Development of Magnesium Boride Etherates as Hydrogen Storage Materials

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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: 35 %

Barriers

Barrier	Project Goals
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: $ 239,102.42 as of 3/31/18

Partners

- HyMARC Consortium
  - **SNL**: High Pressure Hydrogenation
  - **SNL**: Material Characterizations
  - **LLBL** & **LLNL**: Theoretical Modelling
  - **NREL:** Material Characterizations

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	0.045	0.065
Low System volumetric capacity	kg H_2/L system	0.030	0.050
Low System fill times (5.6 kg)	min	3-5	3-5
Min Delivery Pressure	bar	5	5
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		Cycling wt%	
Dehydrogenation Product	Temp ˚C	P atm	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**
$Mg_{0.75}Mn_{0.25}B_2$	380	150	38	225-400	-	>11	**1**
$Mg(B_3H_8)_2(THF)_x/2MgH_2$	200	50	2	180	12	<2.5	
$Mg(B_3H_8)_2/2MgH_2$	250	120	48	250	120	2.7	**2.1**
$Mg(B_{10}H_{10})_2(THF)_x/4MgH_2/X$	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 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.

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Grigorii Soloveichik, Jae-Hyuk Her, Peter W. Stephens, Yan Gao, Job Rijssenbeek, Matt Andrus, and J.-C. Zhao, Inorg. Chem. **2008**, 47, 4290-4298
J. J. Vajo, J Graetz, V Stavila, L Klebanoff, E Majzoub, FY **2015** DOE Annual Progress Report

Relevance: 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.

$$\text{Ether modified } MgB_2 + 4H_2 \longrightarrow Mg(BH_4)_2$$

Mols ether/ Mol MgB_2 (x)	0.70	0.40	0.20	0.10	0.05
Wt % Hydrogen					
$MgB_2(OMe_2)_x$	9.4	11.1	12.8	13.8	14.3
$MgB_2(THF)_x$	7.7	9.7	11.8	13.2	14.0
$MgB_2(OCH_2Me_2)_x$	7.6	9.6	11.7	13.1	14.0
$MgB_2(Dioxane)_x$	7.0	9.0	11.3	12.8	13.8
$MgB_2(polyether)_x$				>12	>12

Minimize ether:MgB_2 ratio

IDEALLY:
Sub-Stoichiometric amounts of ether

Hypothesis Validation

- Lower bulk MgB_2 hydrogenation temperature: From 400 to **300 °C**
- Lower bulk MgB_2 hydrogenation pressure: From >900 to **700 bar**.
- Increase MgB_2 hydrogen sorption rates.

PROOF of CONCEPT

Potential to improve practical hydrogen storage properties of $MgB_2/Mg(BH_4)_2$ system.

Approach: Synthesize, Characterize and Hydrogenate Modified MgB_2 Materials

Experimental Approach: YEAR 1

A. Synthesis of MgB_2 etherates by reactive ball milling and heat treatments from:

- Direct reaction of MgB_2 with ethers in presence/absents of other additives.

B. Hydrogenation reactions:

UH: ≤ 150 bars, ≤ 300 °C. HyMARC-SNL: ≤1000 bars, ≤ 400 °C.

C. Characterizations: FTIR, TGA-DSC, XRD, NMR, TPD.

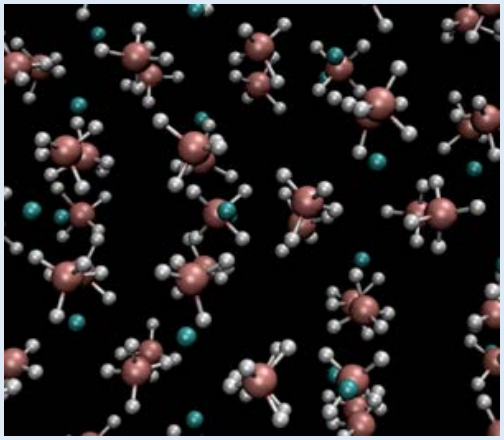
Go/No-Go Decision : Demonstrate ≥7.0 wt % hydrogen uptake by a MgB_2 etherate at ≤300 ˚C, 700 bars 48 hrs and reversible release of ≥ 2 wt% H_2 by at least one MgB_2 etherate: MET

Milestone #	YEAR 2: Project Milestones: (03/01/2018 - 02/28/2019)	Quarter	Accomplished (03/31/2018)
1	Characterize modified MgB_2 by FTIR, NMR, XRD & TGA-DSC.	1	25%
2	Characterize MgB_2 composite by FTIR, NMR, XRD & TGA-DSC.	2	10%
3	Complete design and fabrication of medium pressure reactor.	2	10%
4	Perform 1 round of hydrogenation per quarter: ≤ 700 bar, ≤ 300 °C.	3	0%
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	0%
6	Demonstrate 5 cycles of reversible hydrogenation of modified MgB_2–THF materials to $Mg(BH_4)_2$ at 300 °C and 700 bar.	4	0%
GNG	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 $Mg(BH_4)_2$	4	

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

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 by coordinating species.

HyMARC:LLNL

Dr. B. Wood and Dr. S. Kang

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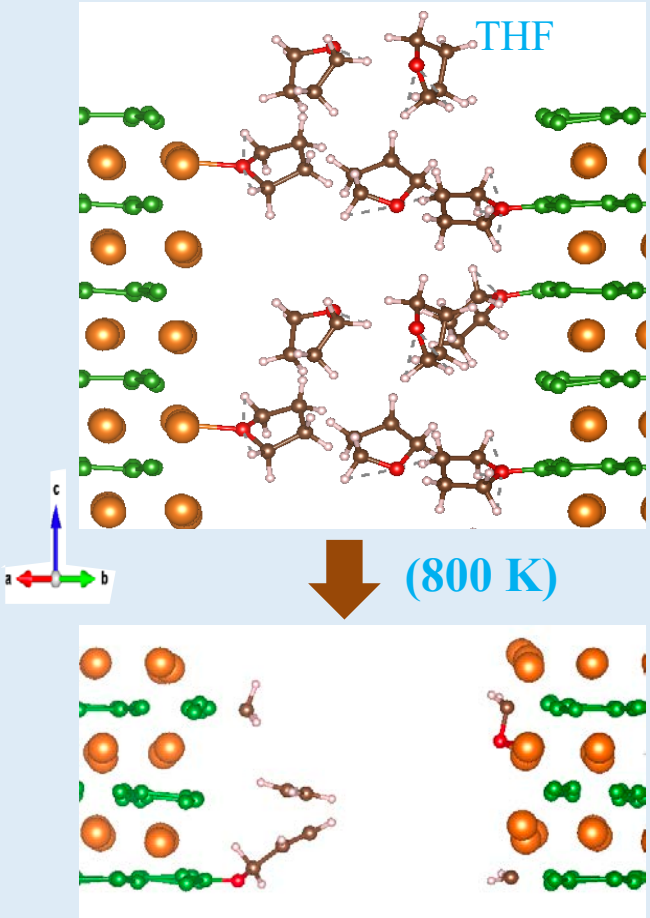
Accomplishments: Molecular Dynamic Simulations

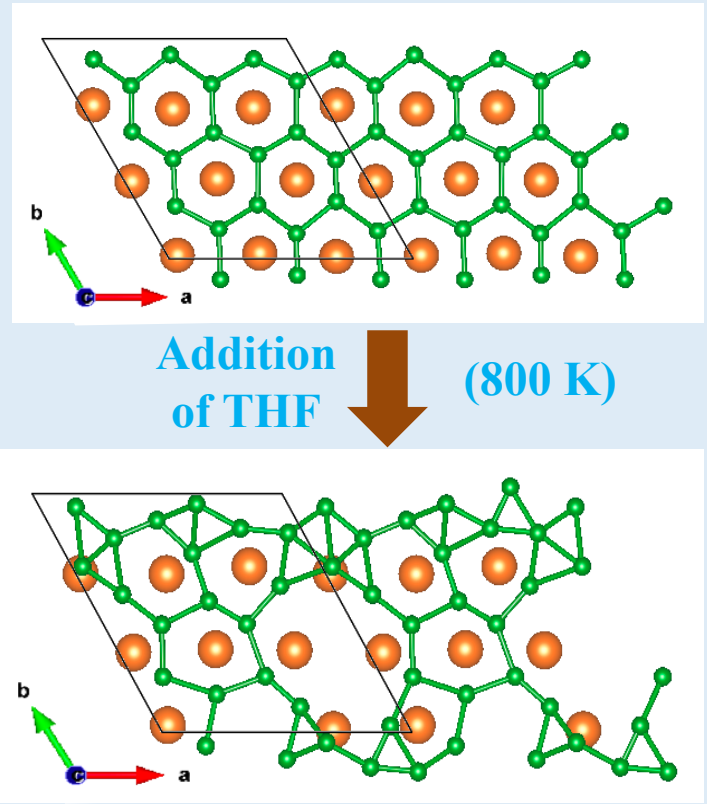
Orientation-dependent reactivity of MgB_2 with THF

