Improving the Kinetics and Thermodynamics of Mg(BH$_4$)$_2$ for Hydrogen Storage

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University of Michigan (H.-C. Yu, K. Thornton)

Project ID# ST118

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## Overview

### Timeline

- **Project start date:** 07/01/2014
- **Project end date:** 07/01/2017

### Barriers addressed

- Lack of understanding of hydrogen chemisorption (Barrier O)
- System weight (Barrier A)
- Charge/discharge rate (Barrier E)

### Budget

- **Total project budget:** $1.2M
  - Total federal share: $1.2M
  - Total received: $200K (FY14), $400K (FY15), $400K (FY16), $200K (FY17)
  - Total funds spent (as of 3/17): $937K

### Team

- **Project Lead:** Lawrence Livermore National Laboratory
- **Funded Partners:**
  - Sandia National Laboratories
  - University of Michigan
Relevance and approach

We integrate theoretical and experimental tools to probe mechanisms and pathways in MgB$_2$/Mg(BH$_4$)$_2$ towards rational tuning of the energy landscape.

How, when, and why can these help?
- **Nanoscaling**
- **Additives**
- Microstructure (physical arrangement)
- State (crystal/amorphous/molecular)
- Mechanical effects/confinement (stress)
- High H$_2$ pressure (far from equilibrium)

Phase I: Thermodynamics

**Predict thermodynamics of (de)hydrogenation**
- Baseline bulk phase diagram and phase fraction prediction by high-level computation
- Validation and calibration from testing and literature data

Phase II: Bulk & nanoscale kinetics

**Understand mechanisms & kinetic pathways**
- Study initial hydrogenation (single-phase) and deeper hydrogenation (multiphase)
- Use theory, spectroscopy, and kinetic rate analysis

Phase III: Additives & optimization

**Assess how energy landscape can be tuned**
- Investigations focused on nanoscaling and additives
- Theory studies of mechanical and microstructural effects
- Identify & test promising improvement strategies
Approach: Combining chemistry and materials science

Our approach adapts tools from chemistry and materials science, with particular emphasis on less-well-understood rehydrogenation.

Local chemistry of $B_xH_y$ complexes
- Single-phase reactions
- DFT/ab initio molecular dynamics
- Soft X-ray spectroscopy & NMR

Evolution of solid phases
- Multi-phase reactions
- Ab initio thermodynamics and phase-field models
- Phase identification via XRD, NMR, FTIR

Multiscale Theory
- Validation
- Controlled Synthesis
- Parameterization
- Characterization

- Bulk materials
- Unconfined size-selected nanoparticles
- Additives/catalysts

Tightly integrated with efforts on the Mg-B-H system within HyMARC (theory tools & high-pressure testing) and HySCORE ($B_xH_y$ dehydrogenation chemistry & NMR)
To boost capacity and isolate size effects without confinement, we use unique nanoparticle synthesis that integrates with theory for mechanistic insight and improvement strategies.

**Nanoparticle synthesis approach:**

1. Use **“surfactant-assisted” ball milling** to create unconfined MgB$_2$ nanoparticles (Y. Wang et al., Nanotechnology 18, 465701 (2007))
2. Employ solvent dispersion techniques to separate out nano and micro size fractions
3. Remove surfactants and solvents from the nanoparticle material
Accomplishment: Reference phase diagram of Mg-B-H

Used combined computational-experimental approach to obtain a reliable baseline phase diagram for further thermodynamic predictions

- Zero-K energies from hybrid DFT and zero-point energies from phonons
- Analytical expression for $\Delta G(T,P)$
- Calibrate temperature against PCT data

Thermal properties from ab initio MD

\[
\beta\text{-Mg(BH}_4\text{)}_2 \rightarrow \text{MgB}_2 + 4 \text{H}_2
\]

- Threshold $T$, $p_{\text{H}_2}$
- Other theory work

- * = PCT from Li et al., Nanotechnology 20, 204013 (2009)
- $1/6 \text{MgB}_{12}\text{H}_{12} + 5/6 \text{Mg} + 3 \text{H}_2$
- $\text{MgB}_2 + 4 \text{H}_2$

- MgB$_{12}$H$_{12}$ is stable over a wide ($P,T$) range, but other MgB$_x$H$_y$ intermediates are not stably formed as isolated solid phases and must exist as molecules or at interfaces
- Including thermal anharmonic effects dramatically changes behavior for $T > 300^{\circ}$C
- Density affects anharmonic modes, suggesting a new pathway for tuning thermodynamics
Accomplishment: Validation experiments at high $H_2$ pressure

