



Hawai'i Natural Energy Institute Research Highlights

Advanced Materials

Magnesium Boride Etherates for Hydrogen Storage

OBJECTIVE AND SIGNIFICANCE: The objective of this project was 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 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 ($\sim 400^\circ C$) 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 $< 200^\circ C$ to give $Mg(B_{10}H_{10})$ with high selectivity. However, these types of materials have much lower hydrogen cycling capacities. This project was 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.

This project is geared towards improving the hydrogen cycling kinetics and cycling capacity of a magnesium boride/magnesium borohydride system, to contribute towards meeting the DOE hydrogen storage ultimate targets. The project aims to 1) synthesize and characterize novel modified magnesium borides, especially ether modified materials, with improved hydrogen cycling kinetics and hydrogen storage capacities compared to unmodified MgB_2 ; and 2) determine if the reversible hydrogenation of the novel modified borides shows vastly improved hydrogen cycling kinetics and cycling capacities to levels that are practically viable.

This HNEI-led project was a collaborative effort between UH (HNEI and the Department of Chemistry) and the DOE-Hydrogen Materials

Advanced Research Consortium (HyMARC) including Sandia National Laboratories, Lawrence Livermore National Laboratory, and National Renewable Energy Laboratory. The HyMARC collaboration enables access to state-of-art experimental capabilities, characterization tools, and theoretical modelling expertise at the U.S. National Laboratories. The project had two critical Go/No-Go decision points associated with main tasks, which were both met: 1) demonstration of ≥ 7.0 wt% hydrogen uptake by a modified MgB_2 at 700 bar and $300^\circ C$; and 2) demonstration of ≥ 8.0 wt% reversible hydrogen uptake by a modified MgB_2 at 400 bar and $300^\circ C$.

PROJECT STATUS/RESULTS: Our research effort focused on the direct syntheses and characterization of modified MgB_2 with improved hydrogen uptake properties. The project continued to be guided by computational calculations led by Lawrence Livermore National Laboratory. The theoretical modelling studies of MgB_2 interaction with ethers was conducted using the Density functional theory (DFT) calculations and *ab initio* molecular dynamic (AIMD) simulations using various MgB_2 surfaces with tetrahydrofuran (THF). The molecular dynamic simulations suggest that additives (e.g. THF or anthracene) can modify the MgB_2 structure. The B-terminated {0001} basal plane of MgB_2 is known to undergo surface reconstruction under ambient conditions, consequently affecting its electronic structure. The AIMD simulations found that THF accelerates such surface reconstruction (Figure 1).

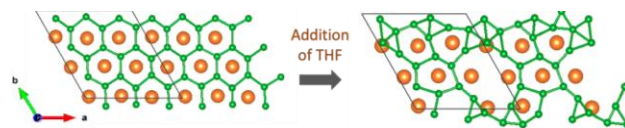


Figure 1. MD Simulations indicating strong coordination of THF to MgB_2 with plausible subsequent defect formation in MgB_2 structure.

Charge density analysis indicates that the electron-deficiency is the key to reconstruct the surface B sheet. It implies the oxidizing role of THF to modify B-B bond properties on MgB_2 surface and facilitate the nucleation of hydrogenated $B_xH_y^{n-}$ units during hydrogenation.

To date, significant progress has been made towards improving the hydrogen storage properties of a

MgB₂/Mg(BH₄)₂ system (Figure 2). The bulk MgB₂ hydrogenation pressure has been reduced from 900 bar to 400 bar and temperatures from 400°C to 300°C, while maintaining the MgB₂ to Mg(BH₄)₂ conversion of greater than 75%. Our results indicate that MgB₂, modified with a unique combination of additives can be hydrogenated to Mg(BH₄)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. Our research efforts towards improving the hydrogen uptake into the bulk of the material over the past period, 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 MgB₂ 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 MgB₂ samples in attempts to correlate any trends of MgB₂ 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 MgB₂ with modifiers, contributed to the higher hydrogen uptake observed in some of the modified MgB₂ samples; c) nuclear magnetic resonance spectroscopy (NMR) to directly confirm the formation of Mg(BH₄)₂ from MgB₂ and; d) scanning transmission electron microscopy (S)TEM to elucidate the microstructure and composition of the as-synthesized and hydrogenated MgB₂-graphene nanoplatelet samples.

