

Development of Magnesium Boride Etherates as Hydrogen Storage Materials

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Merit Review**

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Project ID # ST138

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Overview

Timeline

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

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

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

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

Relevance: Recent Advances in $\text{Mg}(\text{BH}_4)_2$ Research

- Recent improvements in magnesium borohydride research.

Dehydrogenation Product	Hydrogenation			Dehydrogenation		Wt % H_2	
	Temp. ($^\circ\text{C}$)	P (bar)	time (h)	Temp. ($^\circ\text{C}$)	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
$\text{Mg}(\text{B}_3\text{H}_8)_2/2\text{MgH}_2$	250	120	48	250	120	2.7	2.1
$\text{Mg}(\text{B}_{10}\text{H}_{10})_2(\text{THF})_x/4\text{MgH}_2$	200	50	2	200	12	4.9	3.8

$\text{Mg}(\text{BH}_4)_2$ ammoniates

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

$\text{Mg}(\text{BH}_4)_2$ and $\text{MgB}_x\text{H}_y(\text{ether})_z$

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

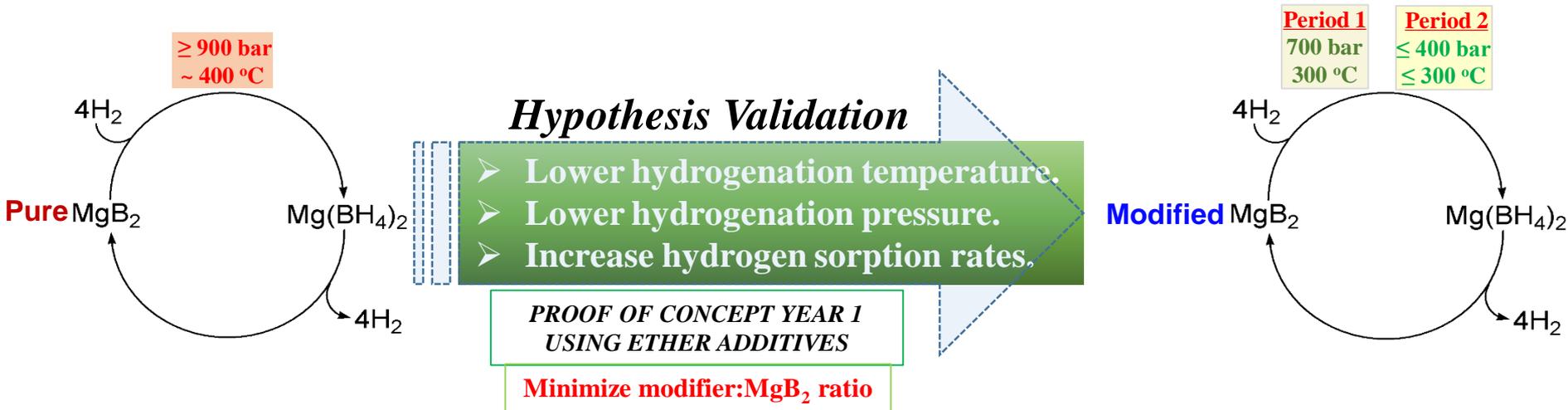
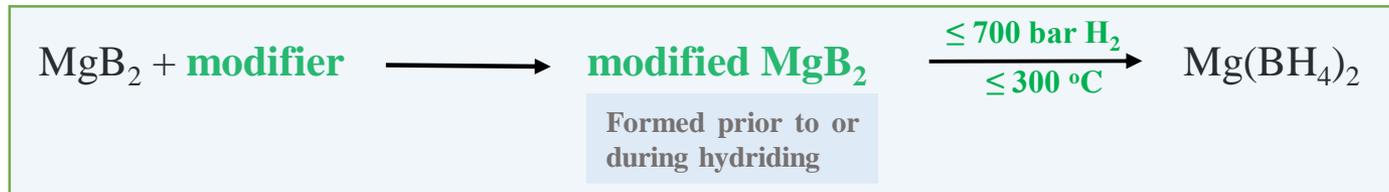
Current state-of-the-art:

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

Efforts show plausibility of continuously enhancing kinetics of $\text{Mg}(\text{BH}_4)_2$ system.

