# 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

Project ID # ST138

# Overview

## Timeline

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

## Barriers

| Barrier | Target |
|---|---|
| Low System Gravimetric capacity | > 7 wt% $H_2$ system |
| Low System volumetric capacity | > 40 g/L system |
| Low System fill times | 1.5 kg hydrogen/min |

## 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.**

| Storage Parameter | Units | 2020 Target | Ultimate Target |
|---|---|---|---|
| Low System Gravimetric capacity | kg $H_2$/kg system | 0.055 | 0.075 |
| Low System volumetric capacity | kg $H_2$/L system | 0.040 | 0.070 |
| Low System fill times (5 kg) | kg $H_2$/min | 1.5 | 2.0 |
| Min Delivery Pressure | bar | 5 | 3 |
| Operational cycle (1/4 tank to full) | cycles | 1500 | 1500 |

Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan: https://energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22

# Relevance: Recent Advances in $Mg(BH_4)_2$ Research

- **Recent improvements in magnesium borohydride research.**

| | Hydrogenation | | | Dehydrogenation | | Wt % $H_2$ | |
|---|---|---|---|---|---|---|---|
| Dehydrogenation Product | Temp. (˚C) | P (bar) | time (h) | Temp. (˚C) | time (h) | Theory | Exp. |
| $MgB_2$ (HP) | >400 | >900 | 108 | 530 | 20 | 14.8 | 11.4 |
| $MgB_2$ (reactive ball milling/HT-HP) | 400 | 10/400 | 10/24 | 390 | - | 14.8 | 4 |
| $Mg(B_3H_8)_2/2MgH_2$ | 250 | 120 | 48 | 250 | 120 | 2.7 | 2.1 |
| $Mg(B_{10}H_{10})_2(THF)_x/4MgH_2$ | 200 | 50 | 2 | 200 | 12 | 4.9 | 3.8 |

$Mg(BH_4)_2$ ammoniates

- Improved kinetics on dehydrogenation even though, $NH_3$, very stable BN products formed.

$Mg(BH_4)_2$ and $MgB_xH_y(ether)_z$

- Improved $H_2$ cycling kinetics on ether coordination,.
- lower $H_2$ storage capacity.

Current state-of-the-art:

- Better $H_2$ cycling kinetics (lower pressures and temperatures).
- **Lower gravimetric $H_2$ storage capacity.**

**Efforts show plausibility of continuously enhancing kinetics of $Mg(BH_4)_2$ system.**

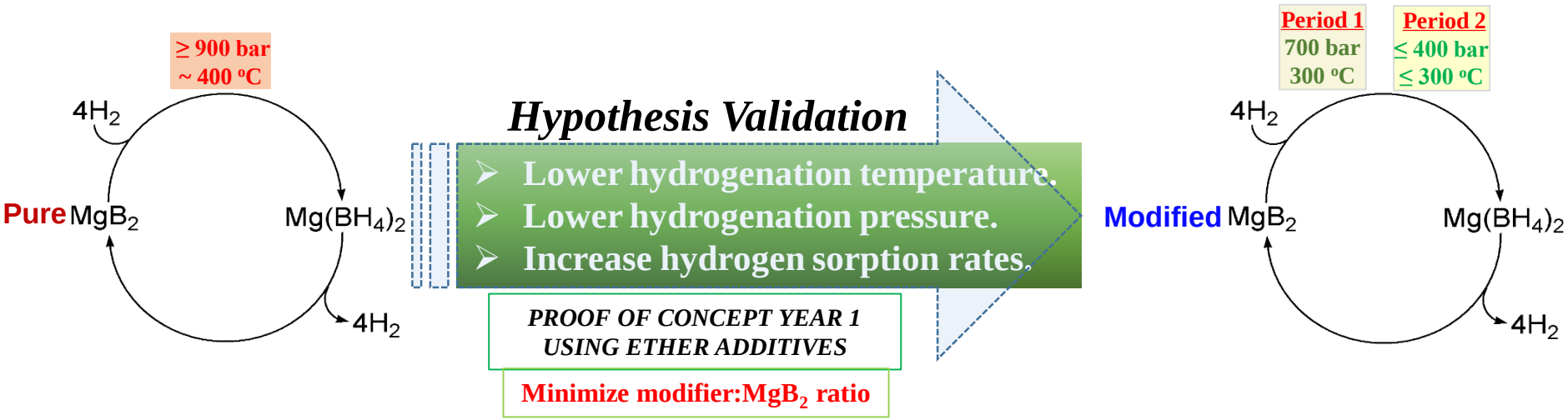
G. Severa, E. Rönnebro, C.M.Jensen; *Chem. Commun.* **2010**, *46*, 421. M. Chong, M. Matsuo, S. Orimo, C.M. Jensen Iinorg. Chem. **2015,** *54*, 4120.; Grigorii Soloveichik, Jae-Hyuk Her, Peter W. Stephens, Yan Gao, Job Rijssenbeek, Matt Andrus, and J.-C. Zhao, Inorg. Chem. **2008**, 47, 4290-4298

