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

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$_2$) 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$_2$ 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$_2$ at ≤300°C, 700 bar, and 48 h.
- Demonstrate reversible release of ≥2 wt% H$_2$ by at least one MgB$_2$ 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].

(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$_2$/kg system
- System Volumetric Capacity of 0.040 kg H$_2$/L system
- Durability/Operability (max H$_2$ delivery temperature) 85°C
- Charging/Discharging Rates (system fill times for 5 kg of H$_2$) 1.5 kg H$_2$/min

FY 2017 Accomplishments

- Formation of novel MgB$_2$ materials from direct reactions with ethers.
- Demonstrated for the first time hydrogenation of a MgB$_2$ material to Mg(BH$_4$)$_2$ at 300°C.
- Demonstrated for the first time hydrogenation of a MgB$_2$ material to Mg(BH$_4$)$_2$ at 700 bar.
- Demonstrated significant weight loss of ~4.9 wt% from MgB$_2$-tetrahydrofuran hydrogenated at 300°C and 1,000 bar.
- $^{11}$B nuclear magnetic resonance (NMR) analyses of a hydrogenated MgB$_2$-tetrahydrofuran, confirmed Mg(BH$_4$)$_2$ formation at 300°C and 700 bar.
- Completed preliminary design of a medium pressure system (350 bar H$_2$, 350°C).
- Theoretical studies indicate plausibility of tetrahydrofuran (THF) coordination to MgB$_2$. ✷ ✷ ✷ ✷ ✷ ✷
INTRODUCTION

Magnesium borohydride, \( \text{Mg(BH}_4 \rangle_2 \), 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 \( \text{Mg(BH}_4 \rangle_2 \) and \( \text{MgB}_2 \) has been accomplished only at high temperature (~400°C) and under high charging pressure (~900 bar). Previous work has shown rapid kinetics at moderate temperatures for the reversible dehydrogenation of magnesium borohydride etereates, \( \text{Mg(BH}_4 \rangle_2 \times(\text{ether})_x \), to magnesium triborane etereates, \( \text{Mg(B}_3 \text{H}_8 \rangle_2 \times(\text{ether})_x \). 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 \( \text{MgB}_2 \times(\text{ether})_x \) 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 \( \text{Mg(BH}_4 \rangle_2 / \text{MgB}_2 \) 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 borides to magnesium borohydride etherate. We therefore intend to team with HyMARC in order to utilize their high pressure capabilities in the hydrogenation of novel magnesium borides with sub-stoichiometric ether content. We considered syntheses of the \( \text{MgB}_2 \) ethers 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.

\[
\text{MgB}_2 + x(\text{ether}) \rightarrow \text{MgB}_2(\text{ether})_x \tag{1}
\]

\[
\text{Mg(B}_3\text{H}_8\rangle_2(\text{THF})_x + 2\text{MgH}_2 \rightarrow 3\text{MgB}_2(\text{THF})_x + 10\text{H}_2 \tag{2}
\]

The direct syntheses of \( \text{MgB}_2 \) etereates 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°C. The only exception was \( \text{MgB}_2 \times\text{tetraglyme} \) samples which showed new
infrared vibrations and an amorphous broad peak at 20° 2θ in XRD spectra. Thermogravimetric analyses (Figure 1) indicated significant mass loss of >15 wt% for the MgB₂-tetraglyme material.

The dehydrogenation of Mg(B₃H₈)(THF)₂/MgH₂ to form MgB₂-THF was also performed at 390°C for 24 h followed by a second low temperature heat treatment in presence of THF. ¹¹B solution NMR of the dehydrogenated material in D₂O indicated no soluble boron species confirming absence of water soluble magnesium borane species (e.g., MgB₁₂H₁₂). Fourier transform-attenuated total reflection spectra showed no B-H stretches in 2,100–2,800 cm⁻¹ region. The surprising absence of MgB₁₂H₁₂ below 400°C points towards plausibility of pathways for forming MgB₂ at lower temperatures. Further investigations are underway to optimize the dehydrogenation reactions of Mg(B₃H₈)(THF)₂.

The syntheses and characterization work was subsequently followed by high pressure hydrogenations of the products of MgB₂ 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 ≤1,000 bar, ≤400°C and ≤72 h, with the assistance of Dr. Stavila, Dr. White, and Dr. Allendorf. Pure, as received MgB₂ and ball milled pure MgB₂ were also hydrogenated and used as controls for comparison with the synthesized MgB₂ 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 MgB₂ etherates and hence reduce contamination of the hydrogenation reactor system. Subsequent characterizations of the hydrogenated samples were performed using XRD, NMR, thermogravimetric analyses-DSC and Fourier transform-attenuated total reflection. The MgB₂-THF synthesized by mechanochemistry was determined to have the best hydrogenation performance. Significant hydrogenation of an MgB₂ material at 300°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 MgB₂-THF hydrogenated at 300°C and 1,000 bar. The XRD of the MgB₂-THF showed new patterns around 20° 2θ attributed to Mg(BH₄)₂ (Figure 3). ¹¹B and ¹H solution NMR spectra confirmed the presence of Mg(BH₄)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 1.** Thermogravimetric analysis of heat treated MgB₂-tetraglyme and MgB₂-THF samples at 5°C/min in Ar

**FIGURE 2.** Thermogravimetric analysis of hydrogenated 9 h ball milled MgB₂-THF indicating significant weight loss (~4.9 wt%) at 300°C and 1,000 bar

**FIGURE 3.** XRD of hydrogenated ball milled samples of pure MgB₂ and MgB₂-THF, confirming Mg(BH₄)₂ formation at 300°C and 1,000 bar
THF. Hydrogenation of this next set of MgB$_2$-THF materials demonstrated for the first time hydrogen uptake by an MgB$_2$ material at 300°C and 700 bar. $^{11}$B solution NMR confirmed presence of Mg(BH$_4$)$_2$ in the MgB$_2$-THF hydrogenated material (Figure 4). No hydrogenation was observed in pure ball milled MgB$_2$ as evidenced by absence of boron species in $^{11}$B solution NMR spectra. This result points towards the THF greatly perturbing the MgB$_2$ structure hence allowing for the increased kinetics of hydrogenation of 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 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 MgB$_2$. The THF is observed to bond to both the Mg and B atoms on edge and basal planes of 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 MgB$_2$ materials have better performance than state-of-the-art pure MgB$_2$. Through this work we have shown for the first time that the 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 MgB$_2$ material was demonstrated at 300°C and 1,000 bar for the first time, using the mechanochemically synthesized MgB$_2$-THF. The improved hydrogenation performance of MgB$_2$-THF indicates the effective interaction of MgB$_2$ and THF allowing the MgB$_2$ material to be hydrogenated at lower temperature and pressure than pure MgB$_2$. Molecular Dynamics Simulations support the plausibility of strong coordination between THF and MgB$_2$. Our work proves it is possible to continuously lower the H$_2$ uptake temperature and pressure of MgB$_2$ hydrogenation to Mg(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.
• Variable hydrogenation time studies at 700 bar and 300°C.
• Demonstration of hydrogen uptake ≥7 wt% at 700 bar and 300°C.
• Hydrogen cycling studies and determining the factors that limit H₂ cycling kinetics.
• Size-dependent stability and morphology of MgB₂ clusters + particles.
• Coordination analysis of solutions and solvent-dependence of stability.

**FY 2017 PUBLICATIONS/PRESENTATIONS**


**REFERENCES**