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.



Towards improving hydrogen storage properties of $\text{MgB}_2/\text{Mg(BH}_4)_2$ system.

Approach: Synthesize, Characterize and Hydrogenate Modified MgB₂ Materials

Experimental Approach: Period 2

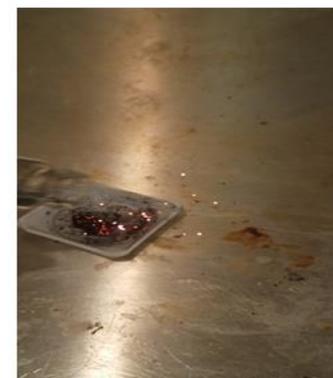
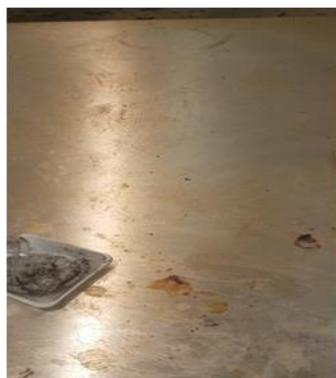
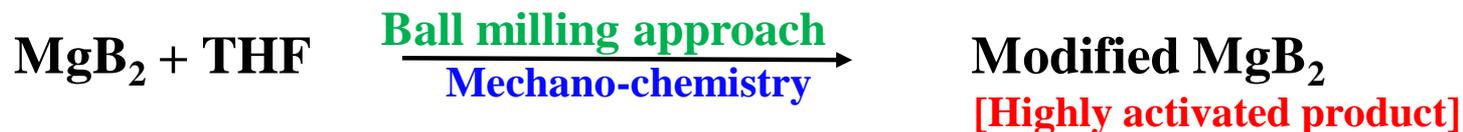
- A. Synthesis of modified MgB₂ materials:** Direct reactions of MgB₂ with additives.
- Reactive ball milling, heat treatment and ultra sonication approaches
- B. Hydrogenation reactions:** UH: ≤ 200 bars, ≤ 200 °C. HyMARC-SNL: ≤700 bars and 300 °C.
- D. Computation Experiments:** HyMARC-LLNL: *Ab initio* 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 dehydrogenation 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 MgB₂ to Mg(BH₄)₂