# Relevance: Potential for Practical Hydrogen Storage Properties using modified $MgB_2$

**Hypotheses: Coordination or incorporation of additives/modifiers can perturb the $MgB_2$ structure resulting in a destabilized $MgB_2$ material with improved hydrogen storage properties.**

$MgB_2$ + **modifier** → **modified $MgB_2$** $\xrightarrow[\leq 300\ ^oC]{\leq 700\ bar\ H_2}$ $Mg(BH_4)_2$

Formed prior to or during hydriding




**Towards improving hydrogen storage properties of $MgB_2/Mg(BH_4)_2$ 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: ≤ 200 bars, ≤ 200 °C. HyMARC-SNL: ≤700 bars and 300 °C.

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

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

| Milestone | Project Milestones: **(03/01/2018 - 08/31/2019)** | Quarter | Accomplished (02/28/2019) |
|---|---|---|---|
| 1 | Characterize modified $MgB_2$ by FTIR, NMR, XRD & TGA-DSC. | 1 | 100% |
| 2 | Characterize $MgB_2$ composite by FTIR, NMR, XRD & TGA-DSC. | 2 | 100% |
| 3 | Tested $MgB_2$ materials on moderate pressure reactor system. | 4 | 80% |
| 4 | Perform 1 round of hydrogenation per quarter: ≤ 700 bar, ≤ 300 °C. | 3 | 95% |
| 5 | Establish if kinetics of dehydriding of modified Mg boranes are limited by B-H or B-B bond formation or nano-structural effects. | 4 | 50% |
| 6 | Demonstrate 3 cycles of reversible hydrogenation of modified $MgB_2$ materials to $Mg(BH_4)_2$ at 300 °C and 400 bar. | 4 | 40% |

**Go/No-Go Decision: Demonstrate reversible hydrogenation of ≥ 8.0 wt % at ≤ 400 bar and ≤ 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 $\xrightarrow[\text{Mechano-chemistry}]{\text{Ball milling approach}}$ Modified $MgB_2$

[Highly activated product]

