IV.A.5b GE Progress within the DOE Metal Hydride Center of Excellence for Hydrogen Storage (Lightweight Intermetallics for Hydrogen Storage)

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Introduction

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 Mg(BH$_4$)$_2$, which has a very high capacity (14.8 wt% H) and attractive heat of formation. The key is to make it reversible. To accomplish this, we are working on both structure identification and combinatorial screening of dopants and catalysts. Crystal structure identification is important for computational simulations to predict potential doping candidates for experimental exploration.

Approach

Combinatorial/high-throughput screening and mechanistic understanding are two major aspects of GE’s approach to hydrogen storage materials discovery. We developed a very robust high-throughput screening tool based on infrared (IR) thermography for the discovery of catalysts and new hydrides. Our apparatus for performing in situ X-ray diffraction along with simultaneous gas sampling has been effective to determine reaction pathways and crystal structure changes during hydriding and de-hydriding processes.

High-resolution X-ray diffraction patterns were collected using a synchrotron source for detailed crystal structure identification. By some truly extraordinary structure analysis, we and our collaborators were able to identify the crystal structures of both the high-temperature and low temperature phases of Mg(BH$_4$)$_2$, and the structure of Mg(BH$_4$)$_2$(NH$_3$)$_2$. The former has one of the largest units cells whose structure was solved based on powder diffraction and had not yet been reported in the literature. The crystal structure information has been communicated to our atomistic modeling partners who will now be able to perform more reliable doping substitution simulations.

Results

The first key objective of our project is to identify the crystal structure of magnesium borohydride, which is the synthetic focus of our project this year. Without the crystal structure, it would be very difficult for the simulation partners, such as Karl Johnson at the University of Pittsburgh, to perform accurate computational screening of dopants. Such computational screening is very important for the exploration of the reversibility of magnesium borohydride. We found that Mg(BH$_4$)$_2$ has two different crystal structures, a low-temperature (LT) phase, that is hexagonal and stable up to 185°C, and a high-temperature (HT) phase above 185°C, that is orthorhombic. We have now completed the crystal structure identification as promised (Figure 1). The LT phase has space group $P6_3$, with $a \approx 10$ Å, $b \approx 10$ Å, and $c \approx 37$ Å. The HT phase is orthorhombic with a space group $Fddd$, and $a \approx 37$ Å, $b \approx 18.5$ Å and $c \approx 11$ Å. The building blocks for both structures are similar: corner-shared Mg(BH$_4$)$_4$ tetrahedra, where Mg$^{2+}$ is at the center, and (BH$_4$)$^-$ is at the vertex. The (BH$_4$)$^-$ unit is also tetrahedral, with B at the center and H at the vertex.

The orientation of (BH$_4$) tetrahedrons was determined, and the B-H bond length was found to be 1.12 and 1.02 Å for the LT and HT phase, respectively. The Mg-B bond lengths are between 2.28 and 2.49 Å for both phases. In both phases, Mg is bonded to eight hydrogen atoms. This work was completed in collaboration with Jae-Yuk Her and Peter Stephens at State University of New York (SUNY) at Stony Brook. Due to the very

\footnote{We learned after this report was first written that Cerny et al had published the low-temperature crystal structure of the Mg(BH$_4$)$_2$ a few weeks before the publication of our paper. Their work was published in R. Cerny, Y. Filinchuk, H. Hagemann and K. Yvon, Angew. Chem., 46 (2007) 5765. They did not report the crystal structure of the high-temperature phase – we reported it here in addition to the low temperature phase.}
of hydrogen pressure to the decomposition products. Understanding the decomposition pathway and products of Mg(BH$_4$)$_2$ is critical to devising a successful recharging strategy. Last year, based on temperature programmed desorption, calorimetry, and simultaneous in situ X-ray diffraction (XRD)-mass spectrometry (MS), we reported that the decomposition takes place via a complex sequence:

![Figure 1. Crystal Structures of Mg(BH$_4$)$_2$](image)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Reaction</th>
<th>wt% H$_2$ released (measured, theoretical)</th>
</tr>
</thead>
<tbody>
<tr>
<td>190</td>
<td>LT Mg(BH$_4$)$_2$ → HT Mg(BH$_4$)$_2$</td>
<td>0, 0</td>
</tr>
<tr>
<td>300-320</td>
<td>HT Mg(BH$_4$)$_2$ → (MgB,H)$_x$ + 2 B$^+$ + 3 H$_2$</td>
<td>9.1, 11.2</td>
</tr>
<tr>
<td>350</td>
<td>MgH$_2$ → (MgB,H)$_x$</td>
<td>0, 0</td>
</tr>
<tr>
<td>380</td>
<td>MgH$_2$ → Mg + H$_2$</td>
<td>3.0, 4.1</td>
</tr>
<tr>
<td>450</td>
<td>Mg + 2 B$^+$ → MgB$_2$</td>
<td>0, 0</td>
</tr>
</tbody>
</table>

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

Note that, immediately after Mg(BH$_4$)$_2$ decomposition, the resulting species are non-crystalline (amorphous) (MgB$_2$H$_x$). Although crystalline MgH$_2$ is formed upon further heating, no crystalline boron phases are detected up to 450°C. Differential scanning calorimetry (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 Mg(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 to perform solid state $^1$H and $^{11}$B nuclear magnetic resonance (NMR) on Mg(BH$_4$)$_2$ before and after decomposition at 450°C. The results thus far are preliminary but hint at some interesting phenomena. 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 approximately 90±10% of the hydrogen had been desorbed. The $^{11}$B NMR shows that the boron formed upon decomposition of Mg(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. The cross-polarized experiments indicated that much, if not all, of the remaining hydrogen is bound to the boron. Extraction into water of the decomposition products yielded NMR…
spectra identical to those of $[\text{B}_3\text{H}_12]^2$ anion. A similar situation was suggested by Ohba et al., [Phys. Rev. B, 74 (2006) 75110] who proposed $\text{Li}_2\text{B}_3\text{H}_4$ was formed upon decomposition of $\text{LiBH}_4$. Further investigations in this direction are ongoing.

We have investigated the possibility of recharging $\text{Mg(BH}_4)_2$ from the non-crystalline state which exists right after decomposition at 320°C. Initial results as observed by in situ XRD were encouraging because we were able to regenerate $\text{Mg(BH}_4)_2$ peaks where there had been none. Under an applied pressure of 1,950 psi (134 bar), the $\text{Mg(BH}_4)_2$ peaks returned beginning at ~200°C and increase in intensity up to ~300°C. At 350°C, the reformed $\text{Mg(BH}_4)_2$ peaks again disappeared. This contrasts with a decomposition temperature of <320°C under vacuum. This shows the effect of hydrogen pressure on the decomposition temperature. Despite the promising initial observations, further investigation showed that rehydrogenation of fully decomposed products was likely not taking place. Although the XRD peaks may disappear by 320°C, the hydrogen evolution continues for several more minutes if kept at temperature. If this hydrogen evolution is allowed to run its course, subsequent hydrogenation does not regenerate any peaks for $\text{Mg(BH}_4)_2$. The peaks only return when the heating is cut off after the XRD peaks have disappeared but before the hydrogen evolution has stopped. Several explanations are possible for these and other observations, but the current most likely explanation is that $\text{Mg(BH}_4)_2$ releases a small but unknown amount of hydrogen to form a glassy disordered phase $\text{Mg(BH}_4)_{2-x}$. This glassy phase, which has no diffraction pattern due to its non-crystalline nature, decomposes to amorphous $\text{MgH}_2$ and boron. If heating is stopped in time, some of this glassy phase remains and this can absorb hydrogen to return to $\text{Mg(BH}_4)_2$. Given the complex structures of $\text{Mg(BH}_4)_2$, the formation of a glassy phase by the removal of a few hydrogen atoms is not surprising. More experiments are needed to fully confirm this. Planned NMR experiments in collaboration with JPL may shed some light on the nature of this non-crystalline state as well as the hydrogenated boron end product. As a footnote to this discussion, Professor Shin-ichi Orimo’s group at Tohoku University in Japan mentioned at a recent conference that there exists an intermediate phase (based on IR signal) during recharging of decomposed $\text{Mg(BH}_4)_2$. They were able to recharge beyond $\text{MgH}_2$ with a pressure of 500 bar. As one can see, the decomposition and recharging process is very complex and further understanding may provide clues for reversibility.

