

IV.A.1s Lightweight Intermetallics for Hydrogen Storage

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Objectives

The objective of this project is to develop a high-capacity lightweight hydride for reversible vehicular hydrogen storage, capable of meeting or exceeding the 2010 DOE/FreedomCAR targets. The current focus of the project is on $\text{Mg}(\text{BH}_4)_2$ and its complexes which have very high capacities and attractive properties. The key is to make them reversible. To accomplish this, we are working on detailed characterization of the decomposition mechanism of $\text{Mg}(\text{BH}_4)_2$ and on the properties of amine complexes of borohydrides.

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Multi-Year Research, Development and Demonstration Plan:

- (D) Durability/Operability
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption
- (E) Charging/Discharging Rates
- (J) Thermal Management

Technical Targets

This project is conducting fundamental studies of the decomposition mechanism of $\text{Mg}(\text{BH}_4)_2$. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the following DOE 2010 hydrogen storage targets:

- Cost: \$4/kWh net
- Specific energy: 2 kWh/kg
- Energy density: 1.5 kWh/L

Accomplishments

- Gained significantly better understanding of the desorption process of $\text{Mg}(\text{BH}_4)_2$ in collaboration with Jet Propulsion Laboratory/California Institute of Technology (JPL/Caltech) using five independent techniques.
- Discovered the formation of an amorphous $\text{MgB}_{12}\text{H}_{12}$ intermediate phase.
- Discovered reversible behavior at about 300°C and 100 bar H_2 pressure from $\text{Mg}(\text{BH}_4)_2$ to $\text{Mg}(\text{BH}_4)_{2-x}$ during the initial decomposition process of $\text{Mg}(\text{BH}_4)_2$.
- Worked with Metal Hydride Center of Excellence (MHCoe) partners (Oak Ridge National Laboratory and JPL/Caltech) to synthesize and characterize a promising aluminoborane compound $\text{AlB}_4\text{H}_{11}$ for hydrogen storage and found very attractive properties.



Introduction

The U.S. Department of Energy (DOE) defines on-board hydrogen storage for mobile vehicles as a “Grand Challenge”. It is one of the biggest hurdles to the implementation of hydrogen-powered vehicles. Metal hydrides have the advantages of the highest volumetric density, relatively low working pressure, and reasonable working temperature range. The disadvantage of current reversible hydrides is a significant weight penalty. Metal borohydrides have among the highest gravimetric hydrogen storage capacities with the potential to meet the DOE gravimetric density targets and to offset the system weight penalties. However, desorption temperature, reversibility and diborane formation during desorption are challenging issues for these materials. This project attempts to develop a high-capacity lightweight hydride for reversible vehicular hydrogen storage, capable of meeting or exceeding the 2010 DOE/FreedomCAR targets.

Approach

Our approach consists of two thrusts. Firstly, we employed several analytical techniques such as nuclear magnetic resonance (NMR), differential scanning calorimetry (DSC), pressure-composition-temperature, in situ X-ray diffraction (XRD), and residual gas analysis to understand the decomposition mechanism of $\text{Mg}(\text{BH}_4)_2$. Such detailed mechanistic study would provide important insight to the boron chemistry in $\text{Mg}(\text{BH}_4)_2$ and might provide clues for reversibility. This is major part of our work in Fiscal Year 2008 and was accomplished through extensive collaboration with the MHCoe partners, especially Robert Bowman at JPL and Dr. Sonjong Hwang at Caltech for the NMR analysis. The second research thrust is exploring new hydrides. Together with Oak Ridge National Laboratory and JPL/Caltech, we synthesized and performed preliminary characterization of the properties of a aluminoborane compound $\text{AlB}_4\text{H}_{11}$. We found attractive properties and partial reversibility.