EDGE PLANE



Reactive MgB_2 edge plane decomposes THF into ethylene etc.

BASAL PLANE



Ethers destabilize surface boron sheet and create structural defects.

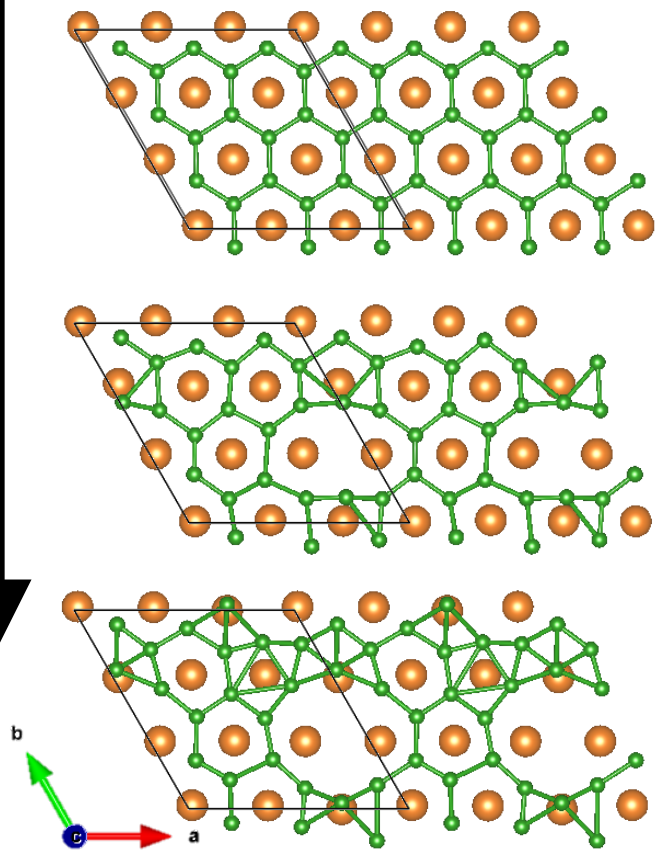
→ Origin of structure deformation?

Accomplishments: Molecular Dynamic Simulations

MgB_2 basal plane structure evolution in presence of THF

Structure evolution in THF

Simulation time

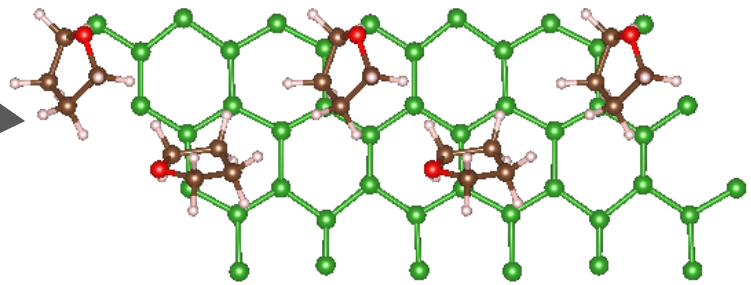


(~0.1 ps)

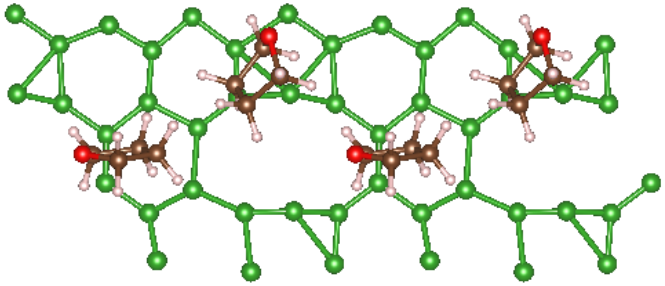
(~0.2 ps)

(~0.3 ps)

THF can induce defect formation in MgB_2 which may facilitate hydrogenation.



