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# 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 a 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 levels that are practically viable.
- Demonstrate capability of modified  $MgB_2$  materials to meet the DOE 2020 hydrogen storage targets.

## Fiscal Year (FY) 2018 Objectives

- Continue to synthesize and characterize novel modified magnesium borides.
- Demonstrate reversible hydrogenation of  $\geq 7.0$  wt% at  $\leq 700$  bar and  $\leq 300^\circ C$  by a modified  $MgB_2$ .
- Determine the factors that limit hydrogen cycling kinetics.

## 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 Plan<sup>1</sup>:

- (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 determining whether the reversible hydrogenation of modified magnesium borides shows vastly improved hydrogen cycling kinetics while extending the cycling capacities to levels that are practically viable. Current improvements in kinetics have been demonstrated by the decrease in both hydrogenation pressure and temperature—to 700 bar and  $300^\circ C$ —of a modified magnesium boride material with at least 6 wt% hydrogen uptake. Insights gained from this project will be applied toward the development of modified boride hydrogen storage materials that meet the following DOE hydrogen storage targets:

- System gravimetric capacity: 0.055 kg  $H_2$ /kg system
- System volumetric capacity: 0.040 Kg  $H_2$ / L system
- Durability/operability (max hydrogen delivery temperature):  $85^\circ C$
- Charging/discharging rates (system fill times for 5 kg hydrogen): 1.5 kg  $H_2$ / min.

## FY 2018 Accomplishments

- The effect of modifiers/additives on enhancing  $MgB_2$  hydrogenation to  $Mg(BH_4)_2$  was proved beyond ethers, and the presence of metals and

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

metal hydrides was observed to improve  $\text{MgB}_2$  hydriding at  $300^\circ\text{C}$  and 700 bar.

- Infrared vibrational spectroscopy (FT-ATR-IR) and  $^{11}\text{B}$  nuclear magnetic resonance (NMR) studies of hydrogenated modified  $\text{MgB}_2$  directly confirmed  $\text{Mg}(\text{BH}_4)_2$  formation.
- Temperature-programmed desorption (TPD) analyses at the National Renewable Energy Laboratory (NREL) confirmed that the  $300^\circ\text{C}$  and 700 bar hydrogenated  $\text{MgB}_2$ -THF-40 mol% Mg and  $\text{MgB}_2$ -THF-5 mol% Mg had a hydrogen uptake of about 6 wt% and 4 wt% hydrogen, respectively, after adjusting for the hydrogen released by the  $\text{MgH}_2$  formed by the hydrogenation of added excess Mg.
- Mass spectroscopy analyses showed that the evolved hydrogen from the hydrogenated modified  $\text{MgB}_2$  samples contained only negligible, trace amounts of impurities.

## INTRODUCTION

Magnesium borohydride,  $\text{Mg}(\text{BH}_4)_2$ , is one of the few materials with a gravimetric hydrogen density (14.7 wt%  $\text{H}_2$ ) that is sufficient to meet the requirements of DOE hydrogen storage targets and also possesses thermodynamics ( $\Delta H^\circ = 39 \text{ kJ/mol H}_2$ ,  $\Delta S = 112 \text{ J/K mol H}_2$ ) 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  $\text{MgB}_2$  has been accomplished only at high temperature ( $\sim 400^\circ\text{C}$ ) and under high charging pressure ( $\sim 900 \text{ bar}$ ). More recently, tetrahydrofuran (THF) complexed to magnesium borohydride has been shown to vastly improve the kinetics of dehydrogenation, 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 because 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 a system hydrogen density that would potentially meet DOE targets. If successful, the solid-state modified  $\text{MgB}_2$  materials would be safer and cheaper than the high-pressure compressed hydrogen (700 bar) or liquid hydrogen alternative onboard storage systems on the market.

