
HyMARC Seedling: Development of Magnesium Boride Etherates as Hydrogen Storage Materials

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Overall Objectives

- Improve the hydrogen cycling kinetics and cycling capacity of magnesium boride/magnesium borohydride system to meet DOE hydrogen storage targets
- Synthesize and characterize novel modified magnesium boride (MgB_2) materials with improved hydrogen cycling kinetics and hydrogen storage capacities
- Determine if the reversible hydrogenation of novel modified borides show vastly improved hydrogen cycling kinetics and cycling capacities to practically viable levels
- Demonstrate the capability of modified MgB_2 materials to meet the Department of Energy (DOE) hydrogen storage targets

Fiscal Year (FY) 2019 Objectives

- Optimize modifier interaction in modified MgB_2 materials for maximum hydrogen uptake.
- Demonstrate reversible hydrogenation of ≥ 8.0 wt % at ≤ 400 bar and $\leq 300^\circ\text{C}$ by a modified MgB_2 .

- Demonstrate cycling stability through 5 cycles of an optimal formulation of a modified MgB_2 to $\text{Mg}(\text{BH}_4)_2$.
- Correlate extent of MgB_2 modification with hydrogen uptake.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan¹:

- (A) System Weight and Volume
- (D) Durability/Operability
- (E) Charging/Discharging Rates
- (O) Lack of Understanding of Hydrogen Physisorption and Chemisorption.

Technical Targets

This project is to determine if the reversible hydrogenation of modified magnesium borides shows vastly improved hydrogen cycling kinetics while extending the cycling capacities to levels that are practically viable. Currently, improvement in kinetics has been demonstrated by the decrease in both hydrogenation pressure and hydrogenation temperature to 250°C and about 200 bar of a modified magnesium boride material, even though the levels of hydrogen uptake are still minimum. Insights gained from this project will be applied toward the development of advanced modified boride hydrogen storage materials that meet the DOE 2020 hydrogen storage targets below:

- System Gravimetric Capacity: 0.045 kg H_2 /kg System
- System Volumetric Capacity: 0.030 kg H_2 / L system
- Durability/Operability (Max H_2 delivery temperature): 85°C
- Charging/Discharging Rates (System fill times for 5.6 kg of H_2): 1.5 kg H_2 / min.

¹ <https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22>

FY 2019 Accomplishments

- Demonstrated the plausibility of continuous improvement in the bulk hydrogenation kinetics of the $\text{MgB}_2/\text{Mg}(\text{BH}_4)_2$ system.
- Significantly moderated the conditions required for hydrogenation of magnesium boride (700 bar/400°C to 400 bar/300°C).
- Discovered new modifiers (graphene and anthracene) that enable the hydrogenation of MgB_2 to $\text{Mg}(\text{BH}_4)_2$ at moderate conditions (≤ 400 bar and $\leq 300^\circ\text{C}$).
- Performed ^{11}B solid MAS- nuclear magnetic resonance (NMR) line fitting analyses of a MgB_2+10 mol% Mg-graphene sample hydrogenated at 400 bar and 300°C, indicating at least 47% conversion of MgB_2 to $\text{Mg}(\text{BH}_4)_2$.

INTRODUCTION

Magnesium borohydride, $\text{Mg}(\text{BH}_4)_2$, is one of the few materials with a gravimetric hydrogen density (14.7 wt% H_2) that is sufficient to meet the requirements of US DOE hydrogen storage targets and also possesses thermodynamics ($\Delta H^\circ = 39$ kJ/mol H_2 , $\Delta S = 112$ J/K mol H_2) that permit reversible hydrogen release under moderate pressure and temperature. However, due to extremely slow kinetics, cycling between $\text{Mg}(\text{BH}_4)_2$ and MgB_2 has been accomplished only at a high temperature ($\sim 400^\circ\text{C}$) and under high charging pressure (~ 900 bar). More recently, THF complexed to magnesium borohydride has been shown to improve the kinetics of dehydrogenation vastly, enabling the rapid release of hydrogen at $< 200^\circ\text{C}$ to give $\text{Mg}(\text{B}_{10}\text{H}_{10})$ with high selectivity. However, these types of materials have much lower hydrogen cycling capacities as a consequence of the weight contribution of the coordinated ethers. However, extending the dehydrogenation to $\text{MgB}_2\cdot(\text{ether})_x$ type materials would result in the hydrogen wt % of the system potentially meeting DOE targets. If successful, the solid-state modified MgB_2 materials could be safer and cheaper than the high pressure compressed hydrogen (700 bar) onboard storage systems on the market.