No THF Decomposition observed



Defect formation also observed in electron deficient solvent free MgB_2,

MD Simulations validate hypothesis and support experimental findings.

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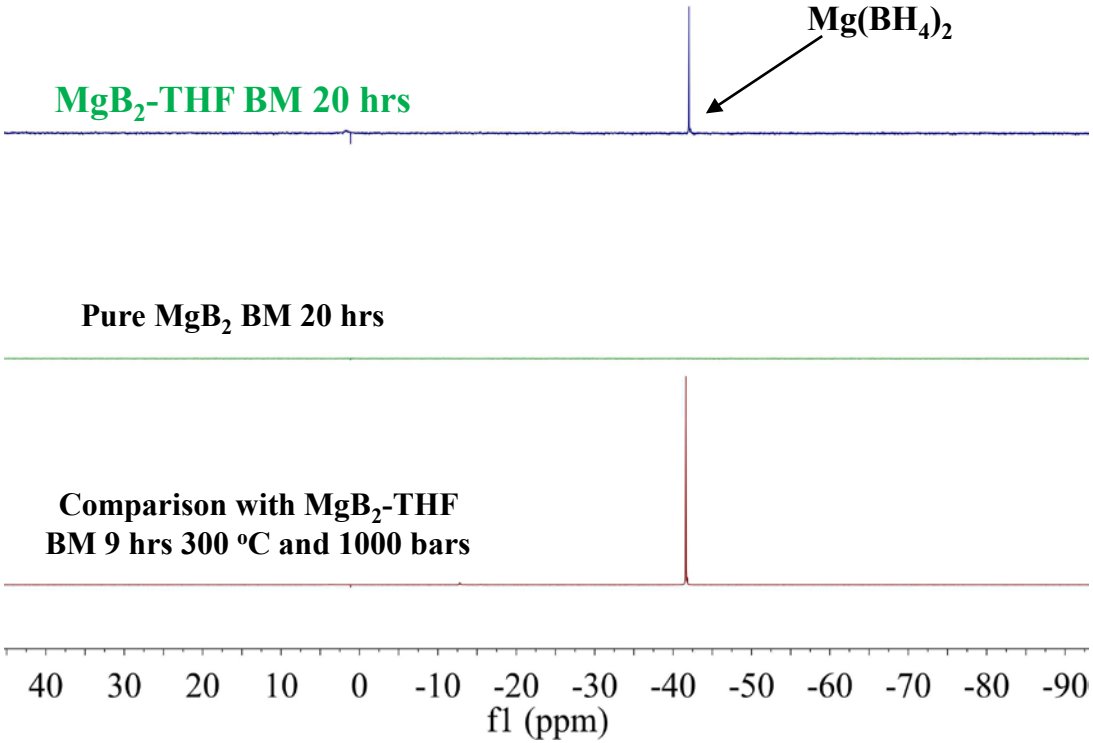
Accomplishments: MgB_2-Ether Hydrogenation Studies

FIRST TIME hydrogenation of MgB_2 to $Mg(BH_4)_2$ at 700 bars!

$$MgB_2\text{-THF} + H_2 \xrightarrow[300\ ^oC]{700\ bar} \text{Magnesium borohydride}$$

Only MgB_2-THF BM samples showed hydrogen uptake at 300 °C and 700 bar.