T = 0 sec

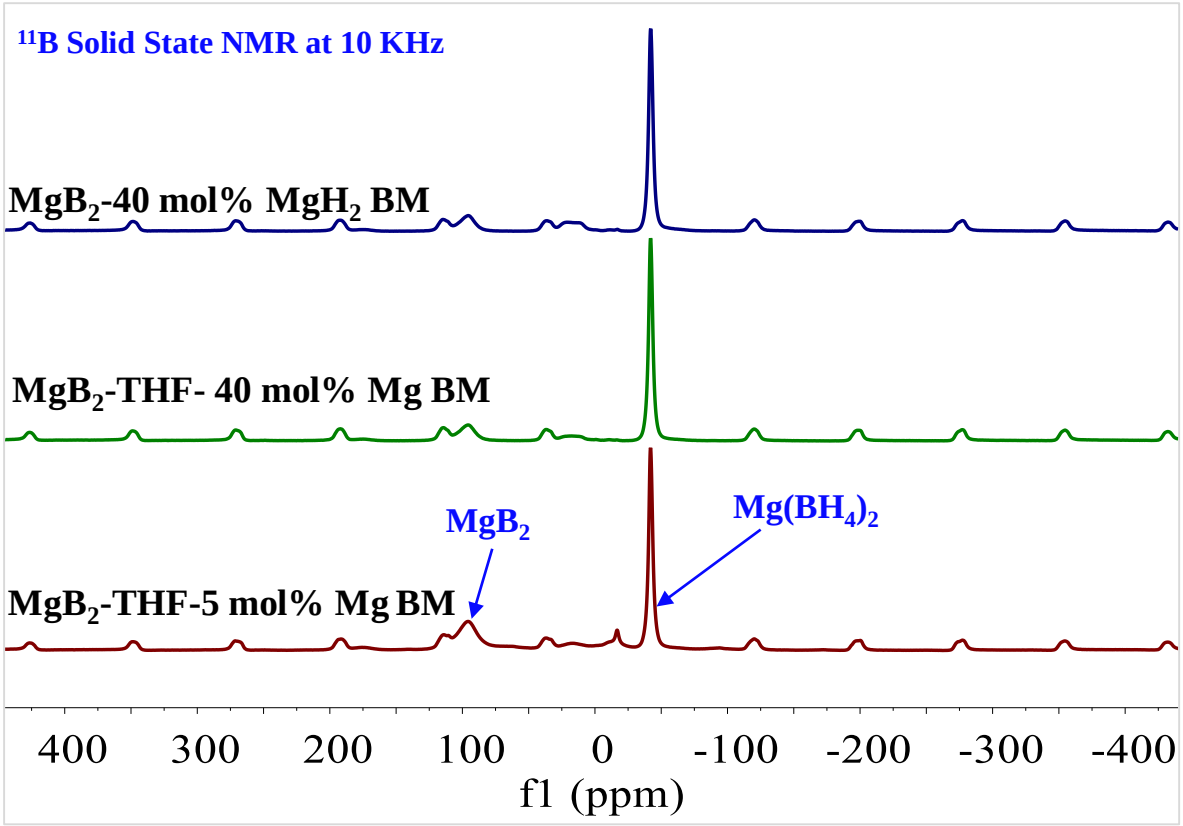
**Evidence of $MgB_2$ modification by THF**

T = t sec
(t > 0)

