

## IV.C.11 HyMARC Seedling: Development of Magnesium Boride Etherates as Hydrogen Storage Materials

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- (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 will determine if the reversible hydrogenation of magnesium boride etherates show vastly improved hydrogen cycling kinetics while extending the cycling capacities to levels that are practically viable. Improvement in kinetics has been demonstrated by the decrease in both hydrogenation pressure and hydrogenation temperature to 300°C and 700 bar of a magnesium boride material. Insights gained from this project will be applied toward the development of boride hydrogen storage materials that meet the DOE hydrogen storage targets.

- System Gravimetric Capacity of 0.055 kg H<sub>2</sub>/kg system
- System Volumetric Capacity of 0.040 kg H<sub>2</sub>/L system
- Durability/Operability (max H<sub>2</sub> delivery temperature) 85°C
- Charging/Discharging Rates (system fill times for 5 kg of H<sub>2</sub>) 1.5 kg H<sub>2</sub>/min

### Overall Objectives

- Improve the hydrogen cycling kinetics and cycling capacity of the magnesium boride/magnesium borohydride system to meet Department of Energy (DOE) hydrogen storage targets.
- Synthesize and characterize novel magnesium boride (MgB<sub>2</sub>) etherate materials with improved hydrogen cycling kinetics and hydrogen storage capacities.
- Determine if the reversible hydrogenation of novel boride etherates show vastly improved hydrogen cycling kinetics and cycling capacities to levels that are practically viable.
- Demonstrate capability of MgB<sub>2</sub> ether materials to meet the DOE 2020 hydrogen storage targets.

### Fiscal Year (FY) 2017 Objectives

- Synthesize and characterize novel magnesium boride etherates.
- Demonstrate uptake of ≥7 wt% H<sub>2</sub> at ≤300°C, 700 bar, and 48 h.
- Demonstrate reversible release of ≥2 wt% H<sub>2</sub> by at least one MgB<sub>2</sub> etherate.

### 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 [1].

### FY 2017 Accomplishments

- Formation of novel MgB<sub>2</sub> materials from direct reactions with ethers.
- Demonstrated for the first time hydrogenation of a MgB<sub>2</sub> material to Mg(BH<sub>4</sub>)<sub>2</sub> at 300°C.
- Demonstrated for the first time hydrogenation of a MgB<sub>2</sub> material to Mg(BH<sub>4</sub>)<sub>2</sub> at 700 bar.
- Demonstrated significant weight loss of ~4.9 wt% from MgB<sub>2</sub>-tetrahydrofuran hydrogenated at 300°C and 1,000 bar.
- <sup>11</sup>B nuclear magnetic resonance (NMR) analyses of a hydrogenated MgB<sub>2</sub>-tetrahydrofuran, confirmed Mg(BH<sub>4</sub>)<sub>2</sub> formation at 300°C and 700 bar.
- Completed preliminary design of a medium pressure system (350 bar H<sub>2</sub>, 350°C).
- Theoretical studies indicate plausibility of tetrahydrofuran (THF) coordination to MgB<sub>2</sub>.



## INTRODUCTION

Magnesium borohydride,  $\text{Mg}(\text{BH}_4)_2$ , is one of the few materials that has a demonstrated gravimetric hydrogen storage capacity greater than 11 wt%, and thus a demonstrated potential to be utilized in a hydrogen storage system capable of meeting DOE hydrogen storage targets. However, due to very 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 ( $\sim 900$  bar). Previous work has shown rapid kinetics at moderate temperatures for the reversible dehydrogenation of magnesium borohydride etherates,  $\text{Mg}(\text{BH}_4)_2 \cdot (\text{ether})_x$  to magnesium triborane etherates,  $\text{Mg}(\text{B}_3\text{H}_8)_2(\text{ether})_x$ . These type of materials have much lower hydrogen cycling capacities as a consequence of the weight contribution of the coordinated ethers. However, extending the dehydrogenation to  $\text{MgB}_2 \cdot (\text{ether})_x$  would result in the  $\text{H}_2$  wt% of the system potentially meeting DOE targets. If successful the solid-state  $\text{MgB}_2$  etherate would be safer and cheaper than the high pressure compressed  $\text{H}_2$  (700 bar) or liquid  $\text{H}_2$  alternative onboard storage systems on the market.

