Kinetic enhancement of bulk, direct hydrogenation of MgB$_2$ to Mg(BH$_4$)$_2$ in presence of modifiers

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Outline

• Motivation
• Background
• Approach
• Results
• Summary
Motivation: Potential of Mg(BH$_4$)$_2$/MgB$_2$ System

High hydrogen storage capacity of pure Mg(BH$_4$)$_2$/MgB$_2$ system.
- Theoretical Gravimetric density: 14.8 wt% H$_2$.

Potential for practical onboard reversible hydrogen storage
- $\Delta H_{\text{dehyd}} = 40\text{-}50 \text{kJ/mol H}_2$
  $\Rightarrow$ plausibility of re-hydrogenation of MgB$_2$ to Mg(BH$_4$)$_2$ at moderate temperatures and pressures.
**Background:** Reversible H₂ cycling of MgB₂ to Mg(BH₄)₂

\[ \text{MgB}_2 \xrightarrow{900 \text{ atm H}_2, 400 \, ^\circ\text{C}} \text{Mg(BH}_4\text{)}_2 \]

Confirmed by XRD, IR, MAS ¹¹B NMR

Demonstrated 11.4 wt % H₂ release from the high pressure synthesized Mg(BH₄)₂

Rönnebro, Severa and Jensen, USPTO, **2012**, Patent 8147788.
**Background:** Reversible Dehydrogenation of Mg(BH$_4$)$_2$ to MgB$_2$

1. Dehydriding Mg(BH$_4$)$_2$ doped with 5mol% TiF$_3$/ScCl$_3$

MgB$_2$ formed with release of up to 14 wt% H$_2$

2. Rehydrogenation at 900 bar and 390 $^\circ$C

Rehydrogenation: 49% for doped sample and 66% for undoped sample observed.

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

- Recent improvements in magnesium borohydride research.

<table>
<thead>
<tr>
<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>
</tr>
<tr>
<td>MgB$_2$ (HP)</td>
<td>&gt;400</td>
<td>&gt;900</td>
<td>108</td>
</tr>
<tr>
<td>MgB$_2$ (reactive ball milling/HT-HP)</td>
<td>/400</td>
<td>10/400</td>
<td>10/24</td>
</tr>
<tr>
<td>Mg(B$_3$H$_8$)$_2$(THF)$_x$/2MgH$_2$</td>
<td>200</td>
<td>50</td>
<td>2</td>
</tr>
<tr>
<td>Mg(B$_3$H$_8$)$_2$/2MgH$_2$</td>
<td>250</td>
<td>120</td>
<td>48</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>
</tr>
</tbody>
</table>

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

- Improved kinetics on dehydrogenation even though, NH$_3$, very stable BN products formed.

**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.

Current state-of-the-art:

- Better H$_2$ cycling kinetics (lower pressures and temperatures).
- Lower gravimetric H$_2$ storage capacity.

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

**Ether activated MgB$_2$: Potential for Practical Hydrogen Storage Properties**

**HYPOTHESIS:** Ether coordination or incorporation can perturb the MgB$_2$ structure resulting in a destabilized MgB$_2$ material with improved hydrogen storage properties.

MgB$_2$ + Ether $\rightarrow$ Ether activated/modified MgB$_2$

<table>
<thead>
<tr>
<th>Mols ether/ Mol MgB$_2$ (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>MgB$_2$(OMe$_2$)$_x$</td>
<td>9.4</td>
<td>11.1</td>
<td>12.8</td>
<td>13.8</td>
<td>14.3</td>
</tr>
<tr>
<td>MgB$_2$(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>MgB$_2$(OCH$_2$Me$_2$)$_x$</td>
<td>7.6</td>
<td>9.6</td>
<td>11.7</td>
<td>13.1</td>
<td>14.0</td>
</tr>
<tr>
<td>MgB$_2$(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>MgB$_2$(polyether)$_x$</td>
<td></td>
<td></td>
<td></td>
<td>&gt;12</td>
<td>&gt;12</td>
</tr>
</tbody>
</table>

**Hypothesis Validation**

- Lower MgB$_2$ hydrogenation temperature.
- Lower MgB$_2$ hydrogenation pressure.
- Increase MgB$_2$ hydrogen sorption rates.