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

Accomplishments: MgB₂ Structure Perturbation by THF



T = 0 sec

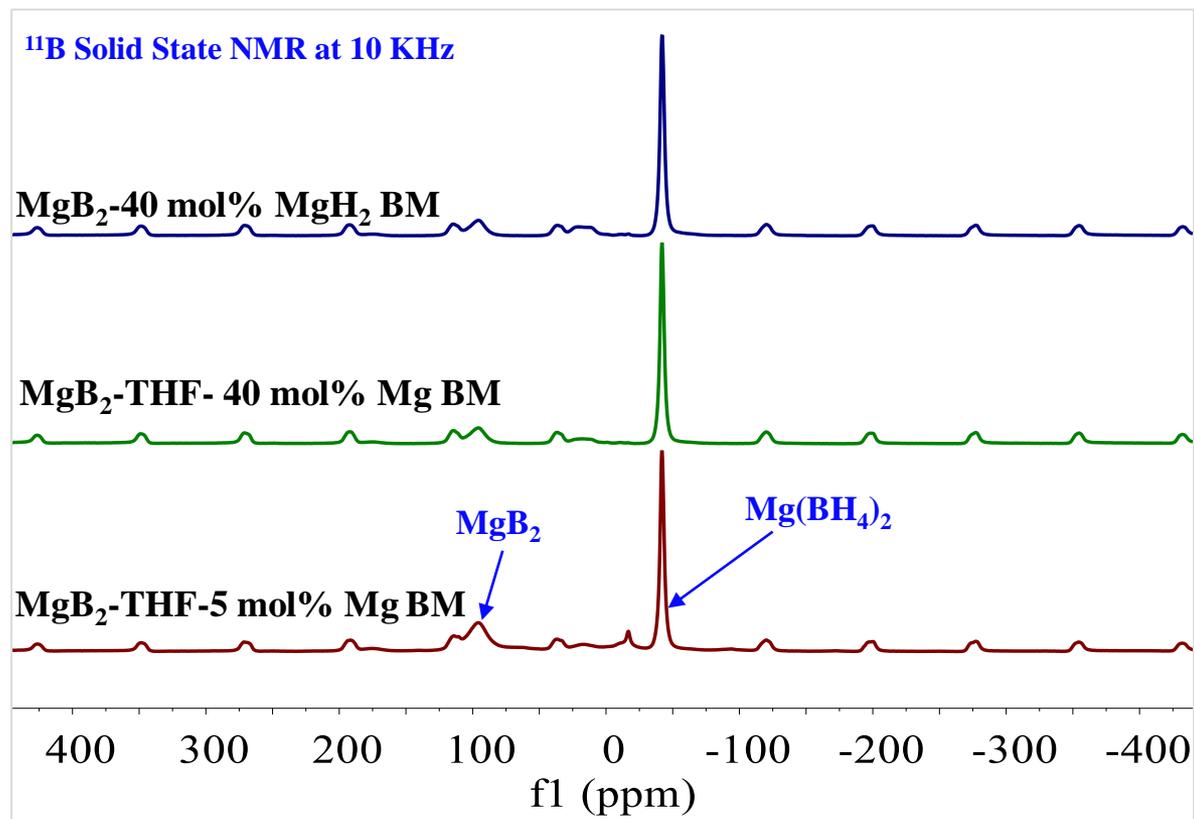
Evidence of MgB₂ modification by THF

T = t sec
(t > 0)

Activated product observed from MgB₂ 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 $\text{Mg}(\text{BH}_4)_2$ by modified MgB_2