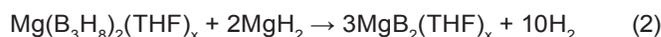
## APPROACH

The project explores the effect of different types of ether ligands and ether stoichiometries on the hydrogen storage properties of the  $\text{MgB}_2$ . In addition to the electronic perturbation caused by the interaction of ethers with the magnesium which may alter the thermodynamics of the reversible hydrogenation of  $\text{MgB}_2$ , the presence of the ethers also results in a 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 ( $\sim 900$  bar), a high-pressure system will be initially utilized for hydrogenation of the borides to magnesium borohydride etherate. We therefore intend to team with HyMARC in order to utilize their high pressure capabilities in the hydrogenation of the magnesium boride etherates as well as their surface characterization equipment. We will determine if the ether-magnesium bonding remains intact during the reversible hydrogenation of boride to borohydrides 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 ether ligand 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  $\text{MgB}_2$  etherate can access new polyborane 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  $\text{MgB}_2/\text{Mg}(\text{BH}_4)_2$  ether 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

The majority of the work in the first year of this project was geared towards synthesis, characterization and hydrogenation of novel magnesium borides with sub-stoichiometric ether content. We considered syntheses of the  $\text{MgB}_2$  etherates from direct reactions of  $\text{MgB}_2$  with various ethers (triglyme, tetraglyme, 1,4-dioxane and 1,3-dioxolane and tetrahydrofuran) and from dehydrogenation of magnesium triborane tetrahydrofuran in accordance to Equations 1 and 2.



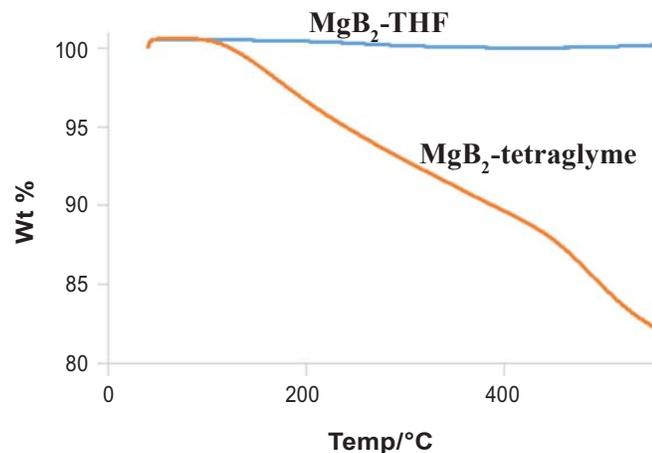
The direct syntheses of  $\text{MgB}_2$  etherates involved the direct reaction of  $\text{MgB}_2$  with ethers using mechanochemistry and heat treatment approaches. The breaking of the  $\text{MgB}_2$  bonds during the high energy mechanical milling was anticipated to create electron deficient reactive sites in the  $\text{MgB}_2$  structure, allowing for the instantaneous reaction and/or binding of sub-stoichiometric amounts of ether. The incorporation of sub-stoichiometric amounts of ether species into the  $\text{MgB}_2$  is key to the maintenance of high gravimetric and volumetric hydrogen densities.

The products of  $\text{MgB}_2$  etherate synthesis from  $\text{MgB}_2$  were characterized by a variety of techniques including solid state and solution  $^{11}\text{B}$  and  $^1\text{H}$  NMR, X-ray diffraction (XRD), infrared vibrational spectroscopy (Fourier transform-attenuated total reflection), thermogravimetric analyses, and differential scanning calorimetry (DSC). Mechanical milling with the ethers reduced crystallinity of the  $\text{MgB}_2$  as evidenced by a reduction of  $\text{MgB}_2$  peak intensity in X-ray diffraction patterns. As expected, no new phases attributable to the minute quantities of coordinated ether were observed in the diffraction pattern. Furthermore, negligible chemical shifts were observed in the  $^{11}\text{B}$  solid state NMR spectra of materials synthesized by mechanical milling process. A similar trend was observed for products from reaction of  $\text{MgB}_2$  and ethers under heat treatment at  $<300^\circ\text{C}$ . The only exception was  $\text{MgB}_2$ -tetraglyme samples which showed new

infrared vibrations and an amorphous broad peak at  $20^\circ 2\theta$  in XRD spectra. Thermogravimetric analyses (Figure 1) indicated significant mass loss of  $>15$  wt% for the  $\text{MgB}_2$ -tetraglyme material.

