Development of Magnesium Boride Etherates as Hydrogen Storage Materials

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DOE Hydrogen and Fuel Cells Program Annual Merit Review

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Project ID # ST138

Overview

Timeline

- Project Start Date: 10/01/2016
- Project End Date: 09/30/2020
- Percent Completion: 60 %

Barriers

Barrier	Target
Low System Gravimetric capacity	> 5.5 wt% H_2 system
Low System volumetric capacity	> 30 g/L system
Low System fill times	1.9 kg hydrogen/min

Budget

- Total Project Budget: $1,204,366
  - Total Recipient Share : $ 214,436
  - Total Federal Share : $989,930
  - Total DOE Funds Spent: $772,936.42 as of 03/31/20

Partners

- HyMARC Consortium
  - **SNL**: High Pressure Hydrogenations.
  - **LLNL**: Computation and XAS studies.
  - **NREL:** TPD and EPR Studies.

Relevance

Objective: Synthesize and Characterize Modified Magnesium Boride Hydrogen Storage Materials Capable of Meeting DOE Targets.

Storage Parameter	Units	2020 Targets	2025 Targets	Ultimate Target
Low System Gravimetric capacity	kg H_2/kg system	0.045	0.055	0.065
Low System volumetric capacity	kg H_2/L system	0.030	0.040	0.050
Low System fill times (5.6 kg)	kg H_2/min	3	3	3
Min Delivery Pressure	bar	5	5	5
Operational cycle (1/4 tank to full)	cycles	1500	1500	1500

DOE Technical Targets for Onboard Hydrogen Storage for Light-Duty Vehicles. https://www.energy.gov/eere/fuelcells/doe-technical-targets-onboard-hydrogen-storage-light-duty-vehicles

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.

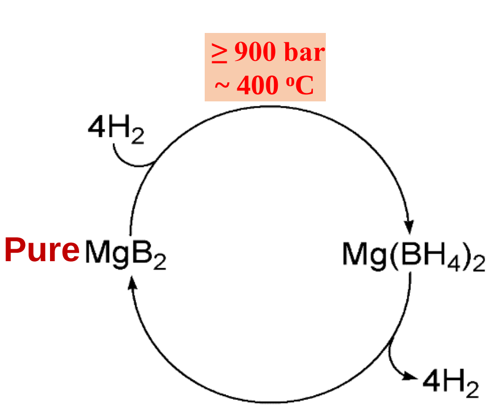
G. Severa, E. Rönnebro, C.M.Jensen; *Chem. Commun.* **2010**, *46*, 421. M. Chong, M. Matsuo, S. Orimo, C.M. Jensen Iinorg. Chem. **2015,** *54*, 4120.; Grigorii Soloveichik, Jae-Hyuk Her, Peter W. Stephens, Yan Gao, Job Rijssenbeek, Matt Andrus, and J.-C. Zhao, Inorg. Chem. **2008**, 47, 4290-4298

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.

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

Formed prior to or during hydriding

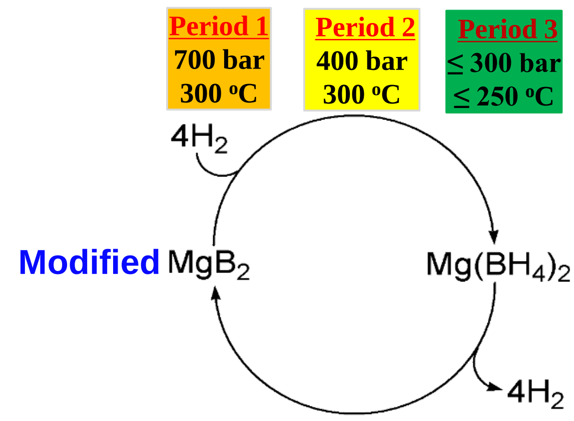


State of art

Hypothesis Validation

- Lower hydrogenation temperature.
- Lower hydrogenation pressure.
- Increase hydrogen sorption rates.

Bulk MgB_2 hydrogenation



Current Project

Towards improving hydrogen storage properties of $MgB_2/Mg(BH_4)_2$ system.

Approach: Synthesize, Characterize and Hydrogenate Modified MgB_2 Materials

<u>Experimental Approach: Period 3</u>

A. **Synthesis of modified MgB_2 materials:** Direct reactions of MgB_2 with additives and dehydrogenation of $Mg(BH_4)_2$ in presence of additives. Emphases on ball milling and heat treatment approaches.