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



<u>11B Solution NMR:</u>
Qualitative evidence of simultaneous lowering of MgB_2 hydrogenation temp and pressure

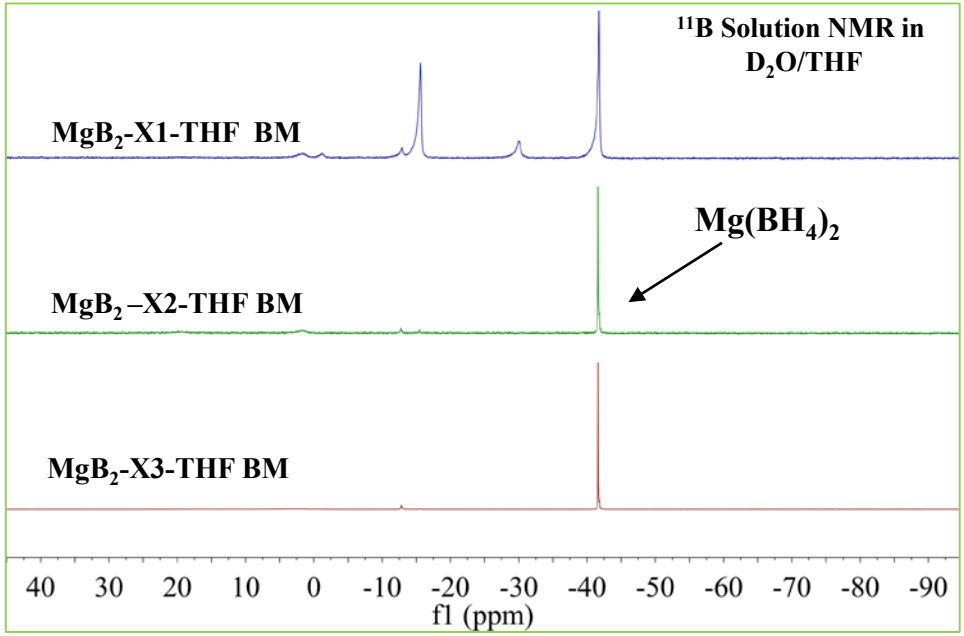
Lowering of PRESSURE required for MgB_2 hydrogenation to 700 bar
Vastly improved kinetics of hydrogenation.

Accomplishments: MgB_2-THF-X Hydrogenation Studies

First time hydrogenation of bulk MgB_2 to $Mg(BH_4)_2$ at 300 °C! and 700 bars!

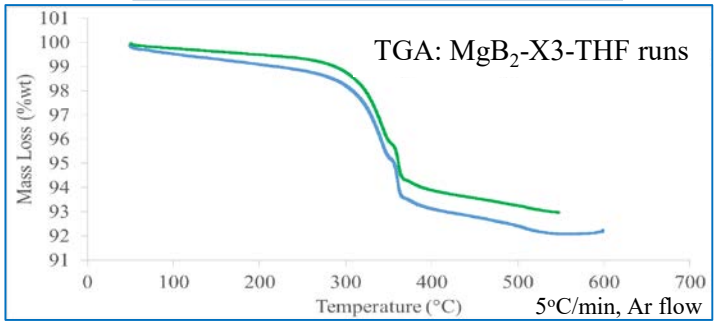
$$MgB_2\text{–X-THF} + H_2 \xrightarrow[300\ ^{o}C]{700\ bar} \text{Magnesium borohydride}$$

Potential of cooperative effects: THF-X additive combination enhanced H_2 uptake of MgB_2 system.



TGA mass loss (%) up to <600 °C for samples H_2 treated at 300 °C, 700 bars & 72 hours

Sample	mass loss (%)
MgB_2 -pure	0
MgB_2-X1-THF	2.5
MgB_2-X2-THF	1.7
MgB_2-X3-THF	6.3-7.2