Successfully validated predicted phase fractions under high-pressure $H_2$ with levels of $MgB_{x}H_{y}$ intermediates depending on $(T,P)$ conditions

Experimental validation at high $P$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Method</th>
<th>$T$ (°C)</th>
<th>$pH_2$ (bar)</th>
<th>Relative mole fractions of products (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Severa (2010)$^1$</td>
<td>$^{11}$B NMR</td>
<td>390</td>
<td>900</td>
<td>MgB$_x$H$_y$ 7</td>
</tr>
<tr>
<td>SNL #1</td>
<td>$^{11}$B NMR</td>
<td>420</td>
<td>1000</td>
<td>MgB$_x$H$_y$ 13</td>
</tr>
<tr>
<td>SNL #2</td>
<td>$^{11}$B NMR</td>
<td>540</td>
<td>500</td>
<td>MgB$_x$H$_y$ 53</td>
</tr>
<tr>
<td>SNL/HyMARC #3</td>
<td>XRD</td>
<td></td>
<td></td>
<td>Mg(BH$_4$)$_2$ 75</td>
</tr>
<tr>
<td>(White/Stavila)</td>
<td></td>
<td>400</td>
<td>1</td>
<td>Mg(BH$_4$)$_2$ 75</td>
</tr>
<tr>
<td></td>
<td></td>
<td>400</td>
<td>70</td>
<td>Mg(BH$_4$)$_2$ 0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>400</td>
<td>350</td>
<td>Mg(BH$_4$)$_2$ 66</td>
</tr>
<tr>
<td></td>
<td></td>
<td>400</td>
<td>700</td>
<td>Mg(BH$_4$)$_2$ 84</td>
</tr>
</tbody>
</table>

$^1$Severa et al., Chem. Commun. 46, 421 (2010)

- Predicted phase diagram and phase fractions are in excellent agreement with NMR & XRD
- Meets Go/No-Go for theory-experiment agreement
- Method for phase fraction prediction published as cover article in Adv. Mater. Interfaces
Theory predicts that nanosizing increases prevalence of MgB$_{12}$H$_{12}$ intermediate, inhibiting full cycling but decreasing onset temperature/pressure for partial (de)hydrogenation.

- Trends explain published dehydrogenation data showing nanoconfinement has biggest destabilizing effect on larger H-rich phases.
- Nano-MgB$_2$: Higher thermodynamic driving force will aid partial rehydrogenation kinetics.
- Confinement in very stiff medium could be thermodynamically beneficial.

**Reaction (@ 1 bar H$_2$)**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Exp. $\Delta T$ upon nanoconfinement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(BH$<em>4$)$<em>2$ $\rightleftharpoons$ (MgB$</em>{12}$H$</em>{12}$, MgH$_2$, H$_2$)</td>
<td>@ 2 nm (DSC)$^1$</td>
</tr>
<tr>
<td>(MgB$<em>{12}$H$</em>{12}$, MgH$<em>2$, H$<em>2$) $\rightleftharpoons$ (MgB$</em>{12}$H$</em>{12}$, Mg, H$_2$)</td>
<td>-20 °C</td>
</tr>
<tr>
<td>(MgB$<em>{12}$H$</em>{12}$, Mg, H$_2$)</td>
<td>-5 °C</td>
</tr>
</tbody>
</table>

$^1$Fichtner et al., Nanotechnology 20, 204029 (2009)
Accomplishment: Developed synthesis procedure for MgB₂ nanoparticles

TEM confirms successful synthesis of MgB₂ nanoparticles that are < 50 nm in diameter

Procedure:
1. Combine high-purity MgB₂ with heptane, oleic acid, and oleylamine in Ar glovebag
2. Use tungsten carbide milling pot and milling balls to ball mill for 20 hrs (for 2 hr increments with 1 hr rest in between)
3. Disperse product in heptane, ultrasonicate, and filter out insolubles (bulk particles)
4. Centrifuge at 5000 rpm for 25 minutes, producing deposit and remaining solution
5. Remove material that deposits (d > 200 nm) coated with surfactant
6. Recover particles from solution (d < 50 nm) by washing 3x with EtOH

• Can now synthesize gram-level amounts to study kinetics and pathways jointly w/ theory
• Enables Phase III: including additives with the MgB₂ nanoparticles
Accomplishment: Confirmed purity of synthesized MgB$_2$ nanoparticles

FTIR shows that NP synthesis removes oleic acid and oleyl amine surfactants, dispersion solvent (heptane), and recovery solvent (ethanol), while avoiding B oxidation.
XAS and elemental analysis further confirm surfactant/solvent removal and show we are not oxidizing or nitriding Mg, but there is ~ 5 mole % of inert C