APPROACH

The project currently explores the effect of additives such as ethers on the hydrogenation properties of MgB_2 to $\text{Mg}(\text{BH}_4)_2$. In addition to the electronic perturbation caused by the interaction of the modifiers with the magnesium or boron, which may alter the thermodynamics of the reversible hydrogenation of MgB_2 , the presence of the modifiers can also result in kinetic enhancement of phase changes in the $\text{Mg}(\text{BH}_4)_2/\text{MgB}_2$ system. Since significant hydrogenation of magnesium boride to magnesium borohydride has only been achieved at very high pressure (~ 900 bar), a high-pressure system will be initially utilized for hydrogenation of the modified borides to magnesium borohydride. We therefore intend to team with several HyMARC lab partners, in order to utilize their high-pressure capabilities in the hydrogenation of the modified magnesium boride as well as their surface characterization equipment. We will determine if the modifier- MgB_2 bonding remains intact during the reversible hydrogenation of boride to borohydride and, if so, what influence it has on the reaction kinetics and thermodynamics.

Of foremost interest will be the reduction of the temperatures and pressures required for the hydrogenation and subsequent dehydrogenation of the boride materials. The ratio of modifier to the MgB_2 will be optimized to allow for the maximum attainable gravimetric and volumetric density without sacrificing hydrogen cycling kinetics at moderate conditions. We will determine whether the modified MgB_2 materials can access new polyboranes reaction pathways which prevent formation of $\text{MgB}_{12}\text{H}_{12}$ during hydrogen cycling. An inherent endeavor of the project will be to understand the mechanisms of kinetic enhancement and intermediates formed during the hydrogenation and dehydrogenation process in order to optimize the hydrogen storage performance of the modified $\text{MgB}_2/\text{Mg}(\text{BH}_4)_2$ materials. A thorough correlation of experiments with theory will be utilized in this effort using HyMARC's multiscale modeling approaches (kinetic Monte Carlo simulation and phase field modeling) to help elucidate the kinetic constraints on hydrogen cycling resulting at both particle surface interfaces and within the bulk of the materials. The results of these studies will provide us with adequate insight to conceivably identify a magnesium boride species whose hydrogen cycling kinetics are adequate to meet the DOE target.

RESULTS

In the third fiscal year of the project we built upon the previous years' successful work on hydrogenating bulk MgB_2 at 700 bar and 300°C, and aimed to determine the plausibility of continually improving the modified MgB_2 hydrogenation kinetics by attempting to further lower the hydrogenation pressure to 400 bar whilst maintaining the temperature at 300°C. Consequently, in the third fiscal year we explored the discovery of modifiers that could further destabilize the MgB_2 structure better than the tetrahydrofuran (THF) based additives, in-order to timely meet our project objectives and further expand our hypotheses of MgB_2 modification. In essence a major effort was placed on demonstrating that the project meets the Go/No-Go criteria of budget period two of hydrogen uptake, of 8 wt %, at 300°C and 400 bars. We continued to emphasize modified MgB_2 syntheses based on the mechano-chemical approach we developed at University of Hawaii. Following the syntheses of the modified MgB_2 materials, hydrogenation experiments of the modified MgB_2 materials were performed at 300°C and 400 bar for ≤ 72 hours at HyMARC's Sandia National Laboratories facility in collaboration with Dr. Stavila, Mr. Davies and Dr. Snider, whilst hydrogenations at ≤ 200 bar and $\leq 300^\circ\text{C}$ for ≤ 72 hours were performed at University of Hawaii.

In FY2019 we continued with the study of the previous year's best performing material, MgB_2 treated with THF and Mg. Furthermore, we began to explore the modification of MgB_2 by other modifiers, including graphene and anthracene. The syntheses were performed by treating MgB_2 with less than 10 mol% of the additives under mechanical milling conditions. The prepared samples we sent to Sandia National Laboratories for hydrogenation at 400 bar and 300°C for less than 72 hours. Following the hydrogenations, the samples were analyzed at University of Hawaii using ^{11}B and ^1H NMR, infrared vibrational spectroscopy and thermogravimetric analyses, and differential scanning calorimetry. ^{11}B solid state NMR proved to be a quick and direct approach to determine the extent of conversion of MgB_2 to $\text{Mg}(\text{BH}_4)_2$. As seen in Figure 1, we can definitively confirm bulk formation of $\text{Mg}(\text{BH}_4)_2$ at 400 bar and 300°C from the modified MgB_2 using the anthracene, graphene, or Mg-THF modifiers. The MgB_2 is observed at a chemical shift of ~ 96 ppm whilst $\text{Mg}(\text{BH}_4)_2$ is observed at ~ -41 ppm. These results indicate the plausibility of the discovery of other modifiers with a higher capability of destabilizing the MgB_2 structure, enabling more efficient hydrogenation of MgB_2 to $\text{Mg}(\text{BH}_4)_2$ at much milder reaction conditions.

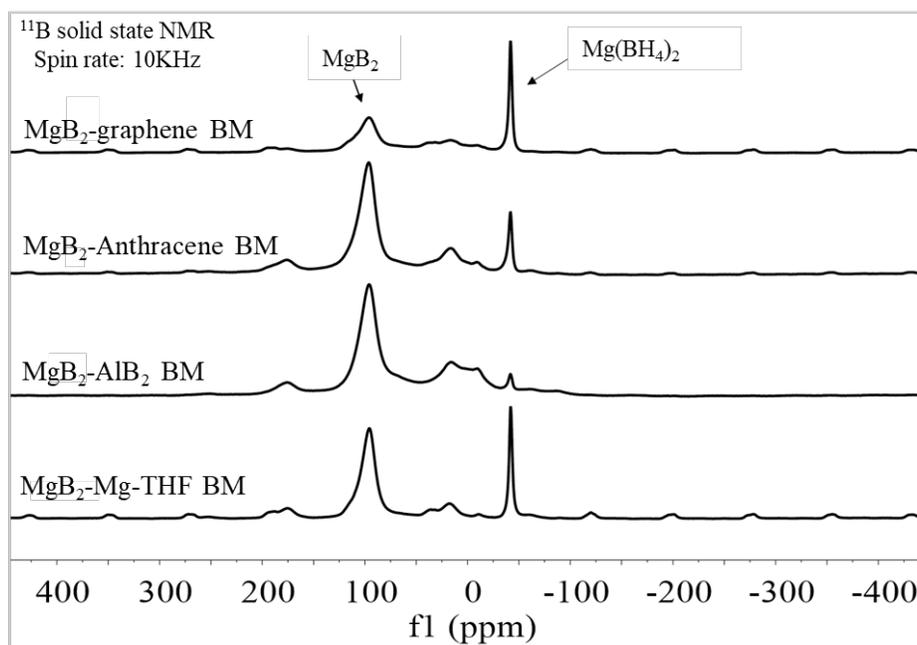


Figure 1. ^{11}B solid state NMR of ball milled; (a) MgB_2 modified with THF and 10 mol % Mg; (b) MgB_2 modified with 10 mol % aluminum boride; (c) MgB_2 modified with 10 mol % anthracene; and (d) MgB_2 modified with 10 mol % graphene; hydrogenated at 400 bar, 300°C and 72 hr.