Results

Understanding the decomposition pathway and products of $\text{Mg}(\text{BH}_4)_2$ is critical to devising a successful recharging strategy. Based on temperature programmed desorption, calorimetry, and simultaneous in situ X-ray diffraction-mass spectrometry (XRD-MS), we reported that the decomposition takes place via a complex sequence:

Temperature (°C)	Reaction	wt% H released measured (theoretical)
190	LT $\text{Mg}(\text{BH}_4)_2 \rightarrow$ HT $\text{Mg}(\text{BH}_4)_2$	0 (0)
300-320	HT $\text{Mg}(\text{BH}_4)_2 \rightarrow (\text{MgB}_x\text{H}_y)^* + 2 \text{B}^* + 3 \text{H}_2$	9.1 (11.2)
350	$(\text{MgB}_x\text{H}_y)^* \rightarrow \text{MgH}_2$	0 (0)
380	$\text{MgH}_2 \rightarrow \text{Mg} + \text{H}_2$	3.0 (4.1)
450	$\text{Mg} + 2 \text{B}^* \rightarrow \text{MgB}_2$	0 (0)

*Indicates non-crystalline structure – gives no diffraction pattern.

Note that immediately after $\text{Mg}(\text{BH}_4)_2$ decomposition the resulting species are non-crystalline (amorphous) (MgB_xH_y) . Although crystalline MgH_2 is formed upon further heating, no crystalline boron phases are detected up to 450°C. DSC experiments show an exothermic signal at 310°C, which corresponds to the formation of crystalline MgH_2 at this point. MgB_2 is formed in some, but not all, experiments after heating at 450°C for extended periods of time.

Based on thermodynamic calculations and measurements, the hydrogen release reaction is expected

to be reversible. Given the difficulties of regenerating $\text{Mg}(\text{BH}_4)_2$ beyond formation of MgH_2 , we theorize that the nature of the decomposition products (especially the B) places significant kinetic barriers on hydrogen absorption. To better understand the nature of the boron end product, we initiated a collaboration with Bob Bowman at JPL and Son-Jong Hwang at Caltech to perform solid state ^1H and ^{11}B NMR on samples taken at various points during the decomposition of $\text{Mg}(\text{BH}_4)_2$. The results have been very helpful in understanding the mechanisms of the entire decomposition process. Prior to decomposition, the NMR spectra are similar to those of LiBH_4 , indicating hindered rotation of BH_4^- groups. The spectra are dramatically different after decomposition. The proton NMR indicated that up to 10% of the hydrogen remained in the sample. The ^{11}B NMR shows that the boron formed upon decomposition of $\text{Mg}(\text{BH}_4)_2$ is distinctly different from traditional off-the-shelf amorphous boron. There is evidence of a small amount of MgB_2 , which is consistent with XRD measurements. Cross-polarized experiments indicated that most remaining hydrogen is bound to boron. Extraction into water of the decomposition products yielded solution, which NMR spectrum is identical to those of $[\text{B}_{12}\text{H}_{12}]^{2-}$ anion. A similar mechanism was suggested by Ohba *et al.* [1] who proposed $\text{Li}_2\text{B}_{12}\text{H}_{12}$ was formed upon decomposition of LiBH_4 . These experiments provided the first conclusive evidence for the formation of this dodecaborane ($\text{B}_{12}\text{H}_{12}$) species.

The assimilation of this unprecedented combination of data on decomposition of $\text{Mg}(\text{BH}_4)_2$ showed that the decomposition reaction occurs via several stages with formation of intermediate magnesium polyboranes that eventually transformed to the most stable magnesium dodecaboranate, Figure 1. Magnesium dodecaboranate decomposes at high temperature (>500°C) to yield magnesium diboride. The formation of $\text{B}_{12}\text{H}_{12}^{2-}$ anion during decomposition was found to be common for many metal borohydrides of lithium, magnesium, scandium and calcium. It should be noted that the existence of multiple steps with different enthalpies makes the task of rehydrogenation very difficult. Therefore, starting the rehydrogenation from the fully decomposed product (MgB_2) may be easier because B_{12} *closo*-structures are kinetically very stable while the possibility of hydrogenation of MgB_2 at reasonable pressures and temperatures was proven in the LiH-MgB_2 system. Clearly, the development of dehydrogenation/hydrogenation catalysts for these intermediate polyborane and boride phases will be required for practical application of magnesium borohydride as a hydrogen storage material. The detailed mechanistic study can be found in our recent publications [2,3]. This part of the work was performed when the principal investigator (PI) was at GE Global Research.

