Hawaiʻi Natural Energy Institute Research Highlights

Advanced Materials

Magnesium Boride Etherates for Hydrogen Storage

Objective and Significance: The objective of this project is to synthesize and characterize novel modified magnesium boride, MgB_2, materials with improved hydrogen cycling kinetics and hydrogen storage capacities and demonstrate their capability to meet the U.S. Department of Energy (DOE) hydrogen storage targets. If successful, the solid-state modified MgB_2 materials would be safer and cheaper than the high pressure compressed H_2 (700 bar) or liquid H_2 alternative onboard vehicle hydrogen storage systems on the market.

Background: Magnesium borohydride, $Mg(BH_4)_2$, 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 meeting U.S. DOE hydrogen storage targets. However, due to extremely very slow kinetics, cycling between $Mg(BH_4)_2$ and MgB_2, has been accomplished only at high temperature (~400°C) and under high charging pressure (~900 bar). More recently, tetrahydrofuran (THF) complexed to $Mg(BH_4)_2$ has been shown to vastly improve the kinetics of dehydrogenation, enabling the rapid release of H_2 at < 200°C to give $Mg(B_{10}H_{10})$ with high selectivity. However, these types of materials have much lower hydrogen cycling capacities. This project is focused on development of modified MgB_2 by either extending the dehydrogenation of magnesium borane etherates to MgB_2 or by direct syntheses of the modified MgB_2 in presence of additives. The immediate goal of the third-year project period is to show hydrogenation at temperatures and pressures below 300 bar and 250°C. This will be a significant improvement over the pre-project state of art (900 bar and 400°C), as well as our previous year project achievement of 400 bar and 300°C.

This HNEI-led project is a collaborative effort between UH (HNEI and the Department of Chemistry) and the DOE-HyMARC Consortium including Sandia National Laboratory, Lawrence Livermore National Laboratory, and National Renewable Energy Laboratory.

Project Status/Results: Our research effort is focused on the direct syntheses and characterization of modified MgB_2 with improved hydrogen uptake properties. The project continues to be guided by computational calculations from Lawrence Livermore National Laboratory (Figure 1). The molecular dynamic simulations suggest that additives e.g. THF or anthracene can modify the MgB_2 structure rendering it susceptible to hydrogen uptake at moderate conditions compared to pure MgB_2.

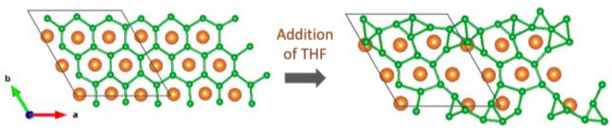

Figure 1. MD Simulations indicating strong coordination of THF to MgB_2 with plausible subsequent defect formation in MgB_2 structure.

To date, significant progress has been made towards improving the hydrogen storage properties of $MgB_2/Mg(BH_4)_2$ system (Figure 2). The bulk MgB_2 hydrogenation pressure has been reduced from 900 bar to 400 bar and temperatures from 400°C to 300°C, while maintaining the MgB_2 to $Mg(BH_4)_2$ conversion of greater than 75%. Recent results indicate that MgB_2, modified with a unique combination of additives can be hydrogenated to $Mg(BH_4)_2$ at the moderate conditions of 160 bar and 250°C. However, the hydrogenation is limited to the surface of the material with minimum hydrogen uptake into the bulk of the material.

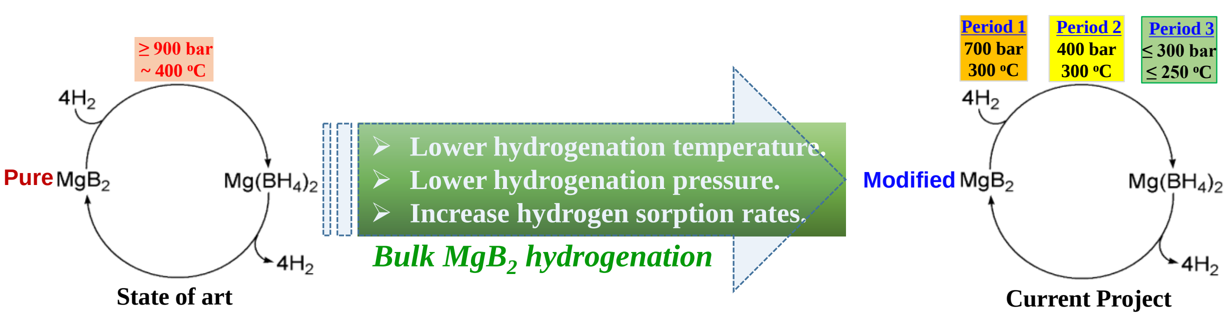

Figure 2. Progression of project efforts towards improving hydrogen storage properties of $MgB_2/Mg(BH_4)_2$ system.

Hawaiʻi Natural Energy Institute | School of Ocean & Earth Science & Technology
University of Hawaiʻi at Mānoa, 1680 East-West Road, POST 109 • Honolulu, HI 96822
Phone: (808) 956-8890 • Fax: (808) 956-2336 • www.hnei.hawaii.edu

Our research efforts towards improving the hydrogen uptake into the bulk of the material over the past year, did not result in significant improvement, at these desirable lower pressure and lower temperature conditions. A variety of characterizations were performed on the as-synthesized and hydrogenated MgB_2 materials (Figure 3). We have utilized: (a) X-ray absorption spectroscopy (XAS) to study the evolution of the boron or magnesium K-edge spectra of the as-synthesized and hydrogenated modified MgB_2 samples in attempts to correlate any trends of MgB_2 perturbation/destabilization to the extent of hydrogen uptake observed experimentally; (b) electron paramagnetic spectroscopy (EPR) to assist with determining if defects created through the ball milling and/or interaction of MgB_2 with modifiers, contributed to the higher hydrogen uptake observed in some of the modified MgB_2 samples; (c) nuclear magnetic resonance spectroscopy (NMR) to directly confirm the formation of $Mg(BH_4)_2$ from MgB_2 and; (d) scanning transmission electron microscopy (S)TEM to elucidate the microstructure and composition of the as-synthesized and hydrogenated MgB_2-graphene nanoplatelet samples.