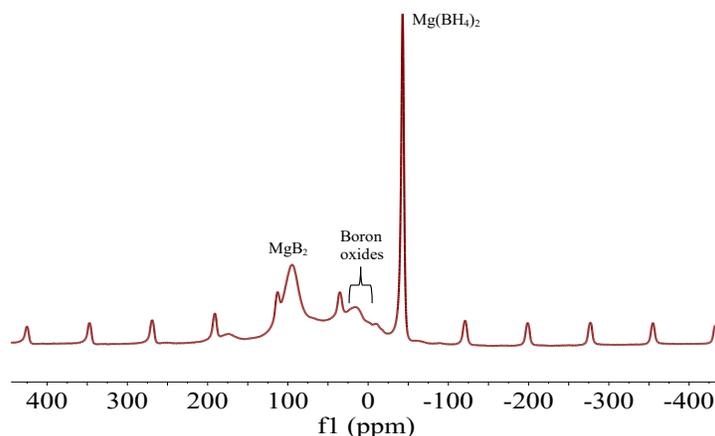


Figure 2. ^{11}B solid-state MAS-NMR of MgB_2 modified with 10 mol % Mg-graphene, after hydrogenation at SNL at 400 bar H_2 , 300 °C and 72-hour showing $\text{Mg}(\text{BH}_4)_2$ formation at -41ppm and boron oxides in the 0-35 ppm region.

After the hydrogenation experiments, large, broad peaks attributable to boron oxide species can be observed in the 0–35 ppm region (Figures 1 and 2). The borate peaks are not present in the pre-hydrogenated samples. The presence of the borate species negatively impacts the weight percent hydrogen uptake by the sample, as well as, the MgB_2 to $\text{Mg}(\text{BH}_4)_2$ percent conversions/yields. ^{11}B solid-state NMR line fitting analyses of the whole spectrum of the graphene-modified sample indicate about a 47% conversion of MgB_2 to $\text{Mg}(\text{BH}_4)_2$. The percent conversion is based on the boron content of $\text{Mg}(\text{BH}_4)_2$ (the $\text{Mg}(\text{BH}_4)_2$ peak area, inclusive of sidebands) versus the total boron content (total boron species peak area, inclusive of sidebands) in the spectra. Exclusion of the contribution of boron trapped as borate species, increases the conversion of MgB_2 to $\text{Mg}(\text{BH}_4)_2$, to about 61%.

We have achieved a significant improvement in the kinetics of the hydrogenation of magnesium MgB_2 to $\text{Mg}(\text{BH}_4)_2$ by the use of modifiers/additives. However, it has not been determined if this enhancement persists through extending cycling or even a single-digit number of cycles. Thus our next step in the evaluation of the practical potential of the modified MgB_2 is to conduct multiple cycle experiments and isothermal kinetic studies of each of the half-cycles.

Theoretical modeling work on the project continues to be led and performed by Dr. Brandon Wood and Dr. Shinyoung Kang. The molecular dynamic simulations of the interaction of MgB_2 layers with tetrahydrofuran or anthracene show strong interactions between the modifiers and MgB_2 (Figure 3). The interactions are seen to consequently lead to the formation of defects in the MgB_2 structure. The defect may act as hydrogenation initiation and propagation sites, hence facilitate MgB_2 hydrogenation at milder conditions than pure, unmodified MgB_2 .