The second part of the research involves synthesizing new hydrogen storage materials. We

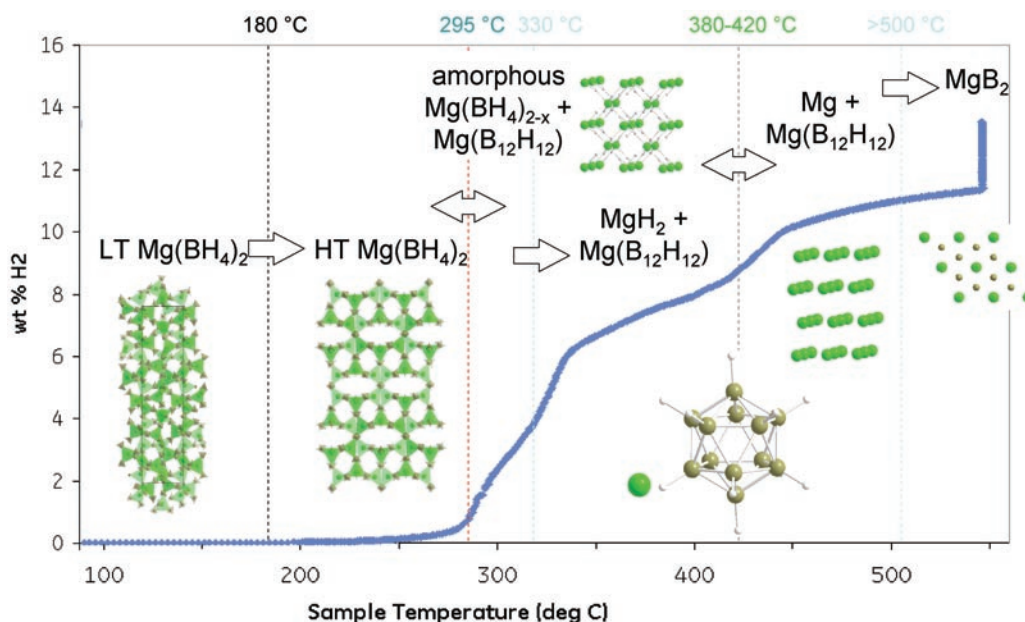


FIGURE 1. Graphic synopsis of the complex decomposition pathway of $\text{Mg}(\text{BH}_4)_2$ revealed from five different measurements.

synthesized several amine complexes of borohydrides and found that NH_3 complexes are a very effective way to fine-tune the thermodynamics of borohydrides. Amine complexes can reduce the desorption temperature (T_{des}) when the borohydride T_{des} is high, e.g. reduce the T_{des} of $\text{Mg}(\text{BH}_4)_2$ from 290°C to $\sim 100^\circ\text{C}$ in $\text{Mg}(\text{BH}_4)_2(\text{NH}_3)_2$. Such complexes increase T_{des} of several borohydrides when their T_{des} is low (too unstable), e.g. increase the T_{des} of $\text{Al}(\text{BH}_4)_3$ and $\text{Zn}(\text{BH}_4)_2$ to ~ 150 - 160°C . We need to understand the mechanism of desorption to take full advantage of this tunability. More work needs to be done to explore the reversibility of such complexes. Early work show partial reversibility at mild conditions for $\text{Mg}(\text{BH}_4)_2(\text{NH}_3)_2$, Figure 2. The reversibility clearly went well beyond the Mg to MgH_2 formation. Such reversibility is very attractive due to the mild recharging conditions.

After the PI moved from GE Global Research to the Ohio State University, he continued to work on the previous two parts, especially on the analyses of experimental results and writing reports and papers. In addition, the PI worked very closely with Oak Ridge National Laboratory and JPL/Caltech on a new hydrogen storage material, aluminoborane compound $\text{AlB}_4\text{H}_{11}$. This compound was reported by Himpsl and Bond [4] in 1981, but the work has eluded the worldwide hydrogen storage community. We synthesized this compound for the first time since the 1981 report and performed preliminary study of its decomposition process and reversibility. The results are shown in Figures 2 and 3. It is clear that the desorption started at $\sim 125^\circ\text{C}$ and ~ 5.5 wt% H was released at