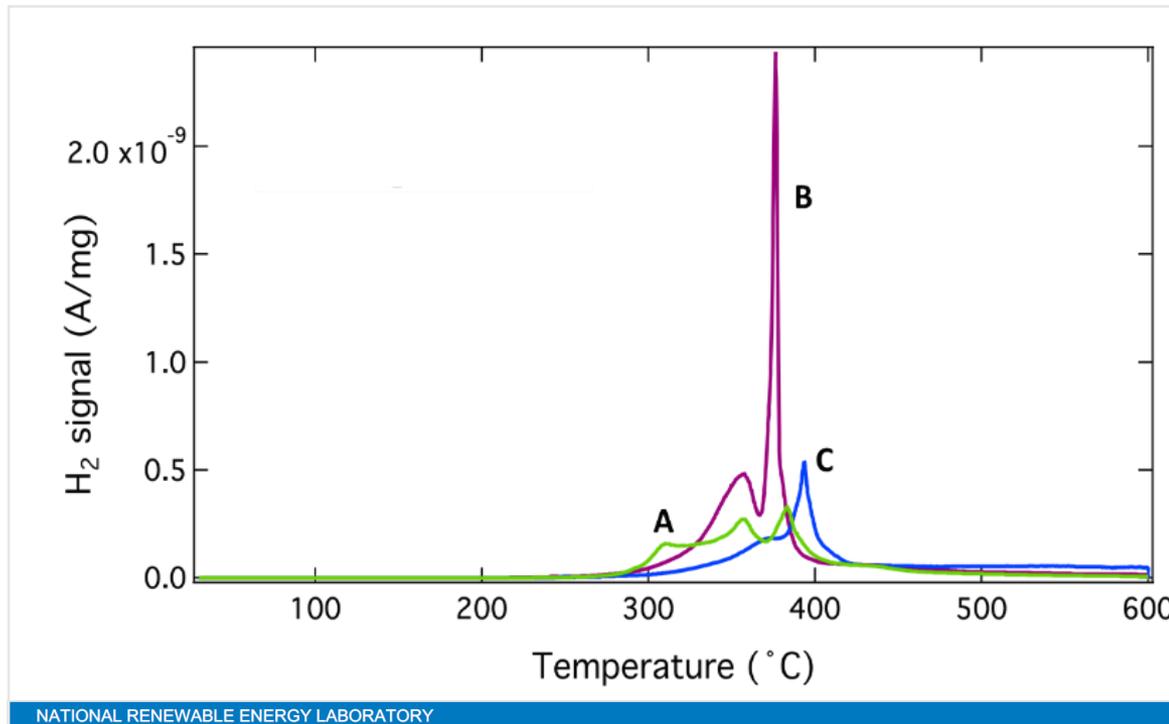


Ball Milled Hydrogenated Samples	^{11}B NMR line fitting analyses % conversion MgB_2 to $\text{Mg}(\text{BH}_4)_2$
MgB_2 -THF-40 mol% Mg	71
MgB_2 -THF-5 mol% Mg	54
MgB_2 -40 mol% MgH_2	68

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



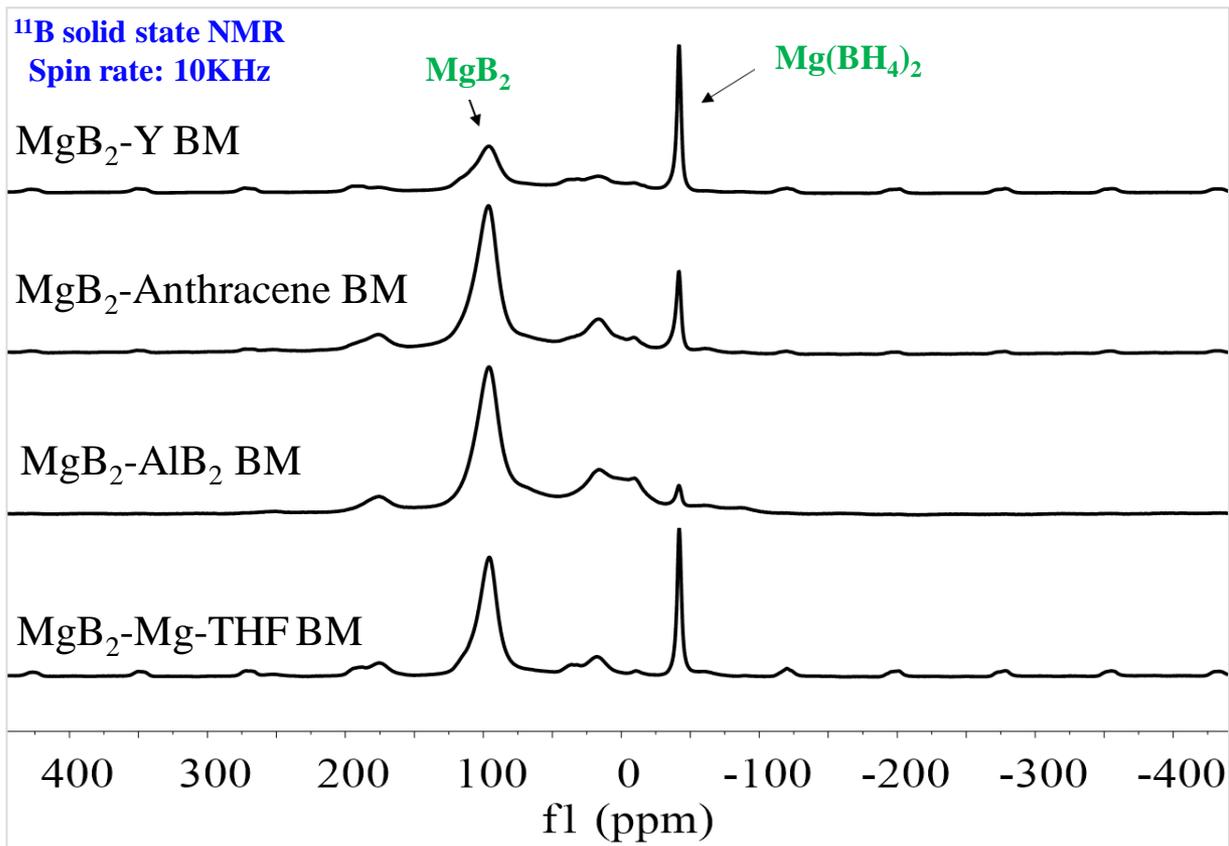
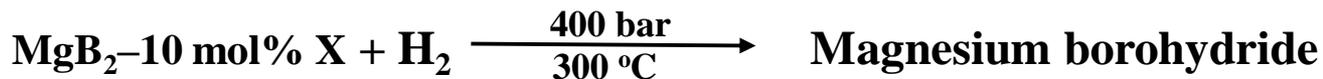
Plausibility of different
intermediate steps
during dehydrogenation
half cycle