B. **Hydrogenation reactions:** <u>UH</u>: ≤ 200 bars, ≤ 300 °C. <u>HyMARC-SNL:</u> ≤400 bars and ≤300 °C.

D. **Computation Experiments:** <u>HyMARC-LLNL:</u> Ab *initio* Molecular Dynamic Simulations.

C. **Characterizations:** TGA, DSC, FT-IR, NMR, <u>HyMARC-PNNL: XRD</u>, <u>HyMARC-NREL:</u> TPD/EPR

Milestone	Project Milestones: **(10/01/2019 - 09/31/2020)**	Quarter	Accomplished (05/28/2020)
1	Establish a correlation of the extent of MgB_2 modification to hydrogen uptake.	1	70%
2	Determine the minimal additives content required to enhance bulk MgB_2 hydrogenation below 200 bar and 300 °C.	2	70%
3	Demonstrate hydrogen cycling by a modified MgB_2 to $Mg(BH_4)_2$.	4	30%
4	Determination of hydrogen cycling conditions for modified MgB_2 to achieve maximum H_2 storage capacity with acceptable kinetics.	4	10%

Period 3 Deliverable: Demonstrate reversible hydrogenation of ≥ 8.0 wt % at ≤ 300 bar and ≤ 250 ˚C and cycling stability through 5 cycles of an optimal formulation of a modified MgB_2 to $Mg(BH_4)_2$.

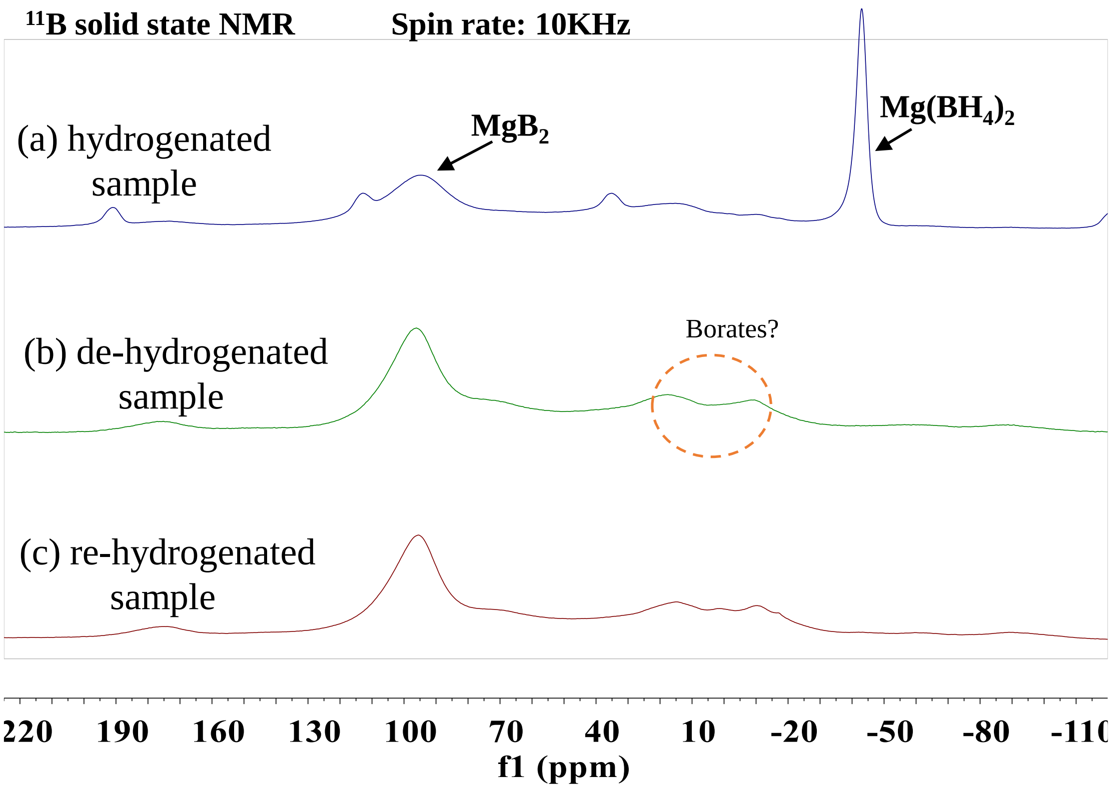
Any proposed future work is subject to change based on funding levels

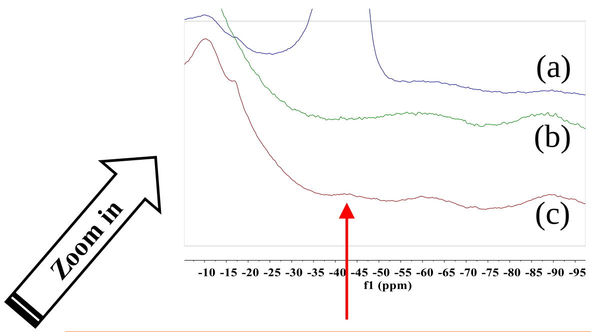
Accomplishments: First hydrogen cycle of modified MgB_2

