1, 2019

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Overview

Timeline

➢ Project Start Date: 10/01/2016
➢ Project End Date: 02/28/2020
➢ Percent Completion: 60%

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/min</td>
</tr>
</tbody>
</table>

Budget

➢ Total Project Budget: $1,204,366
➢ Total Recipient Share: $214,436
➢ Total Federal Share: $989,930
➢ Total DOE Funds Spent: $419,354.74 as of 03/01/19

Partners

▪ HyMARC Consortium
  ➢ SNL: High Pressure Hydrogenations
  ➢ LLNL: Computational Experiments
  ➢ NREL: TPD Studies.
### Relevance

**Objective:** Synthesize and Characterize Modified Magnesium Boride Hydrogen Storage Materials Capable of Meeting DOE 2020 Targets.

<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>Low System volumetric capacity</td>
<td>kg H₂/L system</td>
<td>0.040</td>
<td>0.070</td>
</tr>
<tr>
<td>Low 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(BH₄)₂ Research

- Recent improvements in magnesium borohydride research.

<table>
<thead>
<tr>
<th>Dehydrogenation Product</th>
<th>Hydrogenation</th>
<th>Dehydrogenation</th>
<th>Wt % H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temp. (°C)</td>
<td>P (bar)</td>
<td>time (h)</td>
</tr>
<tr>
<td>MgB₂ (HP)</td>
<td>&gt;400</td>
<td>&gt;900</td>
<td>108</td>
</tr>
<tr>
<td>MgB₂ (reactive ball milling/HT-HP)</td>
<td>400</td>
<td>10/400</td>
<td>10/24</td>
</tr>
<tr>
<td>Mg(B₃H₈)₂/2MgH₂</td>
<td>250</td>
<td>120</td>
<td>48</td>
</tr>
<tr>
<td>Mg(B₁₀H₁₀)₂(THF)ₓ/4MgH₂</td>
<td>200</td>
<td>50</td>
<td>2</td>
</tr>
</tbody>
</table>

Mg(BH₄)₂ ammoniates
- Improved kinetics on dehydrogenation even though, NH₃, very stable BN products formed.

Mg(BH₄)₂ and MgBₓHᵧ(ether)ₓ
- Improved H₂ cycling kinetics on ether coordination.
- Lower H₂ storage capacity.

Current state-of-the-art:
- Better H₂ cycling kinetics (lower pressures and temperatures).
- Lower gravimetric H₂ storage capacity.

Efforts show plausibility of continuously enhancing kinetics of Mg(BH₄)₂ system.
**Relevance:** Potential for Practical Hydrogen Storage Properties using modified MgB₂

**Hypotheses:** Coordination or incorporation of additives/modifiers can perturb the MgB₂ structure resulting in a destabilized MgB₂ material with improved hydrogen storage properties.

\[
\text{MgB}_2 + \text{modifier} \rightarrow \text{modified MgB}_2 \rightarrow \text{Mg(BH}_4\text{)}_2
\]

Formed prior to or during hydriding

\[\leq 700 \text{ bar H}_2 \leq 300 \text{ °C}\]

**Hypothesis Validation**
- Lower hydrogenation temperature.
- Lower hydrogenation pressure.
- Increase hydrogen sorption rates.

**PROOF OF CONCEPT YEAR 1 USING ETHER ADDITIVES**

Minimize modifier:MgB₂ ratio

Towards improving hydrogen storage properties of MgB₂/Mg(BH₄)₂ system.
**Approach:** Synthesize, Characterize and Hydrogenate Modified MgB\(_2\) Materials

**Experimental Approach: Period 2**

A. **Synthesis of modified MgB\(_2\) materials:** Direct reactions of MgB\(_2\) with additives. 
   - Reactive ball milling, heat treatment and ultra sonication approaches

B. **Hydrogenation reactions:** UH: \(\leq 200\) bars, \(\leq 200\) °C. HyMARC-SNL: \(\leq 700\) bars and 300 °C.

D. **Computation Experiments:** HyMARC-LLNL: *Ab initio* Molecular Dynamic Simulations.

C. **Characterizations:** FTIR-ATR, TGA-DSC, NMR, TPD.

<table>
<thead>
<tr>
<th>Milestone</th>
<th>Project Milestones: (03/01/2018  08/31/2019)</th>
<th>Quarter</th>
<th>Accomplished (02/28/2019)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Characterize modified MgB(_2) by FTIR, NMR, XRD &amp; TGA-DSC.</td>
<td>1</td>
<td>100%</td>
</tr>
<tr>
<td>2</td>
<td>Characterize MgB(_2) composite by FTIR, NMR, XRD &amp; TGA-DSC.</td>
<td>2</td>
<td>100%</td>
</tr>
<tr>
<td>3</td>
<td>Tested MgB(_2) materials on moderate pressure reactor system.</td>
<td>4</td>
<td>80%</td>
</tr>
<tr>
<td>4</td>
<td>Perform 1 round of hydrogenation per quarter: (\leq 700) bar, (\leq 300) °C.</td>
<td>3</td>
<td>95%</td>
</tr>
<tr>
<td>5</td>
<td>Establish if kinetics of dehydriding of modified Mg boranes are limited by B-H or B-B bond formation or nano-structural effects.</td>
<td>4</td>
<td>50%</td>
</tr>
<tr>
<td>6</td>
<td>Demonstrate 3 cycles of reversible hydrogenation of modified MgB(_2) materials to Mg(BH(_4))(_2) at 300 °C and 400 bar.</td>
<td>4</td>
<td>40%</td>
</tr>
</tbody>
</table>

**Go/No-Go Decision:** Demonstrate reversible hydrogenation of \(\geq 8.0\) wt % at \(\leq 400\) bar and \(\leq 300\) °C and 50% cycling stability through three cycles of an optimal formulation of a modified MgB\(_2\) to Mg(BH\(_4\))\(_2\).

Any proposed future work is subject to change based on funding levels.
Accomplishments: MgB$_2$ Structure Perturbation by THF

MgB$_2$ + THF $\xrightarrow{\text{Ball milling approach}}$ Mechano-chemistry $\rightarrow$ Modified MgB$_2$ [Highly activated product]

Evidence of MgB$_2$ modification by THF

Activated product observed from MgB$_2$ ball milled with THF
Accomplishments: $^{11}$B Solid State NMR of modified MgB$_2$

700 bar H$_2$ and 300 °C

Direct confirmation of bulk hydrogenation of MgB$_2$ to Mg(BH$_4$)$_2$ by modified MgB$_2$

Potential new pathways for improving kinetics of MgB$_2$ reversible hydrogenation.
Accomplishments: TPD Analyses of modified MgB\textsubscript{2} 700 bar H\textsubscript{2} and 300 °C

Mostly hydrogen evolved from the hydrogenated modified MgB\textsubscript{2} materials

TPD studies showing H\textsubscript{2} release from 300 °C and 700 bar hydrogenated samples of: (A) MgB\textsubscript{2}-THF-5 mol\% Mg (B) MgB\textsubscript{2}-THF-40 mol\% Mg and (C) MgB\textsubscript{2}-40 mol\% MgH\textsubscript{2}

Negligible amounts of impurities were detected in all samples.
Accomplishments: $^{11}$B Solid State NMR of modified MgB$_2$

400 bar H$_2$ and 300 °C

![Graph showing NMR spectra of different samples](image)

1$^1$B solid state NMR
Spin rate: 10KHz

MgB$_2$–10 mol% X + H$_2$ $\xrightarrow{400 \text{ bar} \atop 300 \text{ °C}}$ Magnesium borohydride

First time hydriding of MgB$_2$ to Mg(BH$_4$)$_2$ at 300 °C! and 400 bars!
Accomplishments: $^{11}$B Solid State NMR of modified MgB$_2$ at <200 bar H$_2$ and <250 $^\circ$C