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

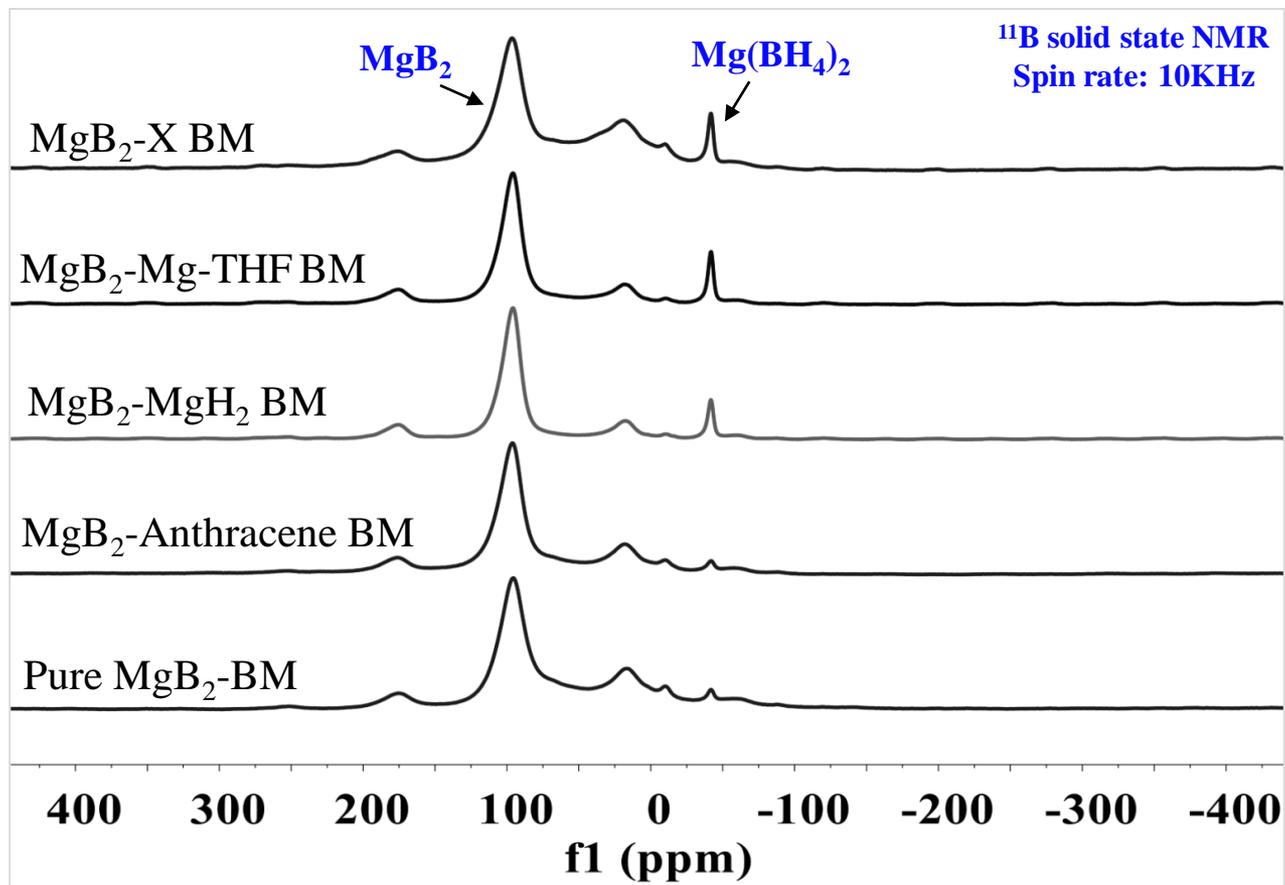
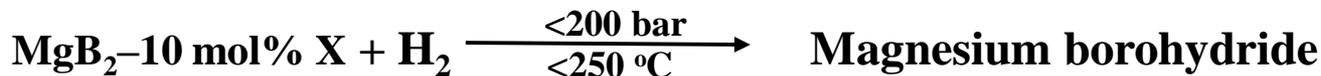
400 bar H_2 and 300 °C