400 bar H_2 and 300 ºC

Cycling study of "MgB_2 + 10mol% Mg-10mol% graphene"

MgB_2–Mg-graphene (hydrogenated 400 bar/300 ºC) → de-hydrogenation ~530 ºC, 2hrs, Ar → **MgB_2–Mg-graphene** (dehydrogenated) → re-hydrogenation 400 bar; 300 ºC → **MgB_2–Mg-graphene** (re-hydrogenated)





Minute reversibility of MgB_2 to $Mg(BH_4)_2$ observed after first re-hydrogenation

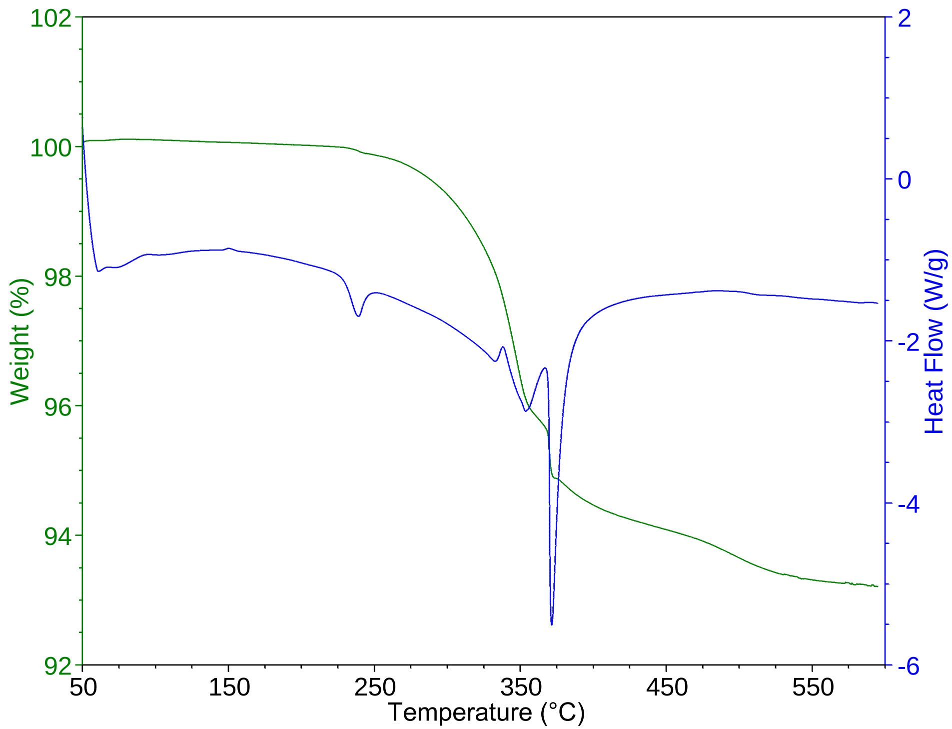
Ball Milled Hydrogenated Samples	11B NMR line fitting analyses (% conversion MgB_2 to $Mg(BH_4)_2$)
Hydrogenated	46
Re-hydrogenated	< 0.1

Preliminary studies indicate minute re-hydrogenation of a modified MgB_2 material.

Accomplishments: Optimization of a modified MgB_2 graphene material for improved H_2 uptake