The continuous improvement of the hydrogenation conditions of MgB_2 from the state of art 900 bar and 400°C to now 160 bar and 250°C shows the plausibility of continuously improving the hydrogenation kinetics of the MgB_2 to $Mg(BH_4)_2$, to conditions relevant for onboard hydrogen storage.

A peer reviewed, journal cover article on discovery of additives for enhancing MgB_2 hydrogenation kinetics has resulted from this work. The final technical report was submitted to DOE-EERE.

Funding Source: U.S. Department of Energy, EERE; Energy Systems Development Special Fund

Contact: Godwin Severa, severa@hawaii.edu

Last Updated: November 2021

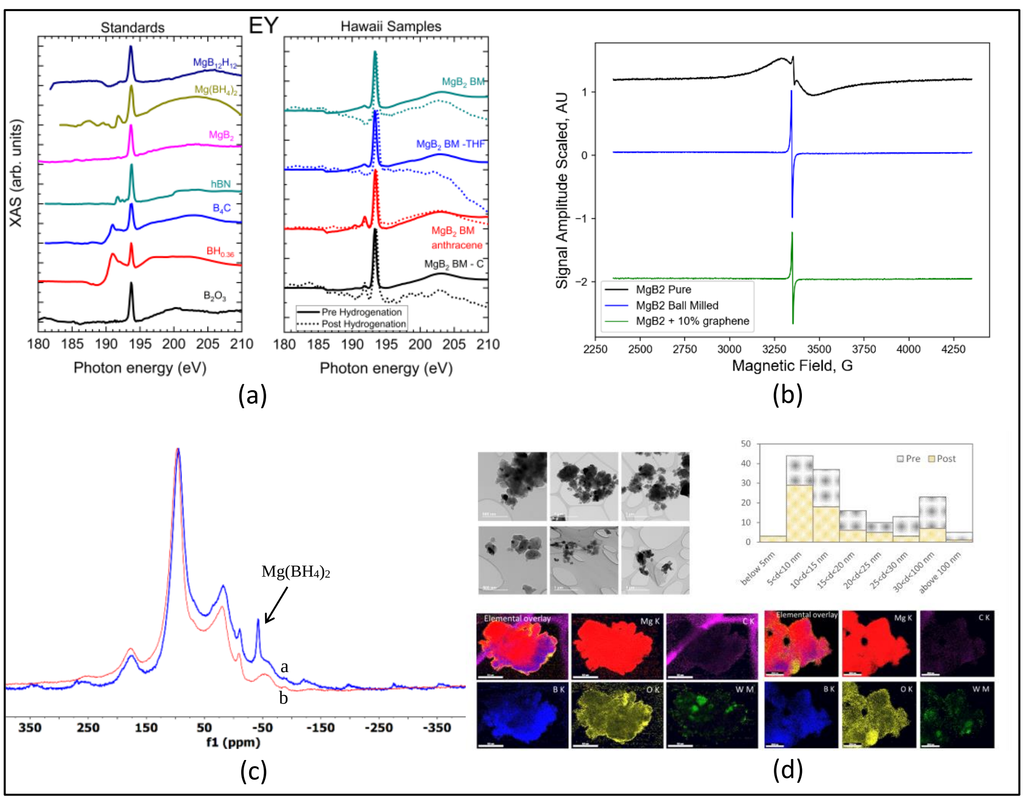

Figure 3. Typical characterizations of modified MgB_2 materials on project; (a) X-ray absorption spectroscopy (XAS), (b) Electron paramagnetic spectroscopy (EPR) (c) nuclear magnetic resonance spectroscopy (NMR) and (d) Scanning transmission electron microscopy (S)TEM.

ADDITIONAL PROJECT RELATED LINKS

TECHNICAL REPORTS:

1. 2020, **HyMARC Seedling: Development of Magnesium Boride Etherates as Hydrogen Storage Materials**, G. Severa, C. Jensen, C. Sugai, S. Kim, 2019 DOE Hydrogen and Fuel Cells Program, Annual Progress Report to the U.S. Department of Energy for Contract Number DE-EE0007654.
2. 2019, **HyMARC Seedling: Development of Magnesium Boride Etherates as Hydrogen Storage Materials**, G. Severa, C. Jensen, C. Sugai, S. Kim, 2018 DOE Hydrogen and Fuel Cells Program, Annual Progress Report to the U.S. Department of Energy for Contract Number DE-EE0007654.
3. 2018, **HyMARC Seedling: Development of Magnesium Boride Etherates as Hydrogen Storage Materials**, G. Severa, C. Jensen, C. Sugai, S. Kim, 2017 DOE Hydrogen and Fuel Cells Program, Annual Progress Report to the U.S. Department of Energy for Contract Number DE-EE0007654.

PAPERS AND PROCEEDINGS:

1. 2019, C. Sugai, S. Kim, G. Severa, J. L. White, N. Leick, M. B. Martinez, T. Gennett, V. Stavila, and C. Jensen, **Kinetic Enhancement of Direct Hydrogenation of MgB2 to Mg(BH4)2 upon Mechanical Milling with THF, MgH2, and/or Mg**, ChemPhysChem, Vol. 20, pp. 1-5.