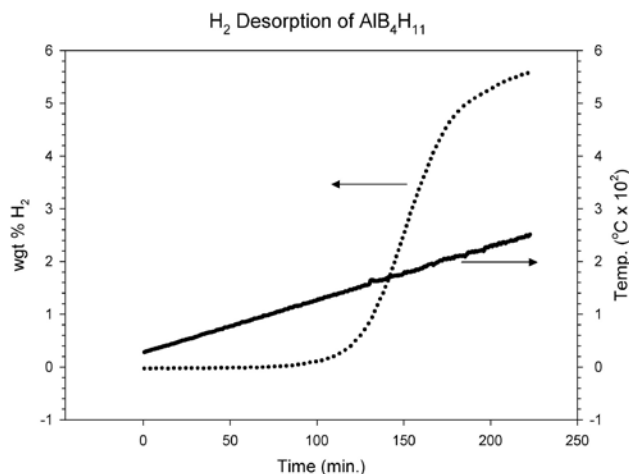


FIGURE 2. Thermal Desorption of $\text{AlB}_4\text{H}_{11}$ Measured with Thermally-Programmed Desorption Mass Spectrometry

200°C . Encouraging evidence of reversibility under mild conditions was observed as shown in Figure 3.

Conclusions and Future Directions

In collaboration with MHCoe partners Robert Bowman (JPL) and Son-Jong Hwang (Caltech), we have gained unprecedented understanding of the complex decomposition processes of $\text{Mg}(\text{BH}_4)_2$. We have identified the intermediate amorphous phase as $\text{MgB}_{12}\text{H}_{12}$ and have found that the formation of such $\text{M}(\text{B}_{12}\text{H}_{12})_x$ intermediates is a common phenomenon

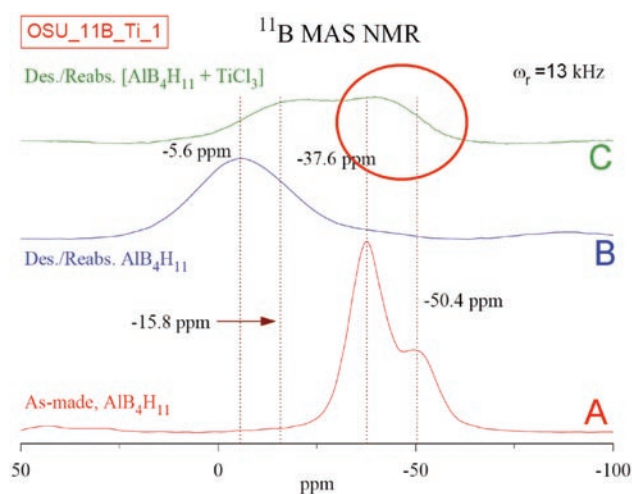


FIGURE 3. Comparison of ^{11}B MAS NMR spectra of as-made, un-desorbed $\text{AlB}_4\text{H}_{11}$ sample (Curve A), sample desorbed at 400°C for 11 hours and then recharged under 90 bar hydrogen at 400°C for 11 hours (Curve B), and sample desorbed at 200°C for 4 hours and recharged at 200°C for 5 hours (Curve C). The catalyzed $\text{AlB}_4\text{H}_{11}$ showed indication of reversibility as shown by the circled overlapping peaks in Curve C that shows intensities corresponding to the as-made (un-desorbed) $\text{AlB}_4\text{H}_{11}$.

in the decomposition process of borohydrides. Partial reversibility at the early stage of the decomposition process of $\text{Mg}(\text{BH}_4)_2$ has been observed. With such understanding, we suggest that exploration of reversibility of this first stage of borohydrides and targeted selection of catalysts may lead to high-capacity hydrogen storage materials. It will be important to see whether solid solution (mixed) compounds in the general formula of $(\text{Li,Na,Mg,K,Ca})_x\text{B}_{12}\text{H}_{12}$ can be synthesized since such compounds may offer sufficient thermodynamic and kinetic flexibilities to allow low temperature reversible borohydrides.

We studied the synthesis and properties of several amine complexes of borohydrides and found attractive thermodynamic tunability. We also found partial reversibility at mild conditions for $\text{Mg}(\text{BH}_4)_2(\text{NH}_3)_2$. Further exploration of this class of materials is planned together with MHCoe partners, Sandia, the University of Hawaii and others.

Working with Oak Ridge National Laboratory and JPL/Caltech, we are exploring a promising aluminoborane compound $\text{AlB}_4\text{H}_{11}$ which has high hydrogen capacity (13.5 wt%), low desorption temperature ($\sim 125^\circ\text{C}$) and partial reversibility under mild conditions (200°C , 90 bar hydrogen pressure). We will continue to explore aluminoborane compounds for hydrogen storage. The amine complexes of borohydrides are also very attractive hydrogen storage materials for further exploration.