**Potential to improve practical hydrogen storage properties of MgB$_2$/Mg(BH$_4$)$_2$ system.**
Experimental Approach: Synthesize, Characterize and Hydrogenate Modified MgB$_2$ Materials

A. Synthesize of modified MgB$_2$ by reactive ball milling and heat treatment approaches:
   1. Syntheses from dehydrogenation reactions of Mg borane etherates and metal hydrides.
   2. Syntheses from direct reactions of MgB$_2$ with additives/modifiers.

B. Hydrogenation reactions: <1000 bars, <400 °C and ≤ 72 hrs. [UH, SNL]

C. Characterizations: FTATR, TGA-DSC, XRD, NMR, TPD-Mass Spec. [UH, NREL, SNL, PNNL, LLNL]

D. Theoretical Studies: HyMARC: [LLNL]
**Computational Approach:** *Ab Initio* 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

*Ab initio* Molecular Dynamic Simulations to identify perturbation of MgB$_2$.

LLNL: Dr. B. Wood, Dr. S. Kang and Dr. S. Wan
Orientation-dependent reactivity of MgB$_2$ with THF

Results: Molecular Dynamic Simulations

**EDGE PLANE**

Reactive MgB$_2$ edge plane decomposes THF into ethylene etc.

**BASAL PLANE**

Addition of THF (800 K)

Ethers destabilize surface boron sheet and create structural defects.

Origin of structure deformation?
**Results: Syntheses of Ether Activated MgB$_2$**

**Preparation By Ball Milling Approach**

MgB$_2$ + ether $\xrightarrow{400\text{ rpm}}$ MgB$_2$-ether

Ether: tetrahydrofuran, dioxane, tetraglyme, triglyme, dioxalane

MgB$_2$ peaks decrease for THF and Triglyme samples.
- Ether role in decreasing MgB$_2$ crystallinity.

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

$^{11}$B MAS-NMR at 10 kHz.

- MgB$_2$ (97.4 ppm)
- MgB$_2$-THF (97.8 ppm)

Solid State $^{11}$B NMR indicates presence of MgB$_2$
**Results:** Lowered Hydrogenation Temperature of MgB$_2$

MgB$_2$-THF + H$_2$ → MgB$_2$-THF → 1000 bar 300 °C, 72 hrs → Magnesium borohydride species

**FIRST TIME** hydrogenation of BULK MgB$_2$ to Mg(BH$_4$)$_2$ at 300 °C

Significant hydrogenation confirmed for the FIRST TIME For Mg(BH$_4$)$_2$ at 300 °C

**Typical Mg(BH$_4$)$_2$ DSC profile**

Lowering of temperature of bulk MgB$_2$ hydrogenation to 300 °C.
Vastly improved kinetics of hydrogenation
FTIR and XRD of hydrogenated MgB$_2$-THF shows typical intense Mg(BH$_4$)$_2$ stretches at 2260 and 1240 cm$^{-1}$.
Results: Solution $^{11}$B NMR of Hydrogenated MgB$_2$-THF

Hydrogenated MgB$_2$-THF Prepared by Ball Milling Approach

MgB$_2$-THF + H$_2$ $\xrightarrow{1000 \text{ bar}, \text{300} \, ^\circ\text{C}, \text{72 hrs}}$ Magnesium borohydride species

$^{11}$B NMR also directly confirmed Mg(BH$_4$)$_2$ formation
Results: Hydrogenation of MgB$_2$-THF at 700 bar & 300 °C

MgB$_2$-THF + H$_2$ $\xrightarrow{700 \text{ bar} \ 300 \degree \text{C}, \ 72 \text{ hrs}}$ Magnesium borohydride

**FIRST TIME** hydrogenation of MgB$_2$ to Mg(BH$_4$)$_2$ at 300 °C and 700 bars

Hydrogen uptake is not a function of ball milling time but due to THF effects

Comparison with MgB$_2$-THF BM hydrogenated at 300 °C and 1000 bars

$^1$H Solution NMR: Qualitative evidence of simultaneous lowering of MgB$_2$ hydrogenation temperature and pressure by THF

Simultaneous lowering of hydrogenation temperature and pressure of a MgB$_2$ material to Mg(BH$_4$)$_2$
**Results: MgB$_2$-THF-X Hydrogenation Studies**

*First time hydrogenation of bulk MgB$_2$ to Mg(BH$_4$)$_2$ at 300 °C! and 700 bars!*

\[
\text{MgB}_2\text{-THF-X} + \text{H}_2 \xrightarrow{700 \text{ bar}, 300 \degree\text{C}} \text{Magnesium borohydride}
\]