**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 $^oC$

**Direct confirmation of bulk hydrogenation of $MgB_2$ to $Mg(BH_4)_2$ by modified $MgB_2$**

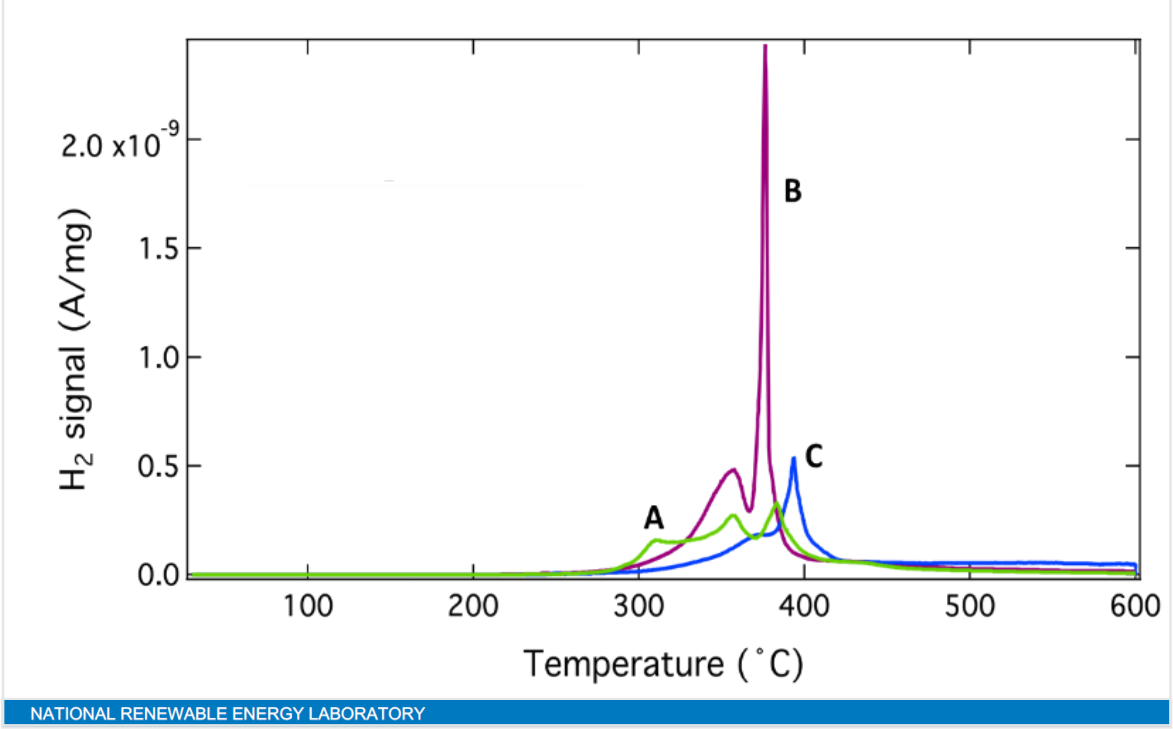



| Ball Milled Hydrogenated Samples | $^{11}B$ NMR line fitting analyses % conversion $MgB_2$ to $Mg(BH_4)_2$ |
|---|---|
| $MgB_2$-THF- 40 mol% Mg | 71 |
| $MgB_2$-THF- 5 mol% Mg | 54 |
| $MgB_2$-40 mol% $MgH_2$ | 68 |

**Potential new pathways for improving kinetics of $MgB_2$ reversible hydrogenation.**

# Accomplishments: TPD Analyses of modified $MgB_2$ 700 bar $H_2$ and 300 °C

**Mostly hydrogen evolved from the hydrogenated modified $MgB_2$ materials**




**Plausibility of different intermediate steps during dehydrogenation half cycle**

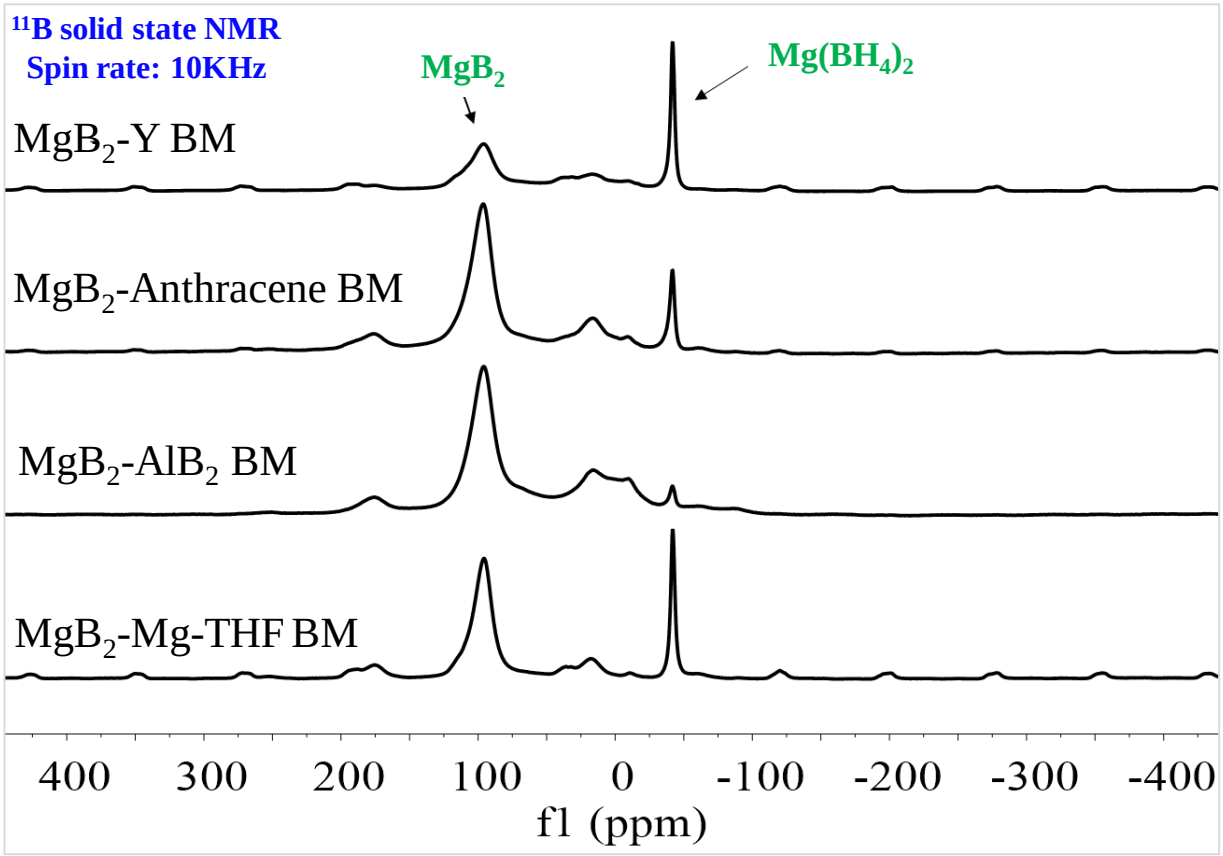
**TPD studies showing $H_2$ release from 300 °C and 700 bar hydrogenated samples of: (A) $MgB_2$-THF-5 mol% Mg (B) $MgB_2$-THF-40 mol % Mg and (C) $MgB_2$-40 mol% $MgH_2$**