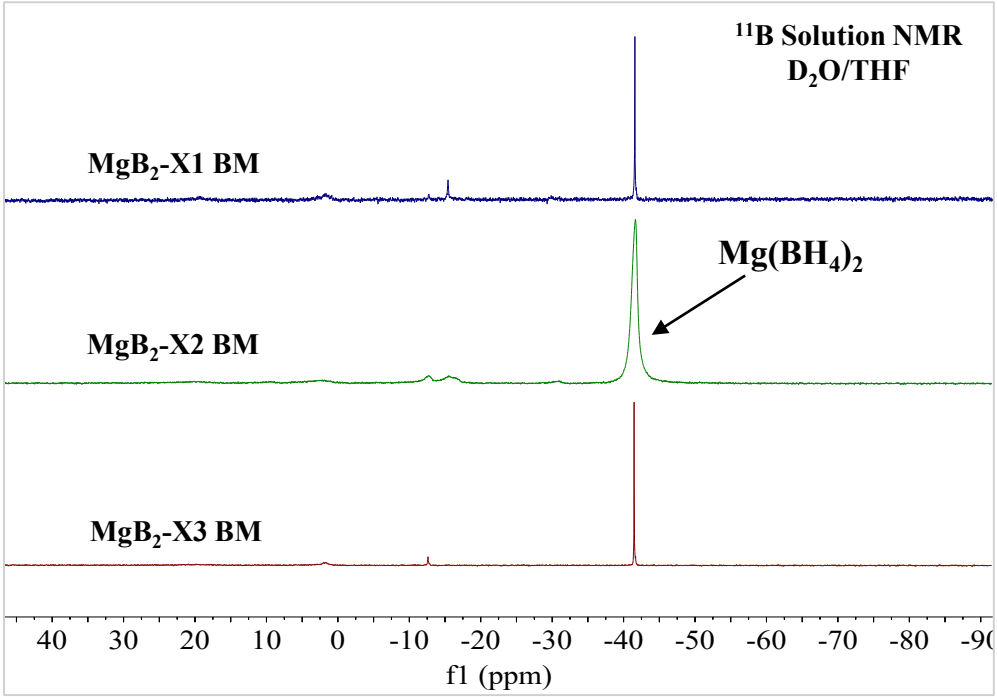
Vastly improved kinetics of hydrogenation of bulk MgB_2 at 300 °C! and 700 bars!

Accomplishments: MgB_2-X Hydrogenation Studies

First time hydrogenation of MgB_2 to $Mg(BH_4)_2$ at 300 °C! and 700 bars! in absence of ether!

$$MgB_2\text{–}X + H_2 \xrightarrow[300\ ^{o}C]{700\ bar} \text{Magnesium borohydride}$$

THF "like effects" on MgB_2, observed with other additives!!!