400 bar H_2 and 300 ºC

MgB_2 + 10 mol% graphene —Ball milling optimization→ **Modified MgB_2**



Rate: 5 ºC/min under Argon flow

TGA-DSC analyses of hydrogenated MgB_2-10 mol% graphene

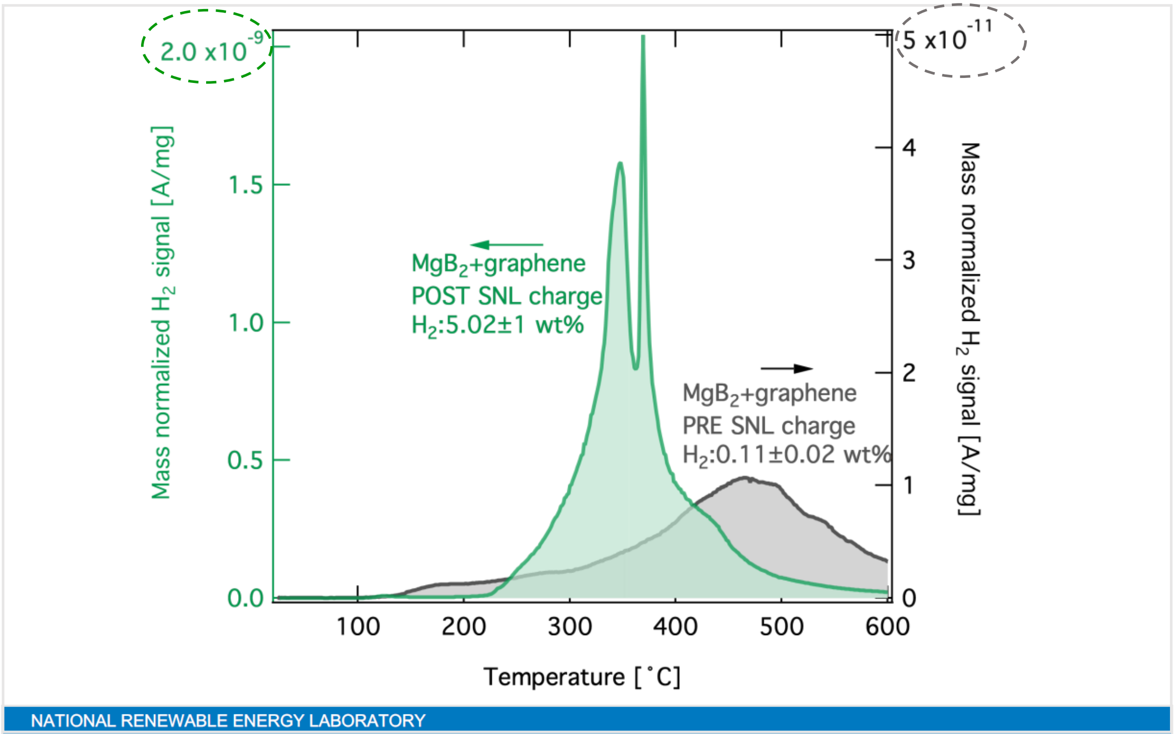
Ball Milled Hydrogenated Sample	TGA mass loss (%)
MgB_2- 10 mol% graphene	6.8

Improved mass loss observed from an optimized modified MgB_2 material hydrogenated at 400 bar and 300 ºC.

Accomplishments: TPD Analyses of the modified MgB_2

400 bar H_2 and 300 ºC

Confirmation of hydrogen evolution from the hydrogenated modified MgB_2



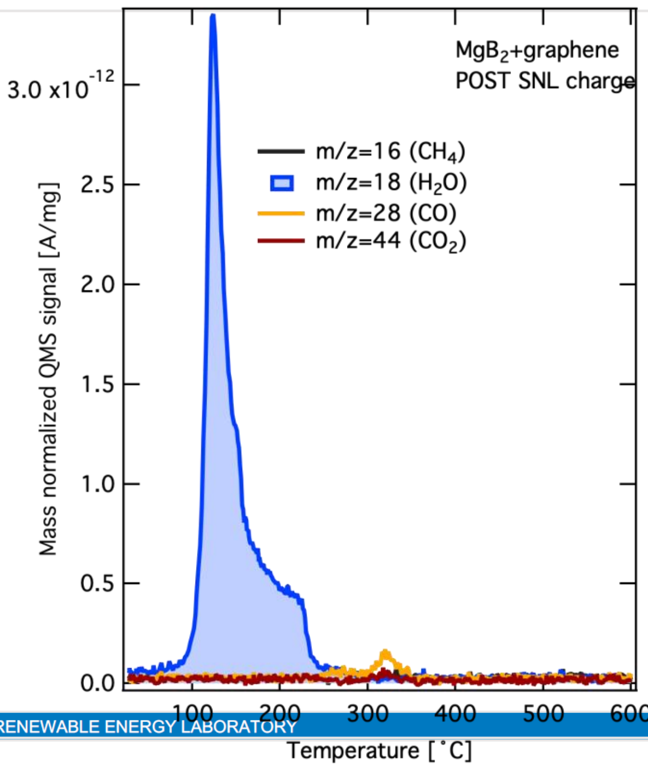
Confirmatory TPD Analyses indicates between 4-6 wt% hydrogen release from the hydrogenated sample