Overall, the project managed to achieve a major reduction in the conditions required for hydrogenation of bulk magnesium boride to magnesium borohydride through the use of modifiers for the first time. The major accomplishments are as follows:

- Demonstrated reduction of the conditions at which MgB₂ can be thermally hydrogenated to Mg(BH₄)₂; from state of art of ~900 bar and ~400°C prior to project to about 160 bar and 250°C. Though this is a remarkable achievement, the yields are still low compared to the 900 bar/400°C conditions.
- Synthesized destabilized MgB₂ materials from direct reactions of MgB₂ with modifiers, especially tetrahydrofuran (THF) using mechanochemistry methods.
- Established correlation of theory and experiment with feedback loop, leading to quick optimization of materials discovery.
- Demonstrated about 8 wt% H₂ release from MgB₂ treated with tetrahydrofuran and 40 mol% Mg, and then hydrogenated at 300°C and 700 bar. This result translates to an uptake of ~6 wt% H₂, after adjusting for the H₂ released by the MgH₂ formed by the hydrogenation of Mg.
- Demonstrated hydrogen cycling of bulk MgB₂ at 400 bar and 300°C with at least 6 wt% H₂ cycling capacity from a MgB₂ treated with 10 mol% graphene nanoplatelets. ¹¹B solid state nuclear magnetic resonance spectroscopy line fitting analyses indicates 85% conversion of MgB₂ to Mg(BH₄)₂.
- Discovered at least five modifiers (graphene, anthracene, Mg-THF, MgH₂ and Mg) capable of improving hydrogen uptake of MgB₂ to Mg(BH₄)₂ at ≤400 bar and ≤300°C.

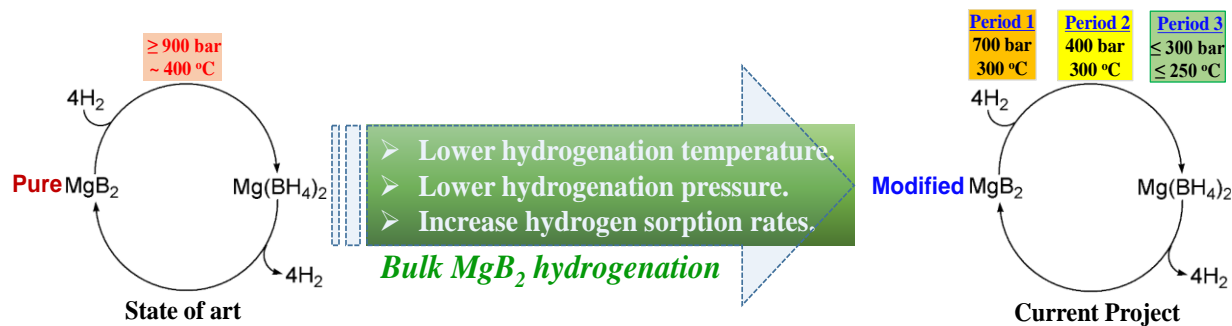


Figure 2. Progression of project efforts towards improving hydrogen storage properties of MgB₂/Mg(BH₄)₂ system.

- Demonstrated the plausibility of enhancing the hydrogen storage properties of the Mg-B-H system using modifiers, with higher capability of chemical or structural modification of MgB₂, enabling more efficient hydrogenation of MgB₂ to Mg(BH₄)₂, towards PEM fuel cell operation conditions. The continuous improvement of the hydrogenation conditions of MgB₂ 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 MgB₂ to Mg(BH₄)₂, to conditions relevant for onboard hydrogen storage.

This project concluded in 2021. In addition to the accomplishments listed above, this work produced:

- 1) a final technical report which was submitted to DOE; 2) the paper "[Kinetic Enhancement of Direct Hydrogenation of MgB₂ to Mg\(BH₄\)₂ upon Mechanical Milling with THF, MgH₂, and/or Mg](#)" published in journal *ChemPhysChem*; and 3) the filing of U.S Patent 11,661,338 "[Activated Magnesium Boride Materials for Hydrogen Storage](#)".