We also synthesized $\text{Mg(BH}_4)_2(\text{NH}_3)_2$ and studied its crystal structure and decomposition process. $\text{Mg(BH}_4)_2(\text{NH}_3)_2$ is orthorhombic ($Pca\bar{b}; a = 17.487$ Å, $b = 9.415$ Å, $c = 8.732$ Å). It consists of isolated tetrahedra of $\text{Mg(BH}_4)_2(\text{NH}_3)_2$, as shown in Figure 2(a). The tetrahedra are weakly connected via B–H—H–N “hydrogen” bonds to form a three-dimensional network. We performed catalyst screening for this material and found effective catalyst additives as shown in Figure 2(b). Catalyzed $\text{Mg(BH}_4)_2(\text{NH}_3)_2$ desorption starts at 80-90°C and can complete at <300°C, giving 13 wt% H (16 wt%H theoretical). Its decomposition process gives off small amounts of $\text{NH}_3$ and $\text{BH}_4$, but their exact amounts were not quantified yet. The high capacity and low desorption temperature make this material very attractive for further study as a hydrogen storage material.

To further reduce the desorption temperature and explore reversibility of $\text{Mg(BH}_4)_2$, we tried to synthesize $\text{Mg(BH}_4)(\text{AlH}_4)$. The synthesis was accomplished in an
Assume 4
1/3
15
1
25
2010
3
30
5
2015
p
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Temperature

Figure 3. Comparison of the Desorption Characteristics of Mg(BH₄)(AlH₃) with Mg(BH₄)₂ Showing Very Attractive Desorption Temperature

Conclusions and Future Directions

We have identified the very complex crystal structures of both the LT and HT phases of the Mg(BH₄)₂, which will allow computational simulation to perform more reliable doping substitution studies. The increased understanding of the complex decomposition and recharging processes of Mg(BH₄)₂, especially the reported intermediate phase and partial reversibility at 500 bar, along with intriguing NMR information and reformation of crystalline Mg(BH₄)₂ from “amorphous” intermediate, call for more detailed studies on the reversibility of Mg(BH₄)₂. We will collaborate with partners such as Sandia National Laboratories, Oak Ridge National Laboratory (ORNL), JPL/Caltech, the University of Pittsburgh, and others in MHCoE to further explore this important topic. We have started working with ORNL to perform borane experiments to study the conditions of reversibility with borane. Recent data from Germany showed the Mg(BH₄)₂ → MgH₂ + 2B + 3H₂ reaction enthalpy to be about 57 kJ/mol H₂, ideal for reversibility. (This information was communicated to us by Dr. Max Fichtner.)

We will continue to perform studies on Mg(BH₄)₂(NH₃)₂ and Mg(BH₄)(AlH₃) since both have very high hydrogen capacity and attractive desorption temperatures. The Mg(BH₄)(AlH₃) is especially attractive since it has a very low desorption temperature and potentially no detrimental gas formation. The current performance of these materials against the DOE targets is shown in Figure 4.

Special Recognitions & Awards/Patents Issued

1. Member of the Organizing Committee, MH2006 - October 1–6, Maui, HI.
2. Co-organizer, Hydrogen Storage Technologies Symposium at the MRS Fall Meeting 2006 - November 27–30, Boston, MA.

FY 2007 Publications/Presentations

1. MH2006 - October 1-6, Maui, HI, “Determination of Crystal Structures and Reaction Pathways of Hydrogen Storage Materials,” Job Rijssenbeek, Yan Gao, Matt Andrus, Grigori Soloveichik, John Lemmon, J. C. Zhao, Jonathan Hanson, Peter Stephens, Qingzhen Huang, Camille Jones, & Brian Toby.
3. MRS Fall Meeting 2006 - November 27–30, Boston, MA, “Discovery and Mechanistic Understanding of Metal Hydrides using Thermography, Gravimetric Analysis and
in-situ Synchrotron XRD,” John P. Lemmon, Jun Cui, Yan Gao, Tom Raber, Job Rijssenbeek, Malgorzata Rubinsztajn, Grigorii Soloveichik and J.-C. Zhao.