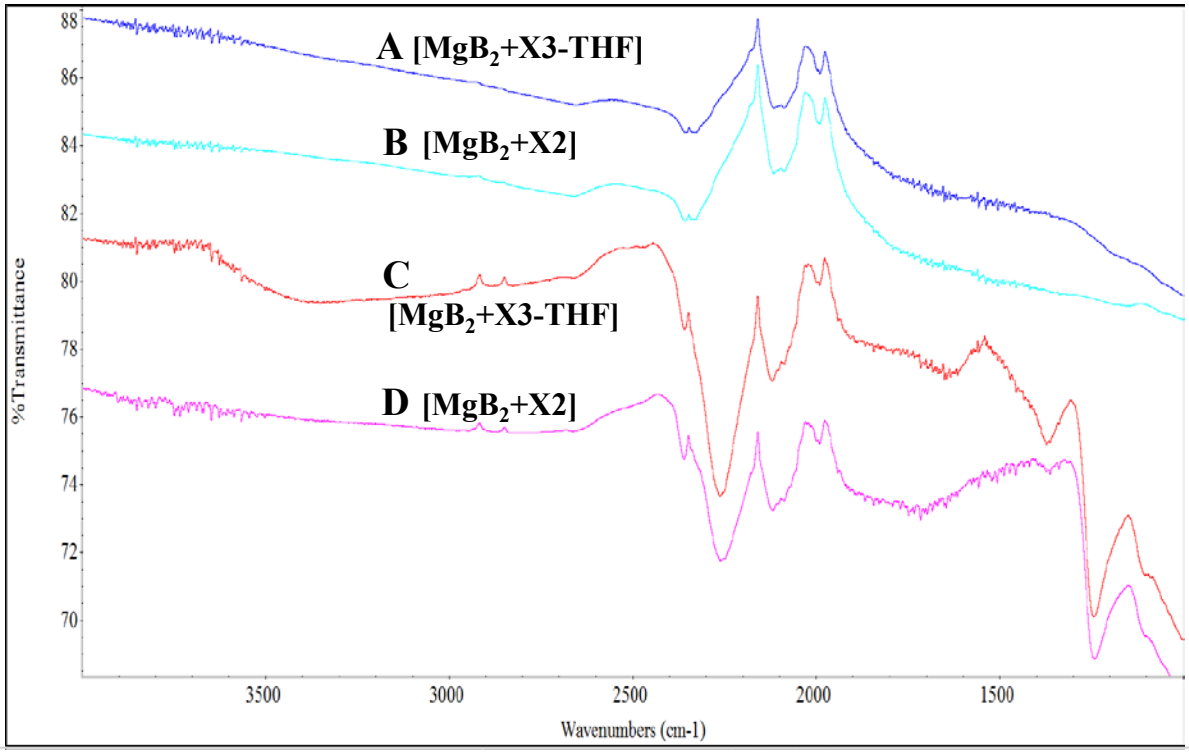


Expansion of MgB_2 perturbation hypothesis beyond ether incorporation

Potential new pathways for improving kinetics of MgB_2 hydrogenation.

Accomplishments: IR Analyses of Hydrogenated Samples

FT-ATR analyses of hydrogenated MgB_2-X3-THF and MgB_2-X2 samples



<u>Pre hydrogenated samples:</u> (A) MgB_2+X3-THF and (B) MgB_2-X2 ;

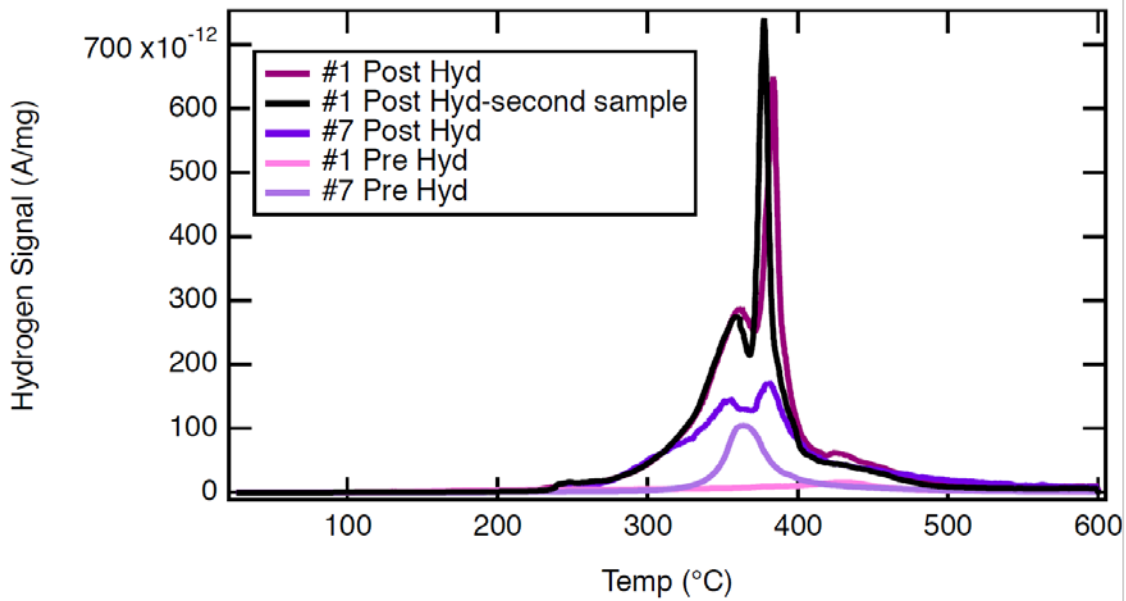
<u>Post hydrogenated samples (700 bar, 300 °C)</u> : (C) MgB_2-X3-THF and (D) MgB_2-X2.

Typical $Mg(BH_4)_2$ vibrations in the 2200-2300 cm^{-1} and 1200-1300 cm^{-1} region are observed after hydrogenation.

Accomplishments: TPD Analyses of Evolved Gases

NREL Data: Phase 1 GNG Data Validation.

Analyses of gases evolved on heat treatment of MgB_2-X3-THF and MgB_2-X1



TPD studies showing H_2 desorbed from MgB_2+X3-THF (#1) and MgB_2+ X2 (#7) samples, Pre and Post hydrogenation (300 °C and 700 bar).

Sample	TPD H_2 wt loss (%)
MgB_2-X2 (#7) [Post-Hyd]	5.2
MgB_2-X3—THF (#1) [Post-Hyd]	7.3-8.1

Mostly hydrogen evolved from the hydrogenated MgB_2 based materials.