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Contact: Godwin Severa, severa@hawaii.edu

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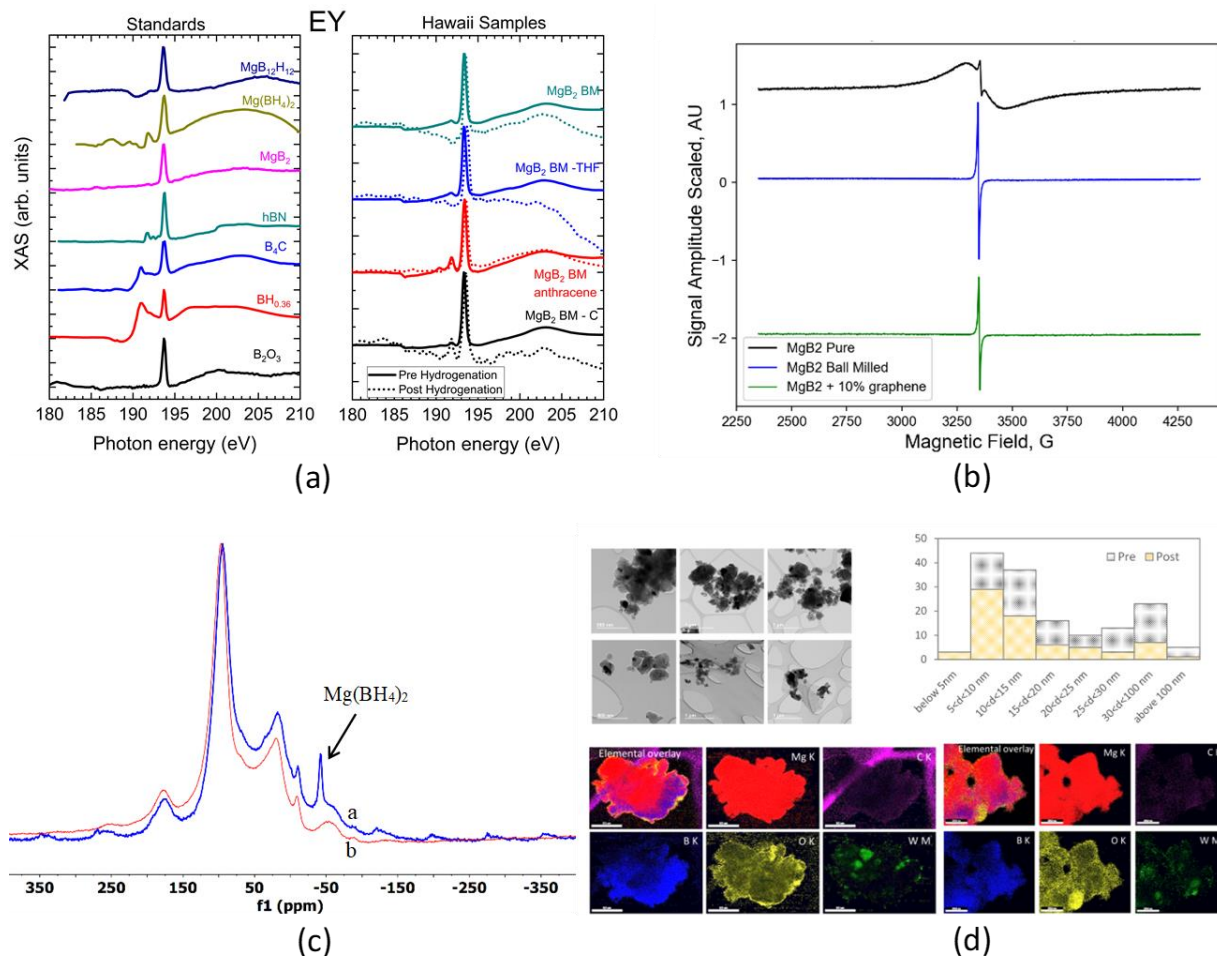


Figure 3. Typical characterizations of modified MgB₂ materials on project; (a) X-ray absorption spectroscopy (XAS), (b) Electron paramagnetic spectroscopy (EPR) (c) nuclear magnetic resonance spectroscopy (NMR) and (d) Scanning transmission electron microscopy (S)TEM.