MgB$_2$–10 mol% X + H$_2$ $\xrightarrow{<200 \text{ bar}}$ $\xrightarrow{<250 \ ^\circ\text{C}}$ Mg(BH$_4$)$_2$

MgB$_2$-X BM
MgB$_2$-Mg-THF BM
MgB$_2$-MgH$_2$ BM
MgB$_2$-Anthracene BM
Pure MgB$_2$-BM

$^{11}$B solid state NMR
Spin rate: 10KHz

Plausibility of discovery of additives for improved kinetics of MgB$_2$ to Mg(BH$_4$)$_2$ at moderate conditions

First time hydriding of MgB$_2$ to Mg(BH$_4$)$_2$ at <250 $^\circ$C! and <200 bars!
Accomplishments: Atomistic modeling of Additive-MgB$_2$ interface

Angle-dependent anthracene-MgB$_2$ interaction energy

Ab initio molecular dynamics of anthracene-MgB$_2$ interface

Joint Theory-Experiments in Progress: Investigation of relative reactivity of MgB$_2$ THF vs. Anthracene.

LLNL Computation Group: Dr. Wood and Dr. Kang
Accomplishments: Responses to 2018 Reviewers’ Comments

• A study demonstrating the dependence of the hydrogenation rate on additive concentration is necessary.
  • Performed hydrogenation of MgB$_2$-THF with 5 mol% Mg and 40 mol% Mg.
  • Non linear variation in hydrogen uptake with additive concentration observed.

• Cycling of the materials should now be the top priority.
  • Currently in the process of performing cycling studies, with target of 3-5 hydrogen cycles at 400 bar and 300 °C.

• X-ray absorption spectroscopy (XAS) will be tremendously useful in validating the suggested mechanism of B-B bond-breaking.
  • Scheduled to perform XAS on pre and post hydrogenated modified MgB$_2$ samples in March and June 2019.

Current and Future Work Addresses AMR Reviewer Comments.

Any proposed future work is subject to change based on funding levels.
Remaining Challenges and Barriers

• Increasing hydrogen uptake to \( \geq 8 \) wt\% at 400 bar at 300 \(^\circ\)C.

• Showing reversibility of the modified MgB\(_2\) materials.

• Understanding mechanism of hydrogenation enhancement in modified magnesium borides.

**Technology Transfer Activities:** Patent filed by University of Hawaii.

## Collaborations

<table>
<thead>
<tr>
<th>Partners</th>
<th>Project Roles</th>
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<tbody>
<tr>
<td>Sandia National Laboratories (HyMARC)</td>
<td>Collaborating with Dr. Stavila and Dr. Allendorf:</td>
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<tr>
<td></td>
<td>➢ High pressure hydrogenation experiments.</td>
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<tr>
<td></td>
<td>➢ XRD analyses.</td>
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<tr>
<td>Lawrence Livermore National Laboratory (HyMARC)</td>
<td>Collaborating with Dr. Wood, Dr. Kang, Dr. Baker:</td>
</tr>
<tr>
<td></td>
<td>➢ Molecular dynamic simulations of magnesium</td>
</tr>
<tr>
<td></td>
<td>boride etherates</td>
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<tr>
<td></td>
<td>➢ XES/XAS studies of modified MgB$_2$.</td>
</tr>
<tr>
<td>National Renewable Energy Laboratory (HyMARC)</td>
<td>Collaborating with Dr. Gennett:</td>
</tr>
<tr>
<td></td>
<td>➢ Temperature programmed desorption.</td>
</tr>
<tr>
<td></td>
<td>➢ Mass spec analyses of desorbed gas.</td>
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</tbody>
</table>

Maximizing HyMARC facilities and Expertise to achieve project objectives.
Proposed Future Work

**Synthesis**
**UH**: HNEI and Dept. of Chemistry. Continue to synthesize modified MgB$_2$ materials using ball milling, ultra sonication and heat treatment approaches.

**Hydrogenations**
• **SNL**: High pressure hydrogenations  
  • Perform hydrogen cycling studies of modified MgB$_2$ materials.  
  • Demonstrate higher gravimetric cycling capacity at $\leq 400$ bar and $\leq 300$ °C.

• **UH**: Moderate pressure hydrogenations.  
  • Perform hydrogenations of modified MgB$_2$ at $\leq 200$ bar and $\leq 300$ °C.

**Characterizations**
• **UH**: $^{11}$B and *in-situ* $^{25}$Mg NMR, FTIR-ATR, TGA, DSC and XRD.

• **HYMARC**: NREL: TPD and LLNL: XES and XAS.

**Computation Experiments**
HYMARC-LLNL: continue joint theory-experiments studies on effect of additives on hydrogenation of MgB$_2$.

*Any proposed future work is subject to change based on funding levels*
## Acknowledgements

**University of Hawaii Team**
- Dr. Godwin Severa
- Prof. C.M. Jensen
- Mr. Cody Sugai
- Mr. Stephen Kim

### Collaborators

<table>
<thead>
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<td>Lawrence Livermore National Laboratory</td>
<td>Dr. Wood, Dr. Kang and Dr Baker:</td>
</tr>
<tr>
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<tr>
<td></td>
<td>➢ XES and XAS studies</td>
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<tr>
<td>Sandia National Laboratories</td>
<td>Dr. Stavila and Dr. White:</td>
</tr>
<tr>
<td></td>
<td>➢ High pressure hydrogenations.</td>
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<tr>
<td>National Renewable Energy Laboratory</td>
<td>Dr. Gennett, Dr. Leick and Ms. Martinez:</td>
</tr>
<tr>
<td></td>
<td>➢ Temperature programmed desorption.</td>
</tr>
<tr>
<td>University of Geneva</td>
<td>Dr. Hagemann and Ms Gigante.</td>
</tr>
<tr>
<td></td>
<td>➢ Raman studies of modified MgB₂</td>
</tr>
</tbody>
</table>

**Project Funding:** US. DOE-EERE’s Fuel Cell Technologies Office
Summary

• Modified MgB$_2$ that can be hydrogenated below 700 bar have been synthesized.
• Demonstrated bulk hydriding of modified MgB$_2$ to Mg(BH$_4$)$_2$ at 300 °C and 400 bar.
• Demonstrated hydrogenation of MgB$_2$ to Mg(BH$_4$)$_2$ at ≤ 250 °C and ≤ 200 bar, Mg(BH$_4$)$_2$ yields currently less than 10%, based on $^{11}$B NMR line fitting analyses.
• Hydrogenation of MgB$_2$ to Mg(BH$_4$)$_2$ at conditions relevant to onboard hydrogen storage appear plausible (< 200 bar and < 200 °C).

<table>
<thead>
<tr>
<th>Bulk MgB$_2$ Hydrogenation Conditions</th>
<th>State of Art [Pure MgB$_2$]</th>
<th>FY 17 Results [modified MgB$_2$]</th>
<th>FY 18 Results [modified MgB$_2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure/ bar</td>
<td>950</td>
<td>700</td>
<td>≤ 400</td>
</tr>
<tr>
<td>Temperature/ °C</td>
<td>~400</td>
<td>300</td>
<td>≤ 300</td>
</tr>
<tr>
<td>Wt % hydrogen</td>
<td>11 wt %</td>
<td>7-8 wt %</td>
<td></td>
</tr>
<tr>
<td>% Conversion: MgB$_2$ to Mg(BH$_4$)$_2$</td>
<td>75 % [Sieverts method: wt% H$_2$]</td>
<td>71 % [11B solid state NMR line fitting method]</td>
<td>36 % [11B solid state NMR line fitting method]</td>
</tr>
</tbody>
</table>

Research shows plausibility of finding additives capable of vastly improving kinetics of MgB$_2$ hydrogenation to Mg(BH$_4$)$_2$