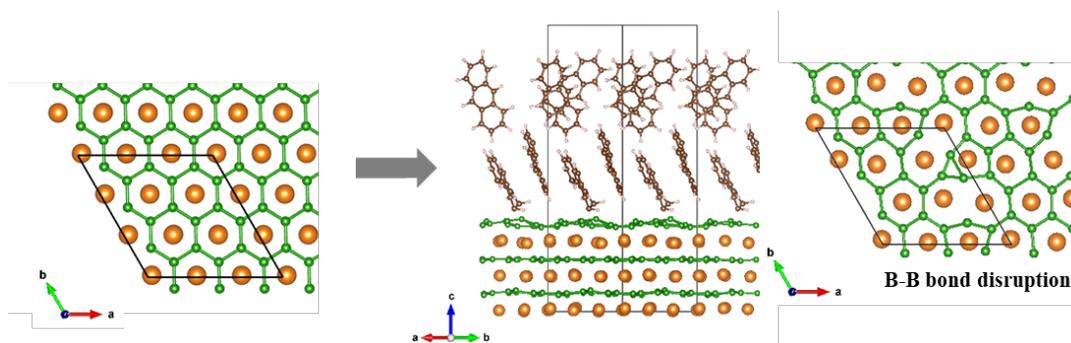


Figure 3. Computational modeling showing boron defect formation on the interaction of MgB_2 and anthracene.

CONCLUSIONS AND UPCOMING ACTIVITIES

In the third fiscal year of the project, we have achieved significant moderation of the conditions required for hydrogenation of magnesium boride, lowering the pressure from 700 bar achieved in the second fiscal year, to 400 bar whilst maintaining temperature at 300°C. Our project demonstrates the plausibility of continuously improving the hydrogenation conditions of this kinetically hindered hydrogen storage system. We have discovered new modifiers, graphene and anthracene that enable the hydrogenation of MgB₂ to Mg(BH₄)₂ at moderate conditions ≤400 bar and ≤300°C. ¹¹B NMR analyses of the hydrogenated modified MgB₂ directly confirmed Mg(BH₄)₂ formation at 300°C and 400 bar. The corresponding ¹¹B solid MAS-NMR line fitting analyses of a “MgB₂+10 mol% Mg-graphene” sample hydrogenated at 400 bar and 300°C, indicates at least 47% conversion of MgB₂ to Mg(BH₄)₂.

Future work guided by the need to attain DOE onboard targets include:

- Optimize modifier interaction in modified MgB₂ materials for maximum hydrogen uptake utilizing high temperature treatments and mechano-chemical approaches.
- Perform in-situ NMR studies of the dehydrogenation of modified Mg boranes
- Demonstrate reversible hydrogen uptake of ≥ 8.0 wt % at ≤ 200 bar and ≤ 250 °C by a modified MgB₂.
- Perform multiple H₂ cycling studies of the modified MgB₂ materials.
- Correlate extent of MgB₂ modification with experimentally observed hydrogen uptake, using X-ray absorption spectroscopy (XAS).

FY 2019 PUBLICATIONS/PRESENTATIONS

1. C. Sugai, S. Kim, G. Severa, J. White, N. Leick, M. B. Martinez, T. Gennett, V. Stavila, and C. M. Jensen, “Kinetic enhancement of direct hydrogenation of magnesium boride to magnesium borohydride upon mechanical milling with THF, MgH₂, and/or Mg,” *ChemPhysChem*, 20 (2019) 1–5
2. G. Severa, C. Jensen, C. Sugai, S. Kim, S. Kang, B. Wood, J. White, T. Gennett, N. Leick, V. Stavila, M. Martinez, “Modified Magnesium Diboride for Moderate Temperature and Pressure Hydrogenation to Magnesium Borohydride.” Presented at the Gordon Research Conferences: Metal Hydrogen Systems, Understanding the Interaction of Hydrogen with Materials from the Atomic Level to Systems; Barcelona, Spain, June 30-July 5, 2019.
3. G. Severa, C. Jensen, C. Sugai, S. Kim, S. Kang, B. Wood, J. White, T. Gennett, N. Leick, V. Stavila, M. Martinez, “Kinetic enhancement of bulk, direct hydrogenation of magnesium boride to magnesium borohydride in presence of modifiers.” Presented at the 16th International Symposium on Metal-Hydrogen Systems, Guangzhou, China, Oct 28-Nov 2, 2018
4. G. Severa, C. Jensen, C. Sugai, S. Kim, “Development of Magnesium Boride Etherates as Hydrogen Storage Materials,” Presentation at the 2019 DOE Annual Merit Review and Peer Evaluation Meeting, Washington, D.C., May 2019.