**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

$$MgB_2\text{–}10\ mol\%\ X + H_2 \xrightarrow[300\ ^oC]{400\ bar} \text{Magnesium borohydride}$$



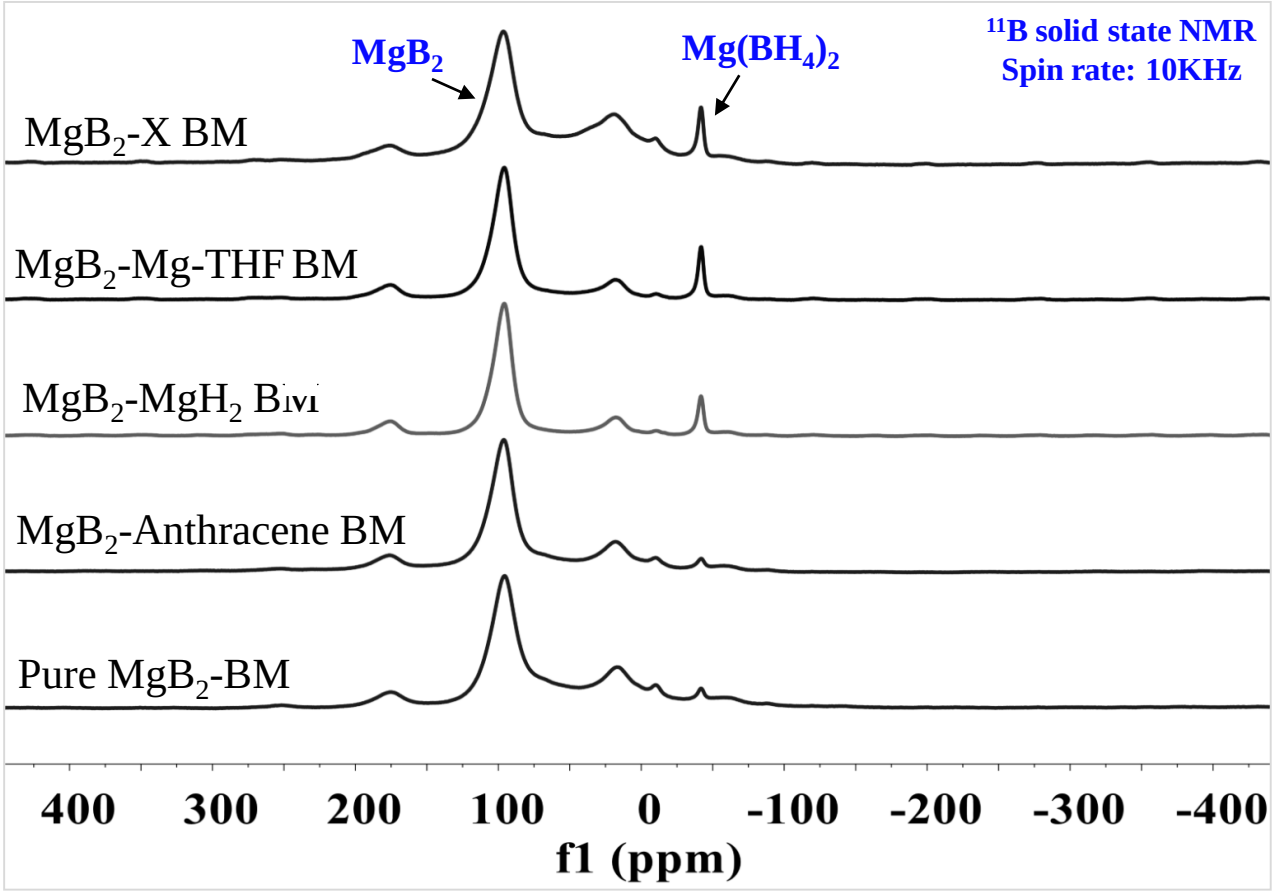

| Ball Milled Hydrogenated Samples | $^{11}B$ NMR line fitting analyses % conversion $MgB_2$ to $Mg(BH_4)_2$ |
|---|---|
| $MgB_2$-THF-Mg BM | 25 |
| $MgB_2$- Y BM | 28 |
| $MgB_2$- Z BM | 36 |