## APPROACH

The project explores the effect of modifiers or additives such as ethers on the hydrogenation properties of  $\text{MgB}_2$  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  $\text{MgB}_2$ , 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. Because significant hydrogenation of magnesium boride to magnesium borohydride has only been achieved at very high pressure ( $\sim 900 \text{ bar}$ ), a high-pressure system will be utilized initially for hydrogenation of the modified borides to magnesium borohydride. We therefore intend to team with the Hydrogen Materials Advanced Research Consortium (HyMARC) 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- $\text{MgB}_2$  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  $\text{MgB}_2$  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  $\text{MgB}_2$  materials can access new polyborane reaction pathways that 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 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 second fiscal year of the project we built upon the first fiscal year's successful validation of the project's core hypotheses: ether or ether-derived species perturb the  $\text{MgB}_2$  material, resulting in improved hydrogenation of a modified  $\text{MgB}_2$  ( $\text{MgB}_2\text{-THF}$ ) to  $\text{Mg}(\text{BH}_4)_2$  compared to the pure  $\text{MgB}_2$ . The major effort in the second fiscal year was on finding approaches to further perturb the  $\text{MgB}_2$  structure in the  $\text{MgB}_2\text{-THF}$  system to enhance hydrogen uptake kinetics to meet project objectives. A major effort was placed on demonstrating that the project meets the go/no-go criteria of Budget Period 1—hydrogen uptake target of 7 wt% and hydrogen release target of 2 wt%—while still maintaining the  $300^\circ\text{C}$  and 700 bar hydrogenation targets achieved in the first fiscal year. Since we had observed hydrogen release in TPD-mass spectroscopy experiments we performed on  $\text{MgB}_2\text{-THF}$  samples in collaboration with Dr. Gennett's group at NREL, we concluded that a hydride or metal species such as  $\text{MgH}_2$  or  $\text{Mg}$  could be playing a role in the hydrogenation of the  $\text{MgB}_2$  under milder conditions. Furthermore, the improved hydrogenation of the  $\text{MgB}_2\text{-THF}$  doped with 5

mol% LiH prepared under milder conditions (9 h BM vs. 20 h for MgB<sub>2</sub>-THF) supported the plausibility of hydride species playing a significant role in the MgB<sub>2</sub> hydrogenation process. As a result, we sought to enhance the species potentially formed during the mechanochemical reactions of MgB<sub>2</sub> and THF that could also be aiding hydrogen uptake kinetics in the MgB<sub>2</sub>-THF samples. We envisioned that such a holistic consideration of the factors impacting the MgB<sub>2</sub> structure could help provide in-depth fundamental understanding on how the THF and/or THF-derived species are perturbing the MgB<sub>2</sub> structure and causing vast improvements in hydrogenation kinetics.

Modified MgB<sub>2</sub> synthesis procedures developed in the first fiscal year at University of Hawaii were utilized, with emphasis on a mechanochemical approach as it was observed to result in better modified MgB<sub>2</sub> materials. Hence, we performed mechanochemical synthesis experiments on improving hydrogen uptake kinetics of a MgB<sub>2</sub>-THF system through use of metal hydride-based modifiers (e.g., ≤40 mol% MgH<sub>2</sub> and ≤40 mol% Mg). Furthermore, due to the envisioned plausibility of the metal hydride or metal modifiers improving the hydrogenation of MgB<sub>2</sub> without ethers, mechanical mixing of these modifiers with MgB<sub>2</sub> were also performed under similar reaction conditions. Following the syntheses of the modified MgB<sub>2</sub> materials at University of Hawaii, hydrogenation experiments of the modified MgB<sub>2</sub> materials were performed at 300°C, 700 bar for ≤72 hours at HyMARC's Sandia National Laboratories facility in collaboration with Dr. White, Dr. Stavila, and Dr. Allendorf. The hydrogenation of ether-modified MgB<sub>2</sub> samples was performed separately from that of the non-ether-modified samples.