The dehydrogenation of  $\text{Mg}(\text{B}_3\text{H}_8)_2(\text{THF})_2/\text{MgH}_2$  to form  $\text{MgB}_2$ -THF was also performed at  $390^\circ\text{C}$  for 24 h followed by a second low temperature heat treatment in presence of THF.  $^{11}\text{B}$  solution NMR of the dehydrogenated material in  $\text{D}_2\text{O}$  indicated no soluble boron species confirming absence of water soluble magnesium borane species (e.g.,  $\text{MgB}_{12}\text{H}_{12}$ ). Fourier transform-attenuated total reflection spectra showed no B-H stretches in  $2,100\text{--}2,800\text{ cm}^{-1}$  region. The surprising absence of  $\text{MgB}_{12}\text{H}_{12}$  below  $400^\circ\text{C}$  points towards plausibility of pathways for forming  $\text{MgB}_2$  at lower temperatures. Further investigations are underway to optimize the dehydrogenation reactions of  $\text{Mg}(\text{B}_3\text{H}_8)_2(\text{THF})_2$ .

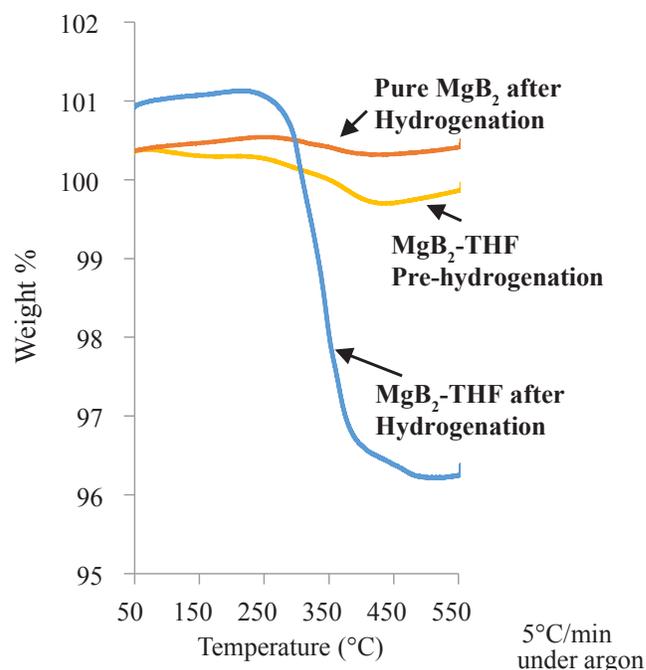
The syntheses and characterization work was subsequently followed by high pressure hydrogenations of the products of  $\text{MgB}_2$  etherate synthesis. The preliminary high pressure hydrogenations were performed to determine the magnesium boride etherate materials with the best potential pathway to meeting DOE hydrogen storage targets. The magnesium boride etherates were hydrogenated at HyMARC-Sandia National Laboratories facility at  $\leq 1,000$  bar,  $\leq 400^\circ\text{C}$  and  $\leq 72$  h, with the assistance of Dr. Stavila, Dr. White, and Dr. Allendorf. Pure, as received  $\text{MgB}_2$  and ball milled pure  $\text{MgB}_2$  were also hydrogenated and used as controls for comparison with the synthesized  $\text{MgB}_2$  etherates. Prior to hydrogenation experiments, all the samples were vacuumed for at least 12 h in the Sandia National Laboratories glovebox antechamber to ensure removal of any residual weakly coordinated ethers on the  $\text{MgB}_2$  etherates and hence reduce contamination of the hydrogenation reactor system. Subsequent characterizations of the hydrogenated samples were performed using XRD, NMR, thermogravimetric