**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 $MgB_2$

## <200 bar $H_2$ and <250 °C

$$MgB_2\text{–}10\ mol\%\ X + H_2 \xrightarrow[<250\ ^oC]{<200\ bar} \text{Magnesium borohydride}$$

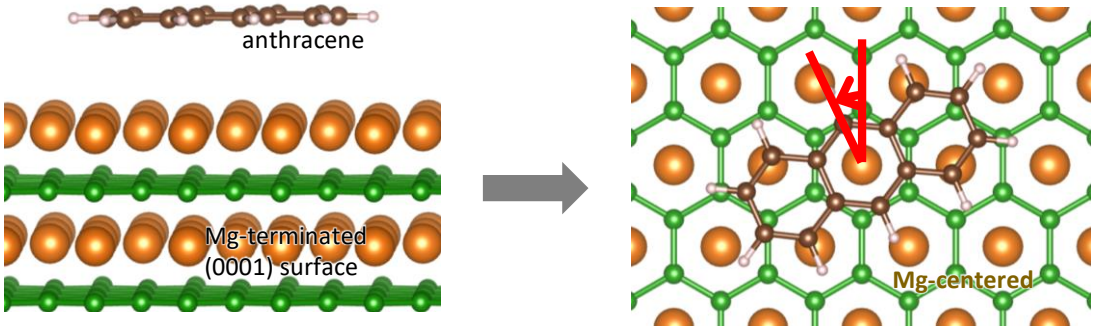


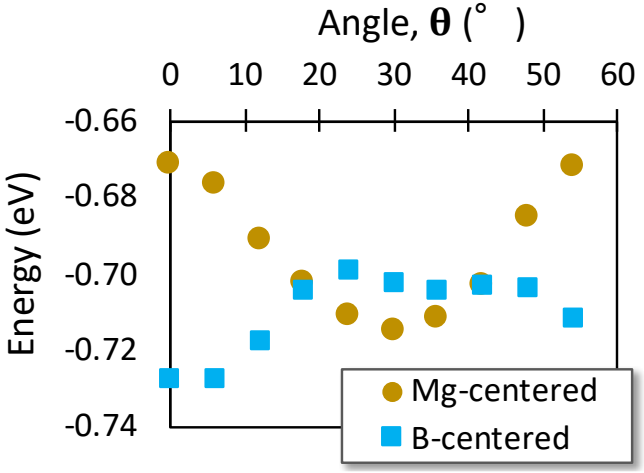

**Plausibility of discovery of additives for improved kinetics of $MgB_2$ to $Mg(BH_4)_2$ at moderate conditions**

**First time hydriding of $MgB_2$ to $Mg(BH_4)_2$ at <250 °C! and <200 bars!**

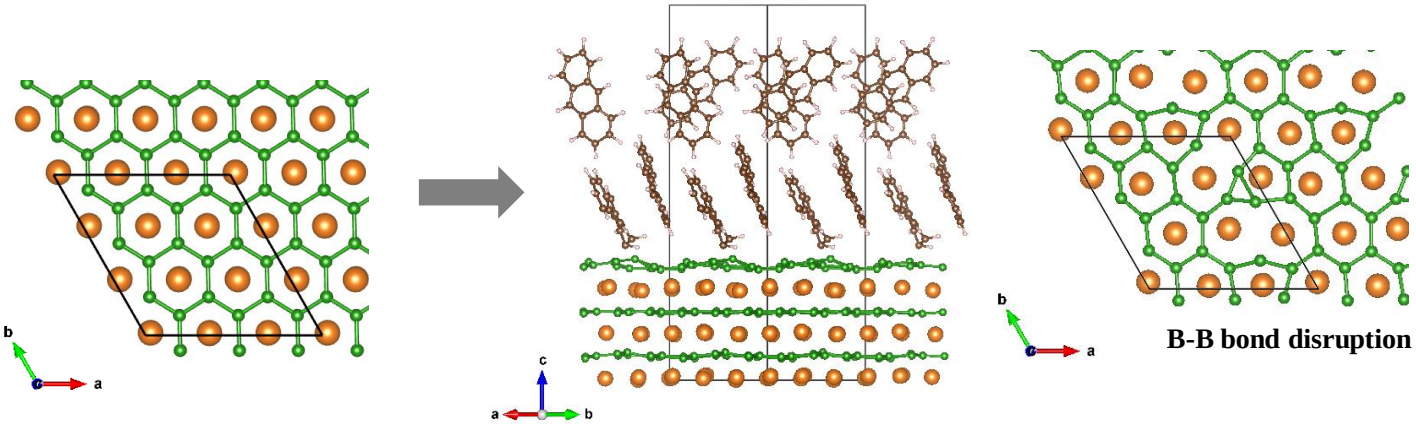
# Accomplishments: Atomistic modeling of Additive-$MgB_2$ interface