Following hydrogenation, the products of hydrogenation were characterized at University of Hawaii by a variety of techniques including solid-state and solution <sup>11</sup>B and <sup>1</sup>H nuclear magnetic resonance (NMR), X-ray diffraction (XRD), infrared vibrational spectroscopy (FT-ATR-IR), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC). TGA of the hydrogenated products was performed at 5°C/min under argon flow of 100 mL/min up to 500°–600°C to determine the extent of hydrogen uptake by the samples. Much higher levels of hydrogen uptake were observed with samples of MgB<sub>2</sub> or MgB<sub>2</sub>-THF materials that were ball milled with the Mg or MgH<sub>2</sub> (Figure 1). However, the amount of hydrogen uptake (after adjusting for the hydrogen released by the MgH<sub>2</sub> added to the reaction mixture or the MgH<sub>2</sub> formed by the hydrogenation of added excess Mg) was highly variable: 1–5 wt% depending upon the level of oxidation to MgO and Mg<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub> that occurred. The extent of hydrogenation was greater than that obtained from the hydrogenation of MgB<sub>2</sub> modified with THF only, at 700 bar and 300°C, which released less than 1 wt% hydrogen. Thus, our results suggest that the hydrogenation of MgB<sub>2</sub>-THF without added MgH<sub>2</sub> or Mg at the milder conditions results in mostly surface hydrogenation. TPD studies coupled with mass spectroscopy analyses were performed at NREL in the range of 1–50 amu on the samples of the reaction mixtures that were found to have undergone high levels of hydrogen uptake (Figure 2). These analyses verified that the evolved hydrogen contained only negligible, trace amounts of impurities. Comparison of these results with those obtained from a TiH<sub>2</sub> standard indicated that the hydrogenation of the MgB<sub>2</sub>-THF-40 mol% Mg, MgB<sub>2</sub>-THF-5 mol% Mg, and MgB<sub>2</sub>-40 mol% MgH<sub>2</sub> resulted in the uptake of 6.0, 4.0, and 3.7 wt% hydrogen, respectively, after adjusting for the hydrogen released by the MgH<sub>2</sub> added to the reaction mixture or the MgH<sub>2</sub> formed by the hydrogenation of added excess Mg. As the high-pressure reactor system did not have the capability to directly measure hydrogen uptake during the high-pressure hydrogenation process, the amount of hydrogen released from the hydrogenated sample using TPD-mass spectroscopy at NREL was used as an indicator of the least amount of hydrogen uptake by the sample. The direct observation of about 8 wt% hydrogen release from TPD-mass spectroscopy analyses of hydrogenated MgB<sub>2</sub>-THF-40 mol% Mg materials confirmed that these materials met the go/no-go hydrogen uptake target of 7 wt% and the go/no-go hydrogen release target of 2 wt%.