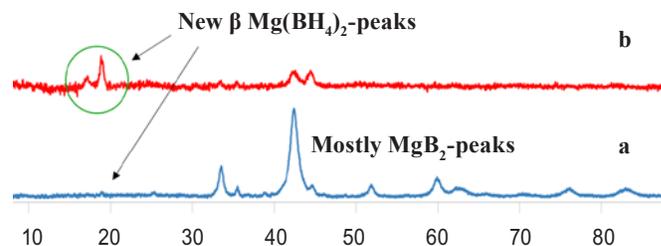
**FIGURE 1.** Thermogravimetric analysis of heat treated  $\text{MgB}_2$ -tetraglyme and  $\text{MgB}_2$ -THF samples at  $5^\circ\text{C}/\text{min}$  in Ar

analyses-DSC and Fourier transform-attenuated total reflection. The  $\text{MgB}_2$ -THF synthesized by mechanochemistry was determined to have the best hydrogenation performance. Significant hydrogenation of an  $\text{MgB}_2$  material at  $300^\circ\text{C}$  and 1,000 bar was demonstrated for the first time using this material. Thermogravimetric analyses (Figure 2) indicated about 4.9% weight loss from the  $\text{MgB}_2$ -THF hydrogenated at  $300^\circ\text{C}$  and 1,000 bar. The XRD of the  $\text{MgB}_2$ -THF showed new patterns around  $20^\circ 2\theta$  attributed to  $\text{Mg}(\text{BH}_4)_2$  (Figure 3).  $^{11}\text{B}$  and  $^1\text{H}$  solution NMR spectra confirmed the presence of  $\text{Mg}(\text{BH}_4)_2$  as major borohydride product in sample.

Following the initial hydrogenations, more effort was placed on direct syntheses of the boride etherates using a mechanochemistry approach with special emphasis on



**FIGURE 2.** Thermogravimetric analysis of hydrogenated 9 h ball milled  $\text{MgB}_2$ -THF indicating significant weight loss ( $\sim 4.9$  wt%) at  $300^\circ\text{C}$  and 1,000 bar



**FIGURE 3.** XRD of hydrogenated ball milled samples of pure  $\text{MgB}_2$  and  $\text{MgB}_2$ -THF, confirming  $\text{Mg}(\text{BH}_4)_2$  formation at  $300^\circ\text{C}$  and 1,000 bar

THF. Hydrogenation of this next set of  $\text{MgB}_2$ -THF materials demonstrated for the first time hydrogen uptake by an  $\text{MgB}_2$  material at 300°C and 700 bar.  $^{11}\text{B}$  solution NMR confirmed presence of  $\text{Mg}(\text{BH}_4)_2$  in the  $\text{MgB}_2$ -THF hydrogenated material (Figure 4). No hydrogenation was observed in pure ball milled  $\text{MgB}_2$  as evidenced by absence of boron species in  $^{11}\text{B}$  solution NMR spectra. This result points towards the THF greatly perturbing the  $\text{MgB}_2$  structure hence allowing for the increased kinetics of hydrogenation of  $\text{MgB}_2$ . Efforts to determine the weight percent hydrogen uptake and complete characterization of the boride materials are underway. We are also collaborating with Dr. Gennett at National Renewable Energy Laboratory on performing temperature programmed desorption studies coupled with mass spectroscopy analyses to attempt to detect the tightly bound ether or ether derived species in the novel  $\text{MgB}_2$  materials. This is necessitated by the current lack of conclusive, direct evidence of the strongly bound ether in most magnesium boride etherates from techniques such as NMR. Theoretical modelling work on the project is concurrently being led and performed by HyMARC groups of Dr. Wood at Lawrence Livermore National and Dr. Prendergarst at Lawrence Berkeley National Laboratory. The molecular dynamics simulations of magnesium boride etherates indicate plausibility of THF coordination to  $\text{MgB}_2$ . The THF is observed to bond to both the Mg and B atoms on edge and basal planes of  $\text{MgB}_2$  sheets. The safe design of a medium pressure (350 bar, 350°C) hydrogenation reactor system was performed in consultation with HyMARC-Sandia National Laboratories personnel. When built this reactor