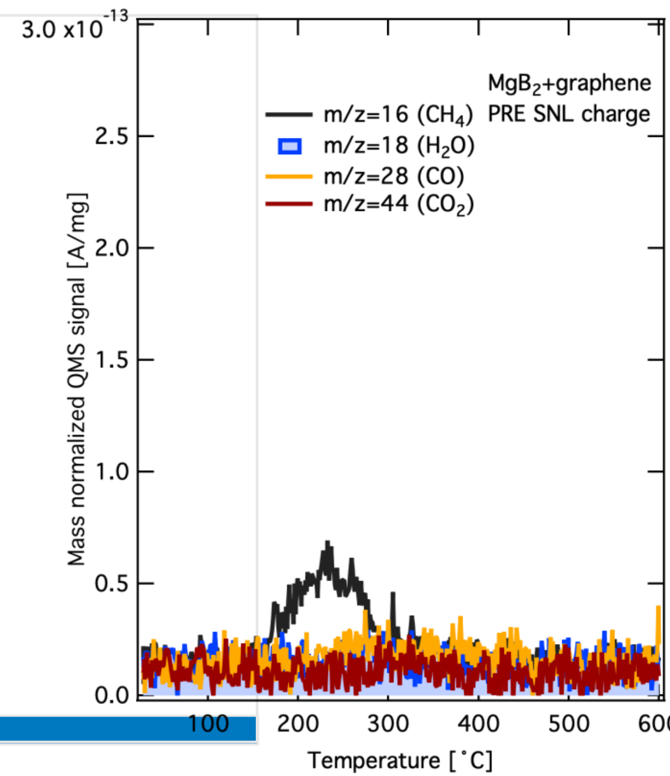
TPD analyses of hydrogen evolution from a MgB_2 -10 mol% graphene nanoplatelets sample before (PRE) and after (POST) hydrogenation at 400 bar and 300 ºC.

Accomplishments: TPD Analyses of the modified MgB_2

400 bar H_2 and 300 °C

Evolved gaseous products from the modified MgB_2 materials





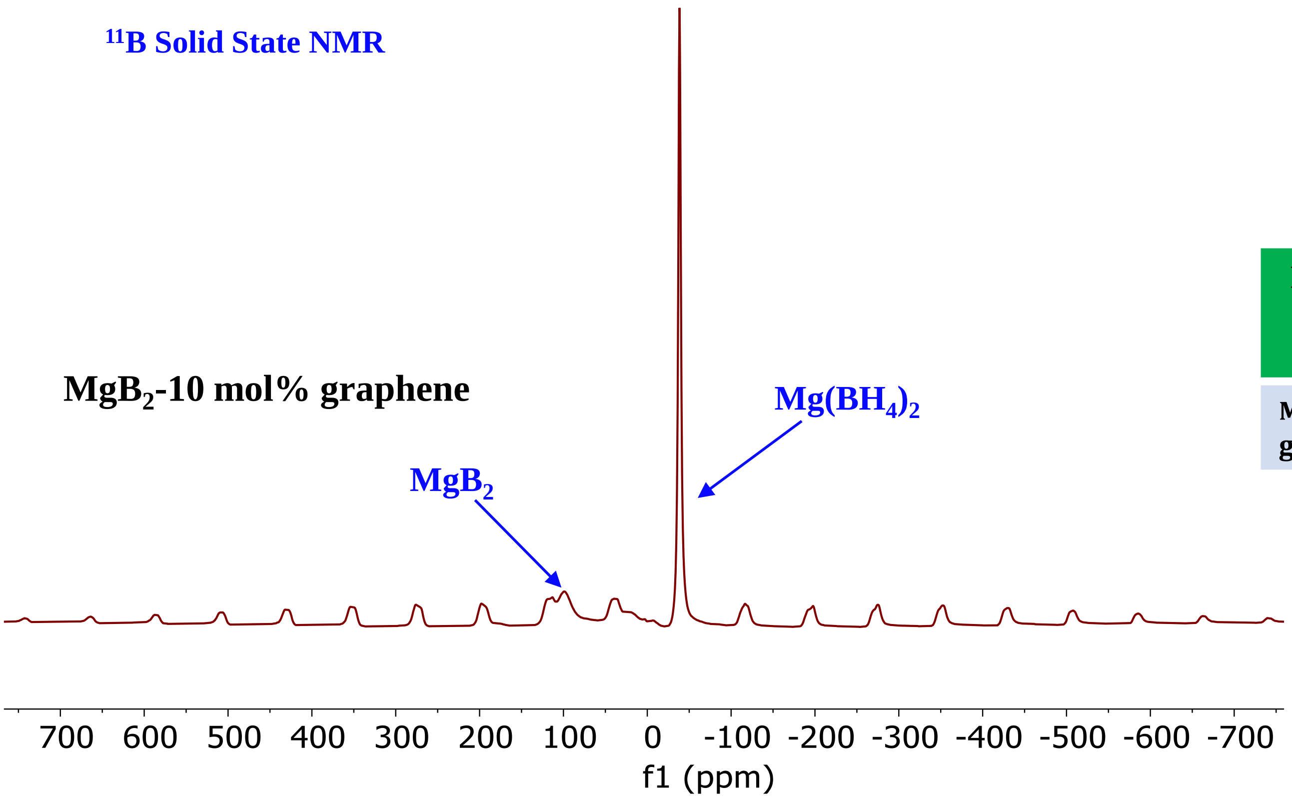
The water impurity is attributed to residual physisorbed H_2O inside the TPD sample vial.

Only trace amounts of graphene or its decomposition products detected.