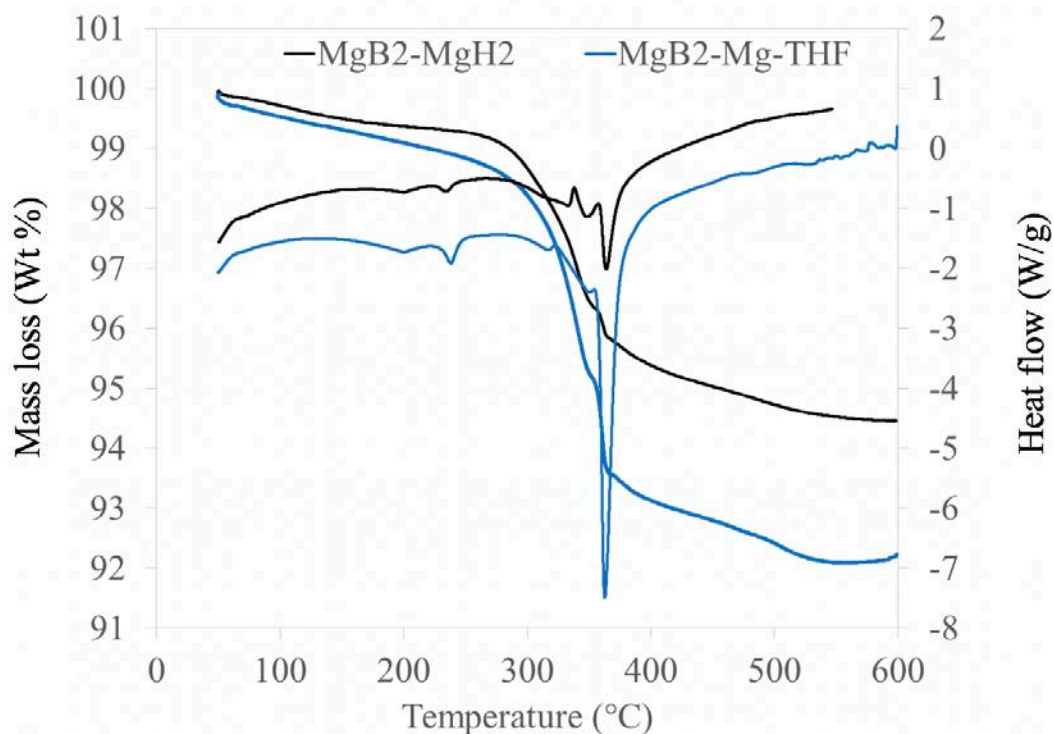


Figure 1. Typical TGA/DSC of  $\text{MgB}_2\text{-THF-40 mol\% Mg}$  and  $\text{MgB}_2\text{-40 mol\% MgH}_2$  hydrogenated at 700 bar and 300°C undergoing dehydrogenation

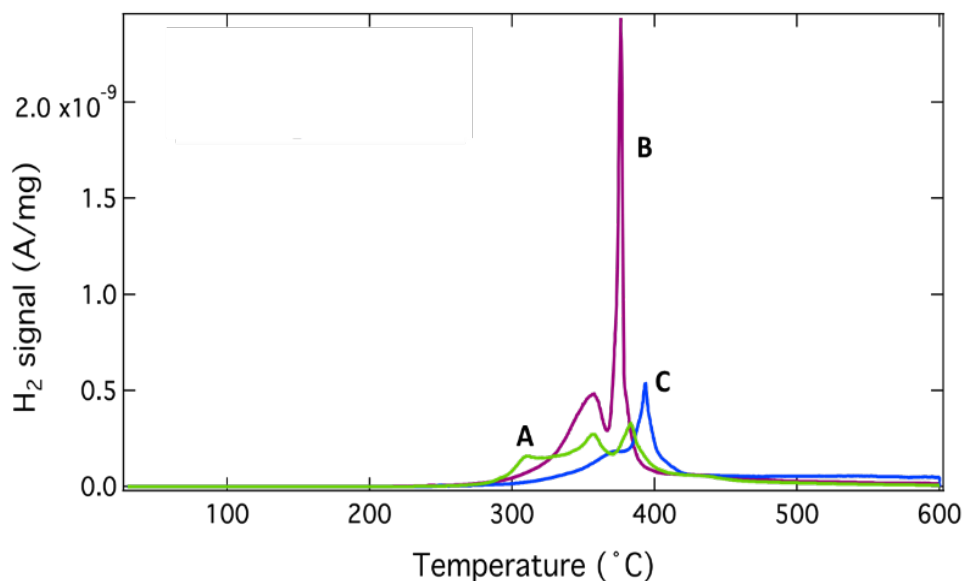


Figure 2. Typical TPD-mass spectroscopy analyses of materials hydrogenated at 700 bar and 300°C. (A)  $\text{MgB}_2\text{-THF-5 mol\% Mg}$ , (B)  $\text{MgB}_2\text{-THF-40 mol\% Mg}$ , and (C)  $\text{MgB}_2\text{-40 mol\% MgH}_2$  products.

Following thermal analyses, solid and solution  $^{11}\text{B}$  and  $^1\text{H}$  NMR spectroscopy was performed. The presence of  $\text{Mg}(\text{BH}_4)_2$  in the hydrogenated samples was confirmed by observance of peaks at about -41 ppm in the  $^{11}\text{B}$  solid-state or solution NMR spectra (Figure 3). The products from the hydrogenation reactions were also analyzed by infrared vibration spectroscopy. The spectra were obtained using a Nicolet iS10 spectrometer with