Ball Milled Hydrogenated Samples	^{11}B NMR line fitting analyses % conversion MgB_2 to $\text{Mg}(\text{BH}_4)_2$
MgB ₂ -THF-Mg BM	25
MgB ₂ - Y BM	28
MgB ₂ - Z BM	36

First time hydriding of MgB_2 to $\text{Mg}(\text{BH}_4)_2$ at 300 °C! and 400 bars!

Accomplishments: ^{11}B Solid State NMR of modified MgB_2 <200 bar H_2 and <250 $^\circ\text{C}$

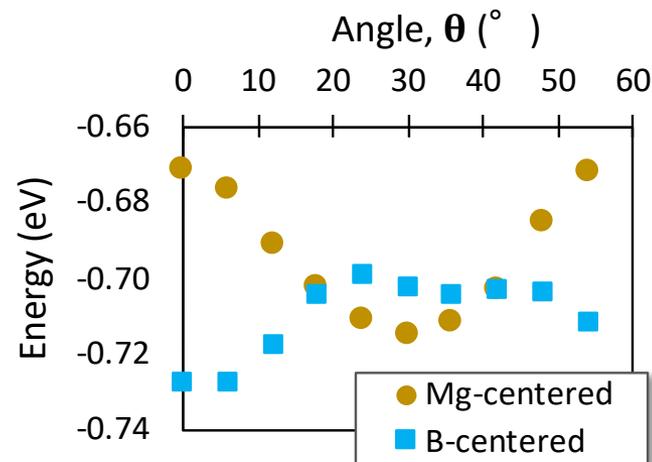
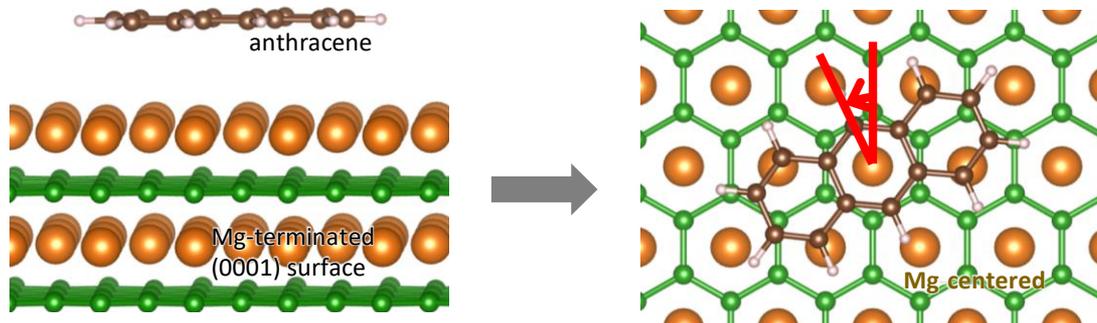


Plausibility of discovery
of additives for
improved kinetics of
 MgB_2 to $\text{Mg}(\text{BH}_4)_2$ at
moderate conditions