<table>
<thead>
<tr>
<th>Sample</th>
<th>C (mol.%)</th>
<th>H (mol.%)</th>
<th>N (mol.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgB₂ nanoparticles (&lt; 200 nm)</td>
<td>5.2</td>
<td>2.8</td>
<td>Not detected</td>
</tr>
<tr>
<td>MgB₂ nanoparticles (&lt; 200 nm) after full cycle at 365 °C, 140 bar H₂</td>
<td>5.2</td>
<td>3.7</td>
<td>Not detected</td>
</tr>
<tr>
<td>Bulk MgB₂</td>
<td>Not detected</td>
<td>Not detected</td>
<td>Not detected</td>
</tr>
</tbody>
</table>

Accomplishment: Confirmed purity of synthesized MgB₂ nanoparticles

No evidence of N or O contamination of Mg

- Erosion of milling balls (stainless steel or tungsten carbide) was initially a major problem, producing high levels (25 mol.%) of metal contamination
- Procedures were developed to reduce metal contamination to < 0.5 mol.%
- Remaining C contaminant is unaffected by cycling and therefore deemed inert
Accomplishment: Initial uptake kinetics of unconfined MgB$_2$ nanoparticles

**Nano-MgB$_2$ shows reduction of activation barriers and significant kinetic improvement for initial hydrogen uptake (0.7 – 0.9 wt.%H)**

- Nanosizing improves initial hydrogenation rates by ~2× and exhibits ~3× lower barriers
- Running higher-pressure uptake and chemical analysis via FTIR, XRD, and NMR (HySCORE)
- Plan to check for agglomeration upon hydrogenation of nano-MgB$_2$
Accomplishment: Determined initial hydrogenation mechanism for MgB$_2$

Bonding probes (FTIR, XAS/XES) w/distinct depth sensitivities (nm to mm) were combined with theory for mechanistic understanding of MgB$_2$ uptake within single-phase regime

- Direct chemical pathway to BH$_4^-$ is feasible
- DFT confirms pathway is energetically favorable
- Mechanism of H bonding to exposed B (at defects or edges) is uniquely consistent with all spectroscopy + simulations
Accomplishment: Semi-empirical multiprocess kinetic modeling

Used energy landscape to parameterize kinetic model for validation of two-step mechanism

- Agreement with experiments confirms two-step dissociation + interface diffusion/binding mechanism (manuscript submitted)
- Importance of interfaces explains why barriers are reduced for nano-MgB$_2$

\[
\begin{align*}
H_2(g) & \leftrightarrow 2H^* \leftrightarrow 2H_{\text{ads}} \\
E_{\text{ads}}(\theta) & \downarrow 0.20 \text{ eV (per H)} \\
H_2(g) & \uparrow 0.91 \text{ eV} \\
2H^* & \downarrow 0.56 \text{ eV} \\
2H_{\text{ads}} & \uparrow
\end{align*}
\]

\[391 \, ^{\circ}\text{C, 140 bar}\]

\[
\begin{align*}
\text{Dissociation:} & \\
\frac{\partial c_{H^*}}{\partial t} &= k_1 \cdot P_{H_2} - \tilde{k}_1 \cdot c_{H^*}^2 - \frac{\partial c_{H_{\text{ads}}}}{\partial t} \\
\text{Surface diffusion/binding (modified Langmuir model):} & \\
\frac{\partial c_{H_{\text{ads}}}}{\partial t} &= k_2 \cdot c_{H^*}^2 \cdot c_s^3 \cdot (1 - \theta)^2 - \tilde{k}_2 \cdot c_s^3 \cdot \theta^2
\end{align*}
\]
Accomplishment: Phase-field simulation of $\text{MgB}_2 \leftrightarrow \text{MgB}_{12}\text{H}_{12}$ kinetics

Performed first full phase-field simulation of (de)hydrogenation for H-poor reaction domain to explore kinetic effects under conditions where Sieverts cannot be performed

- Phase-field models reveal relationship between microstructure, pathway, and kinetics
- Faster mass transport of Mg is predicted to have a large effect on overall kinetics
Accomplishment: Exploration of chemical pathways

Chemical pathways identified by HySCORE were explored using high-T/P ab initio molecular dynamics for additional mechanistic insight and model parameterization

- Simulations of MgB$_2$ hydrogenation show formation of B-H, B-B, and Mg-H bonds
- Closoborane formation during MgB$_2$ hydrogenation may arise from interactions between hexagonal B sheets upon removal and hydriding of Mg
- Can directly observe reaction pathways during dehydrogenation of Mg(BH$_4$)$_2$
- Changes in charge states induce boron chemistry and affect diffusion mobility