Accomplishments: ^{11}B Solid State NMR of the optimized MgB_2-graphene material

400 bar H_2 and 300 ºC

NMR indicates almost complete conversion of the MgB_2 to $Mg(BH_4)_2$



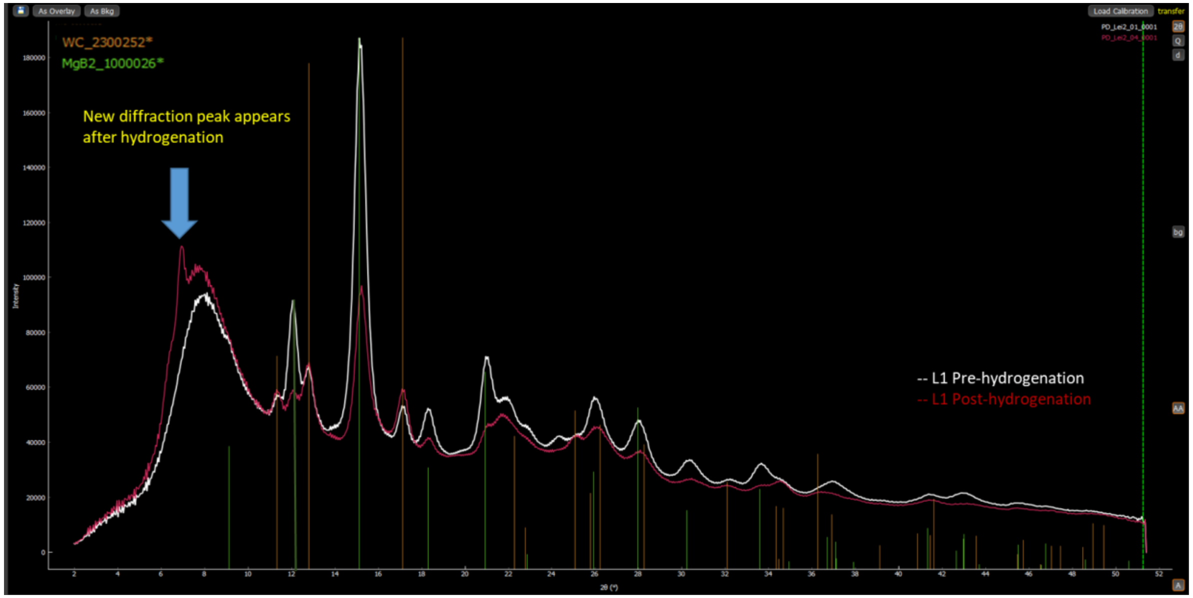
Hydrogenated Sample	Line fitting analyses % conversion MgB_2 to $Mg(BH_4)_2$
MgB_2- 10 mol% graphene	85 %

Minimum impurities of boron species observed in NMR spectrum

Accomplishments: XRD of the optimized MgB_2-graphene material

400 bar H_2 and 300 ^oC

XRD analyses of crystalline phases of boride, borohydride and impurities.



XRD taken in Dera Lab (UH) using single-crystal diffractometer with IuS 3.0 Ag K_α microfocus source.

MgB_2 and WC detected in pre-hydrogenated sample.

- **WC originates from the ware of grinding balls during milling process.**

Large decrease of crystalline phase of MgB_2 observed in hydrogenated material.

- Sharp new diffraction peak is attributed to $Mg(BH_4)_2$ main reflection.

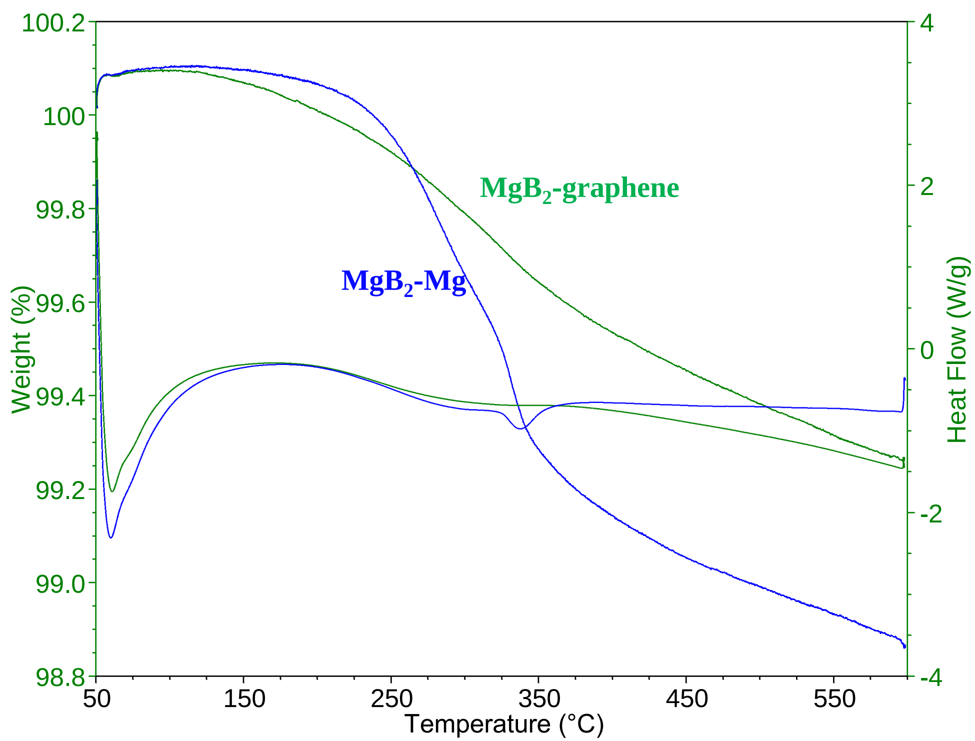
Presence of WC responsible for the unexpected lower wt% H_2 release observed from TPD and TGA analyses.