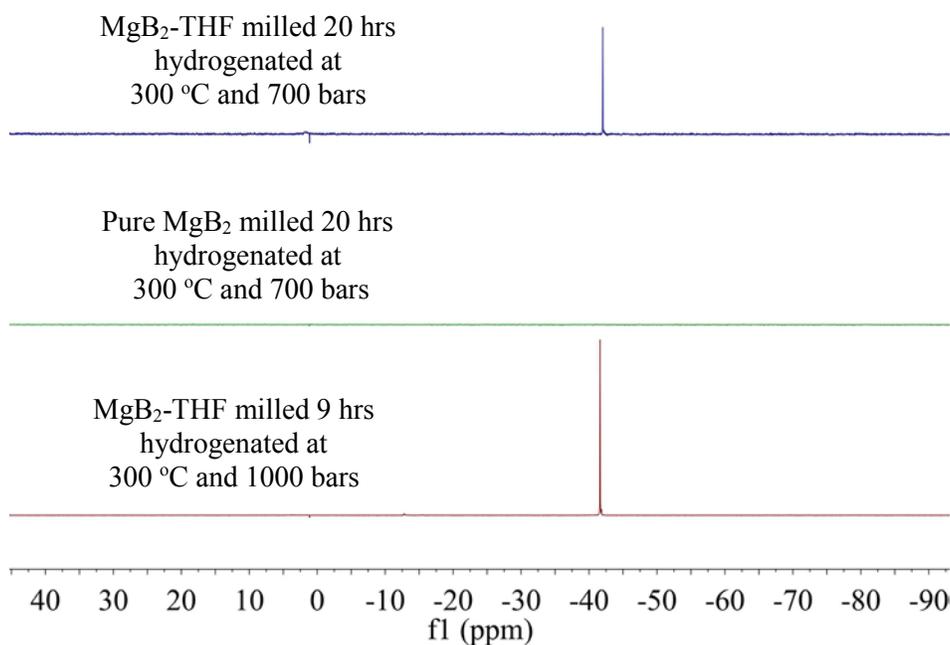
system will assist in the efficient hydrogenation of samples at high and medium pressures.

## CONCLUSIONS AND UPCOMING ACTIVITIES

In this first year of the project we have demonstrated that our novel  $\text{MgB}_2$  materials have better performance than state-of-the-art pure  $\text{MgB}_2$ . Through this work we have shown for the first time that the  $\text{MgB}_2$  system can be hydrogenated at temperatures as low as 300°C and at pressures as low as 700 bar. Significant hydrogenation (up to 4.9 wt%) of an  $\text{MgB}_2$  material was demonstrated at 300°C and 1,000 bar for the first time, using the mechanochemically synthesized  $\text{MgB}_2$ -THF. The improved hydrogenation performance of  $\text{MgB}_2$ -THF indicates the effective interaction of  $\text{MgB}_2$  and THF allowing the  $\text{MgB}_2$  material to be hydrogenated at lower temperature and pressure than pure  $\text{MgB}_2$ . Molecular Dynamics Simulations support the plausibility of strong coordination between THF and  $\text{MgB}_2$ . Our work proves it is possible to continuously lower the  $\text{H}_2$  uptake temperature and pressure of  $\text{MgB}_2$  hydrogenation to  $\text{Mg}(\text{BH}_4)_2$ .

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

- Complete characterization of products of boride etherate synthesis.
- Understanding mechanism of hydrogenation enhancement by ethers.



**FIGURE 4.**  $^{11}\text{B}$  solution NMR of ball milled  $\text{MgB}_2$ -THF samples hydrogenated at 300°C, confirming formation of  $\text{Mg}(\text{BH}_4)_2$  at 1,000 bar and 700 bar

- Variable hydrogenation time studies at 700 bar and 300°C.
- Demonstration of hydrogen uptake  $\geq 7$  wt% at 700 bar and 300°C.
- Hydrogen cycling studies and determining the factors that limit H<sub>2</sub> cycling kinetics.
- Size-dependent stability and morphology of MgB<sub>2</sub> clusters + particles.
- Coordination analysis of solutions and solvent-dependence of stability.

## FY 2017 PUBLICATIONS/PRESENTATIONS

1. “Development of Magnesium Boride Etherates as Hydrogen Storage Materials,” presented at the 2017 DOE Annual Merit Review and Peer Evaluation Meeting, Washington, D.C., June 2017.

## REFERENCES

1. “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>