Initial hydrogenation of MgB$_2$ (1010)

Initial dehydrogenation of Mg(BH$_4$)$_2$ (w/ HySCORE)

Gas-phase ΔH courtesy of PNNL/HySCORE

\[
\text{BH}_4^- + \text{BH}_4^- \xrightarrow{\text{H}^-} \text{B}_2\text{H}_7^- \xrightarrow{\text{H}_2} \text{B}_2\text{H}_5^- \\
\begin{array}{c}
+70.6 \\
+31.5
\end{array}
\text{kJ/mol}
\]
Progress on FY17 and post-AMR FY16 milestones (as of 4/17)

- Synthesize high-purity MgB₂ nanoparticles (~10 nm) (complete)
- Compute thermodynamics of surfaces and interfaces of nano-MgB₂/Mg(BH₄)₂ (complete)
- Establish modeling framework for surface chemical reactions and calculate surface-dependent thermodynamics, migration, and dissociation (complete)
- Measure hydrogen desorption/adsorption rate of nanoparticles and identify key intermediates (75% complete; new samples sent to HySCORE for phase identification)
- Go/No-Go: Demonstrate 75% agreement between model predictions and observed phase diagram/phase fractions, and demonstrate scalable nanoparticle synthesis (complete)
- Identify rate-limiting processes in hydrogenation of nano-MgB₂ (75% complete)
- Measure hydrogen desorption/absorption in catalyst-modified nanoscale MgB₂ and identify intermediates (25% complete)
- Determine sensitivity of reaction kinetics on atomistic processes (50% complete)
- Compute hydrogenation/rehydrogenation kinetics using three-phase model (75% complete)
- Predict ideal particle shape, size, and stress state for optimized thermodynamics and kinetics (20% complete)
Remaining challenges/barriers & mitigation strategies

- **Nanosizing MgB\(_2\)** is unlikely to provide an ultimate solution on its own
  - Our predictions show that nanosizing helps kinetics but does not destabilize intermediates. Our Phase III study of nanoscale catalyzed MgB\(_2\) will determine how additives might additionally help.

- **Extracting barriers for inclusion in free energy landscape is challenging**
  - We will work with HyMARC to improve the free energy landscape description via kinetics studies. We will also use time-dependent data from NMR analysis (HySCORE) of different exposure times at a variety of (T,P) to parameterize the landscape.

- **Phase-field kinetic model should be applied to full reaction pathway**
  - We started with the hydrogen-poor phases because the reaction chemistry is less complex, but the model can be extended to the full phase diagram.

- **Need to translate mechanistic insights into rational design strategies for validation**
  - Future activities will focus on use of mesoscale modeling framework to analyze sensitivity of kinetics to changes in materials properties and guide design, validated and informed by experiments.
Proposed future work

- **Incorporate catalyst additives** (TiCl$_3$/TiF$_3$) into surfactant-assisted ball milling process for nanoparticles and test for kinetics and phase expression (underway)
- **Extend thermodynamic phase-fraction predictions** to account for other B$_x$H$_y$ intermediates, including possible B$_2$H$_6$ formation
- **Extend phase-field kinetic model** to other regions of phase diagram (underway)
- **Inform free energy landscape** with more advanced interfacial reaction and transport models in collaboration with HyMARC and PNNL/HySCORE (underway)
- **Validate kinetic model** against phase expression from NMR, FTIR, XRD, XAS/XES in uncatalyzed and catalyzed nanoparticles as a function of exposure time
- **Use kinetic model to explore sensitivity of kinetics** to additives, nanosizing, and confinement to evaluate best strategies for optimization

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

Collaborations are crucial for realizing theory/characterization/synthesis partnership

Ab initio modeling/multiscale integration
- Dr. Brandon Wood (PI, LLNL)*
- Dr. Keith Ray (LLNL)*
- Dr. ShinYoung Kang (LLNL)*

Mesoscale phase-field modeling
- Prof. Katsuyo Thornton (Univ. Michigan)**
- Dr. Hui-Chia Yu (Univ. Michigan)**
- Dr. Tae Wook Heo (LLNL)*

HySCORE collaborations
- Borohydride chemistry and Mg(BH$_4$)$_2$ dehydrogenation pathways (PNNL)
- $^{11}$B NMR (PNNL)
- Neutron vibrational spectroscopy (NIST)

Nanoparticle synthesis & testing
- Dr. Vitalie Stavila (Sandia)**

Characterization
- Dr. Lennie Klebanoff (Sandia)**
- Dr. Jonathan Lee (LLNL)*
- Dr. Alex Baker (LLNL)*