**Angle-dependent anthracene-$MgB_2$ interaction energy**




***Ab initio* molecular dynamics of anthracene-$MgB_2$ interface**




**Complementary XAS/XES Studies Scheduled**

**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 $^{o}$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 $^{o}$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.
  - Severa, G.; Jensen, C. M.; Sugai, C.; Kim, S. (2018) Activated Magnesium Boride Materials for Hydrogen Storage. PCT International patent (PCT/US2018/052306)

# Collaborations

| Partners | Project Roles |
|---|---|
| Sandia National Laboratories **(HyMARC)** | Collaborating with Dr. Stavila and Dr. Allendorf:<br>➢ High pressure hydrogenation experiments.<br>➢ XRD analyses. |
| Lawrence Livermore National Laboratory **(HyMARC)** | Collaborating with Dr. Wood, Dr. Kang, Dr. Baker:<br>➢ Molecular dynamic simulations of magnesium boride etherates<br>➢ XES/XAS studies of modified $MgB_2$. |
| National Renewable Energy Laboratory **(HyMARC)** | Collaborating with Dr. Gennett:<br>➢ Temperature programmed desorption.<br>➢ Mass spec analyses of desorbed gas. |

**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 $^{o}$C.

- **UH:** Moderate pressure hydrogenations.
  - Perform hydrogenations of modified $MgB_2$ at $\leq$ 200 bar and $\leq$ 300 $^{o}$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

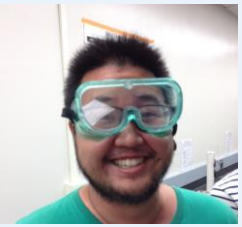
**HYMARC-LLNL:** continue joint theory-experiments studies on effect of additives on hydrogenation of $MgB_2$.

**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 | Contribution |
|---|---|
| Lawrence Livermore National Laboratory | Dr. Wood, Dr. Kang and Dr Baker:<br>➢ Molecular dynamic simulations<br>➢ XES and XAS studies |
| Sandia National Laboratories | Dr. Stavila and Dr. White:<br>➢ High pressure hydrogenations. |
| National Renewable Energy Laboratory | Dr. Gennett, Dr. Leick and Ms. Martinez:<br>➢ Temperature programmed desorption. |
| University of Geneva | Dr . Hagemann and Ms Gigante.<br>➢ Raman studies of modified $MgB_2$ |

**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 $^oC$ and 400 bar.
- Demonstrated hydrogenation of $MgB_2$ to $Mg(BH_4)_2$ at ≤ 250 $^oC$ 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 $^oC$).

| Bulk $MgB_2$ Hydrogenation Conditions | State of Art [Pure $MgB_2$] | FY 17 Results [modified $MgB_2$] | FY 18 Results [modified $MgB_2$] |
|---|---|---|---|
| Pressure/ bar | 950 | **700** | **≤ 400** |
| Temperature/ $^oC$ | ~400 | **300** | **≤ 300** |
| Wt % hydrogen | 11 wt % | 7-8 wt % | |
| % Conversion: $MgB_2$ to $Mg(BH_4)_2$ | 75 % [Sieverts method: wt% $H_2$] | 71 % [$^{11}B$ solid state NMR line fitting method] | 36 % [$^{11}B$ solid state NMR line fitting method] |

**Research shows plausibility of finding additives capable of vastly improving kinetics of $MgB_2$ hydrogenation to $Mg(BH_4)_2$**

# Technical Back-Up Slides

# Reviewer-Only Slides