an attached diamond crystal accessory that allowed the spectra to be collected in an attenuated total reflectance (ATR) mode. As seen in Figure 4, the spectra of the products obtained from the hydrogenation of  $\text{MgB}_2$ -40 mol%  $\text{MgH}_2$  and  $\text{MgB}_2$ -THF-40 mol% Mg verify the formation of  $\text{Mg}(\text{BH}_4)_2$ , as the characteristic absorptions of borohydride are clearly present, the B–H stretches  $2,400\text{ cm}^{-1}$ – $2,200\text{ cm}^{-1}$ , and B–H bends at  $1,100\text{ cm}^{-1}$ – $1,300\text{ cm}^{-1}$ . The NMR and FT-ATR-IR analyses confirmed for the first time  $\text{MgB}_2$  to  $\text{Mg}(\text{BH}_4)_2$  formation from a non-ether-modified  $\text{MgB}_2$  material at  $300^\circ\text{C}$  and 700 bar. These results indicate it is plausible that other modifiers besides ethers, metals, and metal hydrides may be capable of assisting in destabilizing the  $\text{MgB}_2$  structure, enabling hydrogenation of  $\text{MgB}_2$  to  $\text{Mg}(\text{BH}_4)_2$  at much milder reaction conditions. Theoretical modeling work on the project continues to be led and performed by Dr. Wood's group at Lawrence Livermore National Laboratory, including Dr. Shinyoung Kang and Sabrina Wan. The molecular dynamic simulations of the interaction of  $\text{MgB}_2$  layers with THF show strong interaction between THF and  $\text{MgB}_2$ . The THF or THF-derived species are observed to interact with the Mg and B atoms. These interactions are seen to consequently induce defect formation in the  $\text{MgB}_2$  structure, which may facilitate hydrogenation.

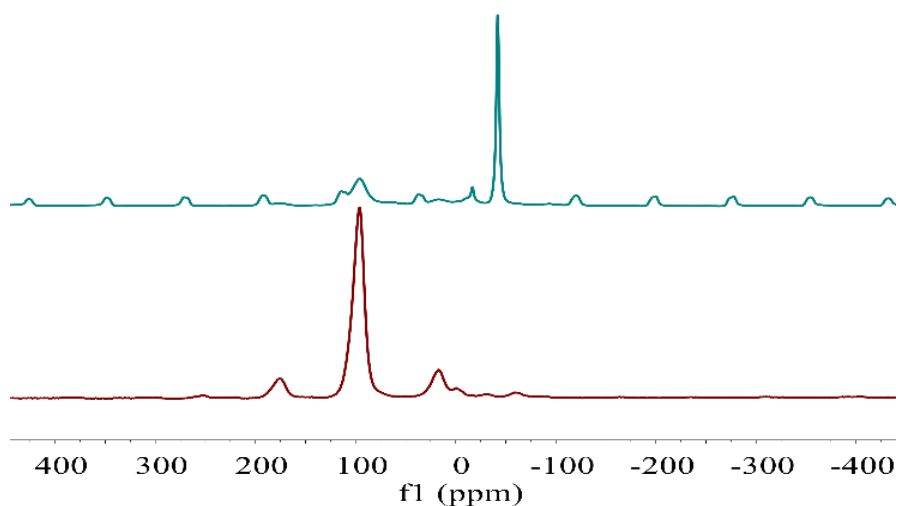


Figure 3. Solid-state  $^{14}\text{B}$  MAS-NMR of product of  $\text{MgB}_2$ -THF-Mg hydrogenation at 700 bar and  $300^\circ\text{C}$ , showing formation of  $\text{Mg}(\text{BH}_4)_2$  at  $-41\text{ ppm}$ ,  $\text{MgB}_{12}\text{H}_{12}$  at  $-15\text{ ppm}$ , and  $\text{MgB}_2$  at  $97\text{ ppm}$ . The boron frequency is  $128.3\text{ MHz}$ . All remaining peaks are spinning side bands.