HyMARC collaborations
- Computational spectroscopy (LBNL)
- Free energy analysis for phase fraction prediction (LLNL)
- Diffuse reactive interface modeling (LLNL)
- High-pressure hydrogenation (SNL)
- Nanoconfining carbons (LLNL)
Summary

Our theory/experiment approach informs mechanisms and improvement strategies

- Validated and applied free energy landscape within a mesoscale kinetic model to explore the sensitivity of H₂ uptake/release to specific kinetic processes
- Demonstrated synthesis of high-purity MgB₂ nanoparticles without confinement
- Showed that it is possible chemically to create molecular Mg(BH₄)₂ directly from MgB₂ and determined associated atomistic mechanism with help from theory
- Elucidated the role of anharmonic molecular rotations in stabilizing Mg(BH₄)₂ and intermediates at higher T, suggesting a pathway for tuning thermodynamics
- Showed that microstructure can play a key role in stability and kinetics
  - Most intermediates (e.g., Mg(B₃H₈)₂) are likely stabilized as molecules at reactive interfaces, so manipulating molecular vs. condensed-phase stability (e.g., via complexation with additives) is a promising strategy
  - For rehydrogenation of MgB₂, introducing interfaces and/or defects will create reaction sites that should aid kinetics (e.g., via ball milling, nanosizing, or additives)
- Predicted and demonstrated that nanosizing MgB₂ without confinement helps kinetics of partial uptake, partly due to stronger thermodynamic driving forces, but it is not predicted to destabilize intermediates
Technical backup slides
Backup: Environment/morphology-dependent thermodynamics

Relative stability of MgBₓHᵧ intermediates depends strongly on environment & morphology

- MgB₂ and Mg(BH₄)₂ have a strong tendency to form bulk condensed phases, whereas other intermediates can form molecules or polymeric chains. This means manipulating molecular vs. condensed phase stability is a promising strategy, which may be one role of solvent additives.

- Of the common intermediates, Mg(B₃H₈)₂ most easily tolerates molecular dissociation (e.g., in THF), followed by MgB₁₂H₁₂, then MgB₁₀H₁₀ and Mg(BH₄)₂. This likely reflects the order of preference for interface segregation, so catalyst additives that segregate to grain boundaries and interfaces will preferentially target MgB₁₂H₁₂ and Mg(B₃H₈)₂.
At 390 °C, 900 bar (reaction conditions of Severa et al. (2010)), anharmonic \( B_xH_y \) rotations are primarily responsible for converting \( \text{MgB}_2 \) to \( \text{Mg(BH}_4)_2 \) without significant intermediates.

\[
\beta\text{-Mg(BH}_4)_2 \leftrightarrow [\frac{1}{6} \text{MgB}_{12}H_{12} + \frac{5}{6} \text{MgH}_2 + \frac{13}{6} \text{H}_2] \\
\leftrightarrow [\frac{1}{6} \text{MgB}_{12}H_{12} + \frac{5}{6} \text{Mg} + 3\text{H}_2] \leftrightarrow [\text{MgB}_2 + 4\text{H}_2]
\]

- Anharmonic modes are strongly density dependent and may be enhanced by grain/phase boundaries or atom substitutions.
Backup: Equilibrium phase fraction predictions

**Computed phase fractions agree with experimental trends in intermediate expression**

$$\beta\text{-Mg(BH}_4\text{)}_2 \leftrightarrow [\frac{1}{6} \text{MgB}_{12}\text{H}_{12} + \frac{5}{6} \text{MgH}_2 + \frac{13}{6} \text{H}_2]$$

$$\leftrightarrow [\frac{1}{6} \text{MgB}_{12}\text{H}_{12} + \frac{5}{6} \text{Mg} + 3\text{H}_2] \leftrightarrow [\text{MgB}_2 + 4\text{H}_2]$$

Based on grand-canonical free energy minimization plus regular solution phase mixing

Amounts of MgB$_{12}$H$_{12}$ and Mg(BH$_4$)$_2$ predicted to be equal at 635 ºC at 500 bar (vs. ≥540 ºC from NMR)

Our work on Li$_3$N demonstrating the method made the cover of *Adv. Mater. Interfaces*, 2017

Meets second Go/No-Go (75% phase fraction theory-experiment agreement)
Backup: Effects of stress and size (isothermal)

Under compressive stress

![Graphs showing under compressive stress at different temperatures (200 °C, 400 °C, 500 °C, 600 °C).](image)

Particle size dependence

![Graphs showing particle size dependence at different temperatures (200 °C, 400 °C, 500 °C, 600 °C).](image)