Accomplishments: Preliminary studies of modified MgB_2 materials under moderate conditions

160 bar H_2 and 250 ^oC

$MgB_2 + \leq 10$ mol% X + H_2 $\xrightarrow[250\ ^oC]{160\ bar}$ Magnesium borohydride

X = Mg, graphene, THF and/or anthracene



TGA analyses indicates less than 1 wt% hydrogen release

Further optimization of modified MgB_2 materials required to ensure lower temperature and pressure hydrogen uptake.

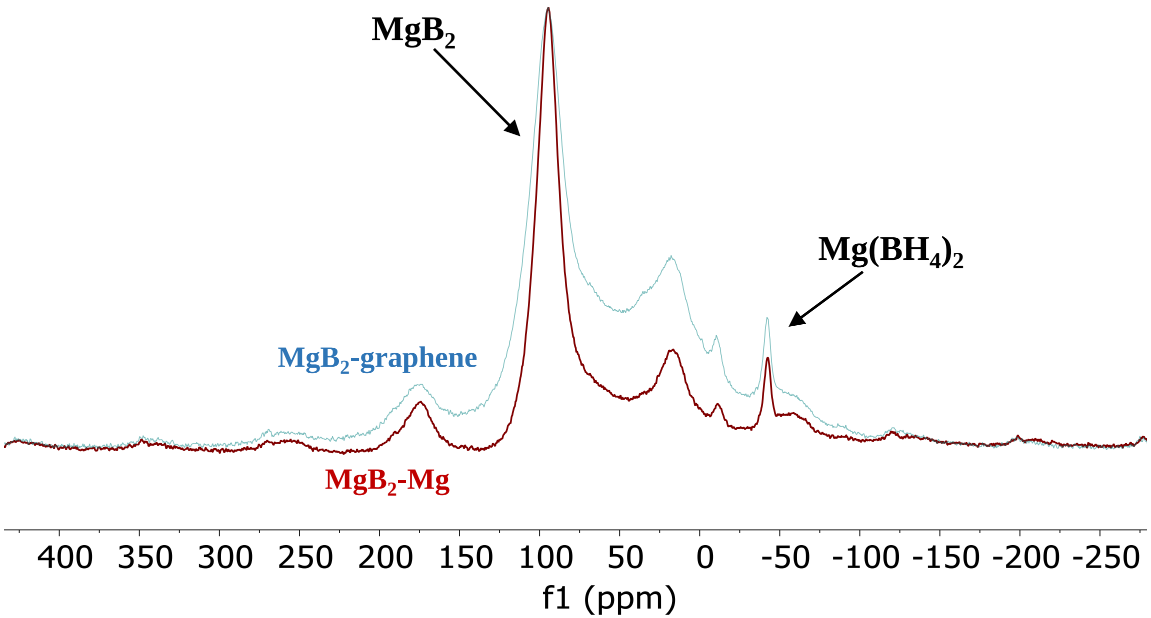
Accomplishments: Preliminary studies of modified MgB_2 materials under moderate conditions

160 bar H_2 and 250 ºC

$$MgB_2 + \leq 10 \text{ mol\% } X + H_2 \xrightarrow[250\ ^oC]{160 \text{ bar}} \text{Magnesium borohydride}$$

X = graphene, Mg, THF and/or anthracene

[11]B Solid State NMR analyses of hydrogenated modified MgB_2 materials.



Confirmation of $Mg(BH_4)_2$ formation in modified materials hydrogenated at moderate conditions

Direct confirmation of $Mg(BH_4)_2$ formation at lower pressures and temperatures

Accomplishments: Responses to 2019 Reviewers' Comments

This project was not reviewed last year.

Remaining Challenges and Barriers

- Increasing hydrogen uptake to $\geq$ 8 wt% at $\leq$ 300 bar and $\leq$ 250 ^oC.
- Showing significant H_2 cycling of a modified MgB_2 to $Mg(BH_4)_2$.
  - Minimize irreversible side products formation during (de)hydrogenation.
- Understanding the process of modifier activation of MgB_2 that enables lower temperature and pressure hydrogenation to $Mg(BH_4)_2$.
- Determining the lower temperature and pressure limits of modifier effects on MgB_2 hydrogenation.

Collaborations

Partners	Project Roles
Sandia National Laboratories **(HyMARC)**	Collaborating with Dr. Stavila, Dr. Snider, Mr. Davis: ➢ High pressure hydrogenations.
Lawrence Livermore National Laboratory **(HyMARC)**	Collaborating with Dr. Wood, Dr. Kang, Dr. Baker: ➢ Molecular dynamic simulations of modified magnesium borides ➢ XAS studies of modified MgB_2.
National Renewable Energy Laboratory **(HyMARC)**	Collaborating with Dr. Gennett and Dr. Leick: ➢ Temperature programmed desorptions. ➢ Mass spec analyses of desorbed gas. ➢ EPR studies of modified MgB_2 materials
Pacific Northwest National Laboratory **(HyMARC)**	Collaborating with Dr. Bowden ➢ XRD studies of modified materials

Continue to maximize HyMARC facilities and expertise to achieve project goals.

Proposed Future Work

Synthesis

UH: HNEI and Dept. of Chemistry. Optimize syntheses of modified MgB_2 materials using ball milling and heat treatment approaches. Emphases on heat treatment approaches for better control of syntheses conditions and products.

Hydrogenations

- Perform hydrogenations of modified MgB_2 at ≤ 200 bar and ≤ 300 ^{o}C at UH.
- Perform hydrogen cycling studies at ≤ 400 bar and ≤ 300 ^{o}C at SNL and UH.

Characterizations

- **UH:** ^{11}B NMR, FTIR-ATR, TGA, DSC.

- **HYMARC:**
  - NREL: TPD and EPR.
  - LLNL: XAS
  - PNNL: XRD

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

Acknowledgements

University of Hawaii Team

Hawaii Natural Energy Institute

Dr. Godwin Severa

Dr. Lei Wang

Ms. Colleen Kelly

Dept. of Chemistry

Mr. Stephen Kim

Prof. C.M. Jensen





Collaborators	Contribution
Lawrence Livermore National Laboratory	Dr. Wood, Dr. Kang and Dr Baker: ➢ Molecular dynamic simulations ➢ XAS studies
Sandia National Laboratories	Dr. Stavila, Dr. Snider, Mr. Davis: ➢ High pressure hydrogenations.
National Renewable Energy Laboratory	Dr. Gennett, Dr. Leick and Ms. Martinez: ➢ Temperature programmed desorption. ➢ EPR studies
Pacific Northwest National Laboratory	Dr. Bowden ➢ XRD studies of modified materials

Project Funding: US. DOE-EERE's Fuel Cell Technologies Office

Summary

- Demonstrated improved hydrogenation of a modified MgB_2 to $Mg(BH_4)_2$ at 300 ^oC and 400 bar.
  - TPD analyses indicates about 5wt% H_2 release from the MgB_2-10 mol% graphene material.
- Demonstrated hydrogenation of MgB_2 to $Mg(BH_4)_2$ at 250 ^oC and 160 bar.
  - TGA analyses indicates about 1wt% mass loss from the modified MgB_2 materials, suggesting surface hydrogenation.
- Further improvements to the hydrogenation of MgB_2 to $Mg(BH_4)_2$ at conditions relevant for onboard hydrogen storage appear plausible (≤160 bar and ≤ 250 ^oC).

Bulk MgB_2 Hydrogenation	**State of Art** **[Pure MgB_2]**	**Period 1** **[modified MgB_2]**	**Period 2** **[modified MgB_2]**	**Period 3** **[modified MgB_2]**	**Period 3** **[modified MgB_2]**
Pressure/ bar	950	**700**	**400**	**400**	**160**
Temperature/ ^oC	~400	**300**	**300**	**300**	**250**
Wt % hydrogen	11 wt % (Sieverts)	7-8 wt % (TPD)		4-6 wt% (TPD)	~1 wt% (TGA)
% Conversion: MgB_2 to $Mg(BH_4)_2$	75 % [Sieverts method: wt% H_2]	71 % [^{11}B solid state NMR line fitting method]	46 % [^{11}B solid state NMR line fitting method]	85 % [^{11}B solid state NMR line fitting method]	

Research shows plausibility of continuous improvements in kinetics of MgB_2 hydrogenation to $Mg(BH_4)_2$, to fuel cell relevant conditions.