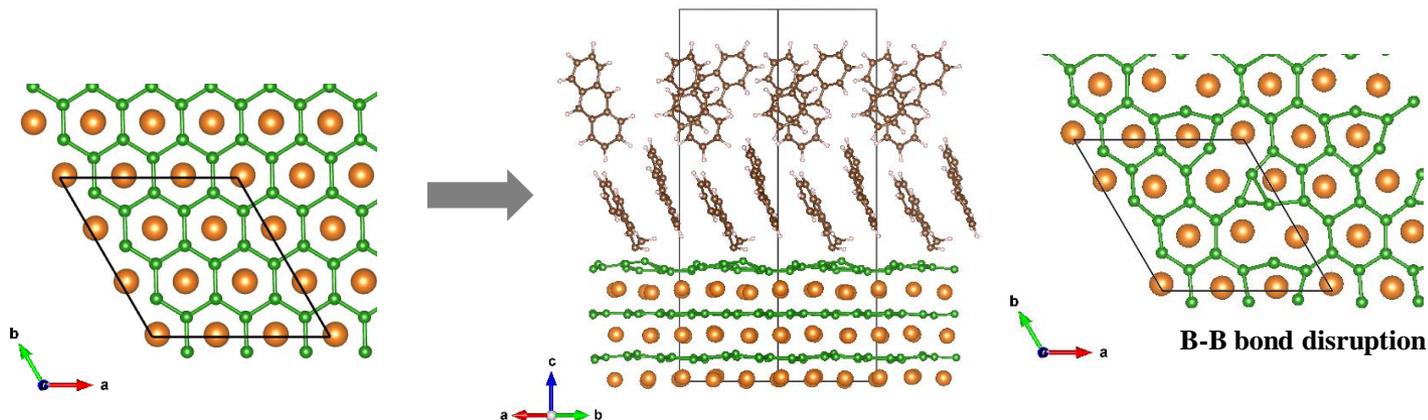
First time hydriding of MgB_2 to $\text{Mg}(\text{BH}_4)_2$ at <250 $^\circ\text{C}$! and <200 bars!

Accomplishments: Atomistic modeling of Additive-MgB₂ interface

Angle-dependent anthracene-MgB₂ interaction energy



Ab initio molecular dynamics of anthracene-MgB₂ interface



Complementary
XAS/XES
Studies
Scheduled

Joint Theory-Experiments in Progress: Investigation of relative reactivity of MgB₂ THF vs. Anthracene.

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 ≥ 8 wt% at 400 bar at 300 °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: <ul style="list-style-type: none">➤ High pressure hydrogenation experiments.➤ XRD analyses.
Lawrence Livermore National Laboratory (HyMARC)	Collaborating with Dr. Wood, Dr. Kang, Dr. Baker: <ul style="list-style-type: none">➤ Molecular dynamic simulations of magnesium boride etherates➤ XES/XAS studies of modified MgB_2.
National Renewable Energy Laboratory (HyMARC)	Collaborating with Dr. Gennett: <ul style="list-style-type: none">➤ Temperature programmed desorption.➤ 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 ≤ 400 bar and ≤ 300 °C.
- **UH:** Moderate pressure hydrogenations.
 - Perform hydrogenations of modified MgB_2 at ≤ 200 bar and ≤ 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	Contribution
Lawrence Livermore National Laboratory	Dr. Wood, Dr. Kang and Dr Baker: <ul style="list-style-type: none">➤ Molecular dynamic simulations➤ XES and XAS studies
Sandia National Laboratories	Dr. Stavila and Dr. White: <ul style="list-style-type: none">➤ High pressure hydrogenations.
National Renewable Energy Laboratory	Dr. Gennett, Dr. Leick and Ms. Martinez: <ul style="list-style-type: none">➤ Temperature programmed desorption.
University of Geneva	Dr . Hagemann and Ms Gigante. <ul style="list-style-type: none">➤ Raman studies of modified MgB₂

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 $\text{Mg}(\text{BH}_4)_2$ at 300 °C and 400 bar.
- Demonstrated hydrogenation of MgB_2 to $\text{Mg}(\text{BH}_4)_2$ at ≤ 250 °C and ≤ 200 bar, $\text{Mg}(\text{BH}_4)_2$ yields currently less than 10%, based on ^{11}B NMR line fitting analyses.
- Hydrogenation of MgB_2 to $\text{Mg}(\text{BH}_4)_2$ at conditions relevant to onboard hydrogen storage appear plausible (< 200 bar and < 200 °C).

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/ °C	~400	300	≤ 300
Wt % hydrogen	11 wt %	7-8 wt %	
% Conversion: MgB_2 to $\text{Mg}(\text{BH}_4)_2$	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 $\text{Mg}(\text{BH}_4)_2$