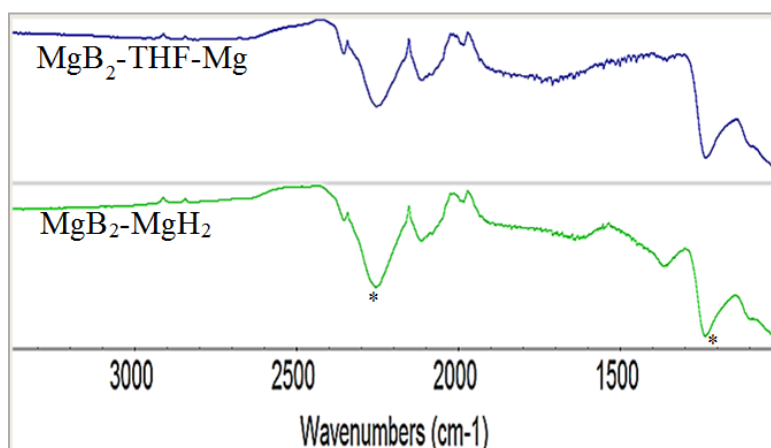


Figure 4. Typical FT-ATR-IR of hydrogenated materials, showing new intense vibrations (asterisked) at  $2,200$ – $2,400\text{ cm}^{-1}$  and  $1,200$ – $1,300\text{ cm}^{-1}$  due to borohydride. Peaks at  $\sim 2,100\text{ cm}^{-1}$  are characteristic of the unreacted  $\text{MgB}_2$ .

## CONCLUSIONS AND UPCOMING ACTIVITIES

In the second fiscal year of the project we have managed to expand our initial hypotheses of  $\text{MgB}_2$  perturbation beyond ether interaction, hence potentially offering new pathways for improving the kinetics of  $\text{MgB}_2$  hydrogenation to  $\text{Mg}(\text{BH}_4)_2$ . We have developed modified  $\text{MgB}_2$  materials from direct mechanochemical reactions of  $\text{MgB}_2$  with metals and metal hydrides in the presence or absence of THF. Improved hydrogenation of  $\text{MgB}_2$  to  $\text{Mg}(\text{BH}_4)_2$  at 300°C and 700 bar was observed from the modified  $\text{MgB}_2$  materials compared to the  $\text{MgB}_2$ -THF only or pure  $\text{MgB}_2$ . FT-ATR-IR and  $^{11}\text{B}$  NMR analyses of hydrogenated modified  $\text{MgB}_2$  directly confirmed  $\text{Mg}(\text{BH}_4)_2$  formation at 300°C and 700 bar. TPD studies performed in collaboration with NREL verified that the evolved hydrogen from hydrogenated products contained only negligible, trace amounts of impurities. The TPD analyses confirmed that the hydrogenation of the  $\text{MgB}_2$ -THF-40 mol% Mg,  $\text{MgB}_2$ -THF-5 mol% Mg, and  $\text{MgB}_2$ -40 mol%  $\text{MgH}_2$  at 300°C and 700 bar results in the uptake of 6.0, 4.0, and 3.7 wt% hydrogen, respectively, after adjusting for the hydrogen released by the  $\text{MgH}_2$  added to the reaction mixture or the  $\text{MgH}_2$  formed by the hydrogenation of added excess Mg. Theoretical studies indicated THF interaction with  $\text{MgB}_2$  with subsequent defect formation in  $\text{MgB}_2$ .

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

- Synthesize novel modified magnesium boride materials.
- Continue to lower hydrogenation temperature and pressure of modified magnesium borides to DOE 2020 target-relevant conditions.
- Perform multiple hydrogen cycling studies of the modified  $\text{MgB}_2$  materials.
- Demonstrate reversible hydrogen uptake of  $\geq 8$  wt% at 400 bar and 300°C.
- Demonstrate 50% cycling stability through three cycles of an optimal formulation of a modified  $\text{MgB}_2$  to  $\text{Mg}(\text{BH}_4)_2$ .
- Perform in situ NMR studies of dehydrogenation of modified Mg boranes.
- Understand mechanisms of hydrogenation enhancement by modifiers.
- Study size-dependent stability and morphology of  $\text{MgB}_2$  clusters + particles.

## FY 2018 PUBLICATIONS/PRESENTATIONS

1. G. Severa and C. Jensen, “Development of Magnesium Boride Etherates as Hydrogen Storage Materials,” Presentation at the 2018 DOE Annual Merit Review and Peer Evaluation Meeting, Washington, D.C., June 2018.
2. G. Severa, C. Jensen, C. Sugai, S. Kim, S. Kang, J. White, V. Stavila, M. Allendorf, and B. Wood, “Activated Magnesium Boride Based Materials for Hydrogen Storage,” Presentation at the 255th ACS National Meeting, New Orleans, LA, March 15–22, 2018.
3. G. Severa, C.M. Jensen, C. Sugai, and S. Kim, “Activated Magnesium Boride Materials for Hydrogen Storage,” PCT International patent, pending (2018).