Special Recognitions & Awards/Patents Issued

1. Two Invited talks (by J.-C. Zhao and Job Rijssenbeek) at Gordon Research Conference on Hydrogen-Metal Systems, Waterville, Maine, July 8-12, 2007.

FY 2008 Publications/Presentations

1. Materials Innovation in an Emerging Hydrogen Economy Meeting (H_2 2008), Cocoa Beach, Florida, February 25th to 27th, 2008 (Invited talk) "Exploration of Mg-Containing Borohydrides and Their Complexes for On-board Hydrogen Storage", Grigori Soloveichik, Sergei Kniajansky, Job Rijssenbeek, Yan Gao, Robert C. Bowman, Jr. and Son-Jong Hwang, and J.-C. Zhao.
2. IEA Task 22 International Hydrogen Experts Meeting, Sacacomie, Quebec, Canada, March 2nd to 5th, 2008, "Exploration of Mg-Containing Borohydrides and Their Complexes for On-board Hydrogen Storage", Grigori Soloveichik, Sergei Kniajansky, Job Rijssenbeek, Yan Gao, Robert C. Bowman, Jr. and Son-Jong Hwang, and J.-C. Zhao.
3. "Magnesium Borohydride Complexed by Tetramethylethylenediamine", Grigori Soloveichik, Matt Andrus, and E.B. Lobkovsky, *Inorg. Chem.*; 2007; 46(10); 3790-3791.
4. "Metal borohydrides as hydrogen storage materials", Grigori Soloveichik, *Material Matters (Aldrich)*, 2007; 2 (2) 11-14.
5. "Structure of unsolvated magnesium borohydride $\text{Mg}(\text{BH}_4)_2$ ", J.-H. Her, P. Stephens, Y. Gao, G. Soloveichik, J. Rijssenbeek, M. Andrus, and J.-C. Zhao, *Acta Cryst. B.*, 2007; B63, 561-568.
6. "Magnesium borohydride as a hydrogen storage material. I. Synthesis of unsolvated $\text{Mg}(\text{BH}_4)_2$," Grigori L. Soloveichik, Matthew Andrus, Yan Gao, Sergei Kniajanski, and J.-C. Zhao, *Inter. J. Hydrogen Energy*, Accepted July 2008.
7. "Ammine magnesium borohydride complex as new material for hydrogen storage: structure and properties of $\text{Mg}(\text{BH}_4)_2 \cdot 2\text{NH}_3$ ", Grigori Soloveichik, Jae-Hyuk Her, Peter W. Stephens, Yan Gao, Job Rijssenbeek, Matt Andrus, and J.-C. Zhao. *Inorg. Chem.*, 2008; 47; 4290-4298.
8. "NMR Confirmation for Formation of $\text{B}_{12}\text{H}_{12}$ Complexes during Hydrogen Desorption from Metal Borohydrides", S.-J. Hwang, R.C. Bowman, Jr., J.W. Reiter, J. Rijssenbeek, G.L. Soloveichik, J.-C. Zhao, H. Kabbour, and C.C. Ahn. *J. Phy. Chem. C.*, 2008; 112; 3164-3168.
9. "Magnesium Borohydride as a Hydrogen Storage Material. II. Properties of Unsolvated $\text{Mg}(\text{BH}_4)_2$," G.L. Soloveichik, Y. Gao, J. Rijssenbeek, M. Andrus, R.C. Bowman, Jr., S.-J. Hwang, and J.-C. Zhao. *Inter. J. Hydrogen Energy*, Accepted July 2008.
10. "Rapid Synthesis and Characterization of Aluminides for Hydrogen Storage by *In-situ* Thermal Imaging and X-ray Diffraction," John P. Lemmon, Jun Cui, Yan Gao,

Thomas R. Raber, Job Rijssenbeek, Malgorzata Rubinsztajn, Grigorii L. Soloveichik, and J.-C. Zhao. In final preparation.

11. "Application of *in-situ* X-ray diffraction to the study of novel hydrogen storage compounds," Job Rijssenbeek, Yan Gao, Grigorii L. Soloveichik, and Ji-Cheng Zhao. To be submitted in 2008.

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