**Potential of cooperative effects:** THF-X additive combination enhanced H$_2$ uptake of MgB$_2$ system.

**11B Solution NMR in D$_2$O/THF**

- MgB$_2$-THF-X1 BM
- MgB$_2$-THF-X2 BM
- MgB$_2$-THF-X3 BM

**TGA mass loss (%) up to <600 °C for samples H$_2$ treated at 300 °C, 700 bars & 72 hours**

**Vastly improved kinetics of hydrogenation of bulk MgB$_2$ at 300 °C! and 700 bars!**
Results: MgB₂-X Hydrogenation Studies

First time hydrogenation of MgB₂ to Mg(BH₄)₂ at 300 °C! and 700 bars! in absents of ether!

\[
\text{MgB}_2{-X} + \text{H}_2 \xrightarrow{\text{700 bar} \atop \text{300 °C}} \text{Magnesium borohydride}
\]

THF “like effects” on MgB₂, observed with other additives!!!

Expansion of MgB₂ perturbation hypothesis beyond ether incorporation

Potential new pathways for improving kinetics of MgB₂ hydrogenation.
**Results: IR Analyses of Hydrogenated Samples**

FT-ATR analyses of hydrogenated MgB$_2$-X3-THF and MgB$_2$-X2 samples

**Pre hydrogenated samples:** (A) MgB$_2$-THF-X3 and (B) MgB$_2$-X2;  
**Post hydrogenated samples (700 bar, 300 °C):** (C) MgB$_2$-THF-X3 and (D) MgB$_2$-X2.

Typical Mg(BH$_4$)$_2$ vibrations in the 2200-2300 cm$^{-1}$ and 1200-1300 cm$^{-1}$ region are observed after hydrogenation.
Results: TPD Analyses of Evolved Gases

Analyses of gases evolved on heat treatment of MgB$_2$-THF-X3 and MgB$_2$-X2

<table>
<thead>
<tr>
<th>Sample</th>
<th>TPD H$_2$ wt loss (%)</th>
</tr>
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<tbody>
<tr>
<td>MgB$_2$-X2 (#7) [Post-Hyd]</td>
<td>5.2</td>
</tr>
<tr>
<td>MgB$_2$-THF-X3 (#1) [Post-Hyd]</td>
<td>7.3-8.1</td>
</tr>
</tbody>
</table>

Mostly hydrogen evolved from the hydrogenated MgB$_2$ based materials.
• Modified MgB$_2$ that can be hydrogenated under milder conditions have been prepared.
• Demonstrated hydrogenation of bulk MgB$_2$ to Mg(BH$_4$)$_2$ at 300 °C and 700 bar.
• Hydrogenation of MgB$_2$ to Mg(BH$_4$)$_2$ at 300 °C and 700 bar has been proven in absents of tetrahydrofuran.
• MD simulations indicate orientation-dependent reactivity of MgB$_2$ with THF.
• Greater than 7 wt% H$_2$ released from MgB$_2$-X-THF material hydried at 300 °C and 700 bar.

<table>
<thead>
<tr>
<th>Bulk MgB$_2$ Hydrogenation Conditions</th>
<th>State of Art</th>
<th>Project Results</th>
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</thead>
<tbody>
<tr>
<td>Pressure/ bar</td>
<td>≥900</td>
<td>≤ 700</td>
</tr>
<tr>
<td>Temperature/ °C</td>
<td>~400</td>
<td>≤ 300</td>
</tr>
</tbody>
</table>

**Summary**

Simultaneous lowering of bulk MgB$_2$ hydrogenation conditions from 900 bar and 400 °C to 700 bar and 300 °C has been demonstrated for first time.
# Acknowledgements

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<tr>
<th>HYMARC Partners</th>
<th>Partner Roles</th>
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<tr>
<td>Lawrence Livermore National Laboratory</td>
<td>Dr. Wood, Dr. Kang and Dr. Wan:</td>
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<td>➢ Molecular dynamic simulations of modified magnesium borides.</td>
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<tr>
<td>Sandia National Laboratories</td>
<td>Dr. Stavila and Dr. White:</td>
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<td>➢ High pressure hydrogenation experiments.</td>
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<td>National Renewable Energy Laboratory</td>
<td>Dr. Gennett, Dr. Leick and Dr. Martinez:</td>
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<tr>
<td></td>
<td>➢ Temperature programmed desorption.</td>
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<td></td>
<td>➢ Mass spec analyses of desorbed gas.</td>
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**Project Funding:** US. DOE-EERE’s Fuel Cell Technologies Office
THANK YOU