Accomplishments: Responses to Previous Year Reviewers' Comments

- **Explore how catalysts/other additives affect the H_2 sorption kinetics in the MgB_2-ether system, consider adding that to the future work plan.**
  - Exploring MgB_2-THF-X system.
  - Targeting to make composite MgB_2 materials that can be hydrogenated at much lower pressures and temperatures.
- **Feedback-driven syntheses.**
  - Results from hydrogenation and computational experiments are being utilized to optimize syntheses of improved modified MgB_2 materials.
- **More interaction with HyMARC modeling team.**
  - Enhanced collaboration with Dr. Wood's group with feed back loops between computation and experiments.
  - Ab *initio* MD simulation integrated into experimental tasks in SOPO.
  - Monthly meetings with HyMARC modelling team.

Current and Future Work Addresses AMR Reviewer Comments.

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

Remaining Challenges and Barriers

- Lowering of hydrogenation pressure to 400 bar at 300 ^{o}C whilst improving hydrogen uptake to $\geq$8 wt%.

- Hydrogen cycling of the modified MgB_2 materials.

- Understanding mechanism of hydrogenation enhancement in defected or composite magnesium borides.

Technology Transfer Activities: Provisional patent filed by University of Hawaii on the modified MgB_2 materials.

Collaboration

Partners	Project Roles
Sandia National Laboratories (HyMARC)	Collaborating with Dr. Stavila and Dr. Allendorf: ➢ High pressure hydrogenation experiments. ➢ Characterization of samples by XRD and TGA-DSC.
Lawrence Livermore National Laboratory (HyMARC)	Collaborating with Dr. Wood and Dr. Kang: ➢ Molecular dynamic simulations of magnesium boride etherates.
Lawrence Berkeley National Laboratory (HyMARC)	Collaborating with Dr. Prendergast's Group: ➢ Reactive quantum molecular dynamics simulations of MgB_xH_y in etherate liquids.
National Renewable Energy Laboratory (HySCORE)	Collaborating with Dr. Gennett: ➢ Temperature programmed desorption. ➢ Mass spec analyses of desorbed gas.

Proposed Future Work

UH Synthesis

- Synthesis of modified magnesium boride materials.
- Optimize MgB_2-X-THF system

Hydrogenations

- **SNL:** Demonstrate higher gravimetric cycling capacity at lower hydrogenation pressures.
  - One round hydrogenation of modified MgB_2 materials per quarter at ≤ 700 bar & ≤ 300 °C.
  - Hydrogen Cycling Studies.
    - THF modified MgB_2 material from Year 1
    - Multiple Cycling Studies of modified MgB_2 materials
- **UH:** Moderate pressure hydrogenation.
  - Set up ≤350 bar, ≤350 °C sys.
  - Screening modified MgB_2 at ≤350 bar and ≤350 °C.

Characterizations

UH: XRD, FTATR, Raman, PCT, (^{11}B, ^{1}H, ^{25}Mg) NMR, TGA, DSC, TEM. NREL: TPD-Mass spec.
HYMARC: Advanced Spectroscopy Techniques (LEIS, XES, XAS).

- In situ NMR studies of dehydrogenation of modified Mg boranes
- Determine the factors that limit H_2 cycling kinetics.

Computations: HYMARC-LLNL

- Effect of additives on hydrogenation of MgB_2.

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

Summary

- 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 ^oC and 700 bar.
- Hydrogenation of MgB_2 to $Mg(BH_4)_2$ at 300 ^oC and 700 bar has been proven in absence 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 hydrided at 300 ^oC and 700 bar.

Bulk MgB_2 Hydrogenation Conditions	State of Art	FY 17 Results
Pressure/ bar	≥900	**700**
Temperature/ ^oC	~400	**300**

Simultaneous lowering of bulk MgB_2 hydrogenation conditions from 900 bar and 400 ^oC to 700 bar and 300 ^oC has been demonstrated for first time.

Acknowledgement

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Prof. C.M. Jensen
Mr. Stephen Kim
Mr. Cody Sugai

HyMARC Consortium: Making facilities and expertise available to the Project.

HySCORE Consortium: Making TPD, Mass spec and expertise available to the Project.

EERE's Fuel Cell Technologies Office: Funding.

Technical Back-Up Slides