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 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$_2$.

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.
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 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.

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.

A peer reviewed, journal cover article on discovery of additives for enhancing MgB₂ hydrogenation kinetics has resulted from this work. The final technical report was submitted to DOE-EERE.

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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.
ADDITIONAL PROJECT RELATED LINKS

TECHNICAL REPORTS:

PAPERS AND PROCEEDINGS: