IV.A.1s Lightweight Intermetallics for Hydrogen Storage

J.-C. Zhao (Primary Contact), 1 Jun Cui, 2
Yan Gao, 2 Sergei Kniajansky, 2 John Lemmon, 2
Thomas Raber, 2 Job Rijssenbeek, 2 and
Grigorii Soloveichik 2

1 The Ohio State University
286 Watts Hall, 2041 College Road
Columbus, OH 43210
Phone: (614) 292-9462; Fax: (614) 292-1537
E-mail: zhao.199@osu.edu

2 GE Global Research
1 Research Circle
Niskayuna, NY 12309

DOE Technology Development Manager:
Ned Stetson
Phone: (202) 586-9995; Fax: (202) 586-9811
E-mail: Ned.Stetson@ee.doe.gov

DOE Project Officer: Paul Bakke
Phone: (503) 275-4916; Fax: (503) 275-4753
E-mail: Paul.Bakke@go.doe.gov

Contract Number: DE-FC3605GO15062
Project Start Date: January 1, 2005
Project End Date: August 29, 2009

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 Mg(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 Mg(BH$_4$)$_2$ and on the properties of amine complexes of borohydrides.

Technical Targets

This project is conducting fundamental studies of the decomposition mechanism of Mg(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 Mg(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 MgB$_{12}$H$_{12}$ intermediate phase.
- Discovered reversible behavior at about 300˚C and 100 bar H$_2$ pressure from Mg(BH$_4$)$_2$ to Mg(BH$_4$)$_{2-x}$ during the initial decomposition process of Mg(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 AlB$_3$H$_{11}$ for hydrogen storage and found very attractive properties.

Introduction

The U.S. Department of Energy (DOE) defines onboard 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 Mg(BH$_4$)$_2$. Such detailed mechanistic study would provide important insight to the boron chemistry in Mg(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 AlB$_{11}$H$_{11}$. We found attractive properties and partial reversibility.

**Results**

Understanding the decomposition pathway and products of Mg(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:

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Reaction</th>
<th>wt% H released measured (theoretical)</th>
</tr>
</thead>
<tbody>
<tr>
<td>190</td>
<td>LT Mg(BH$_4$)$_2$ $\rightarrow$ HT Mg(BH$_4$)$_2$</td>
<td>0 (0)</td>
</tr>
<tr>
<td>300-320</td>
<td>HT Mg(BH$_4$)$_2$ $\rightarrow$ (MgB$<em>4$H$</em>{11}$)$^{-}$ + 2 B$^{+}$ + 3 H$_2$</td>
<td>9.1 (11.2)</td>
</tr>
<tr>
<td>350</td>
<td>(MgB$<em>{11}$H$</em>{11}$)$^{-}$ $\rightarrow$ MgH$_2$</td>
<td>0 (0)</td>
</tr>
<tr>
<td>380</td>
<td>MgH$_2$ $\rightarrow$ Mg + H$_2$</td>
<td>3.0 (4.1)</td>
</tr>
<tr>
<td>450</td>
<td>Mg + 2 B$^{+}$ $\rightarrow$ 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$_{11}$H$_{11}$). 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 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 and Son-Jong Hwang at Caltech to perform solid state $^1$H and $^{11}$B NMR on samples taken at various points during the decomposition of Mg(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 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. 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 [B$_{12}$H$_{12}$]$^{2-}$ anion. A similar mechanism was suggested by Ohba et al. [1] who proposed LiB$_{12}$H$_{12}$ was formed upon decomposition of LiBH$_4$. These experiments provided the first conclusive evidence for the formation of this dodecaborane (B$_{12}$H$_{12}$) species.

The assimilation of this unprecedented combination of data on decomposition of Mg(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 B$_{12}$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
synthesized several amine complexes of borohydrides and found that NH\textsubscript{3} complexes are a very effective way to fine-tune the thermodynamics of borohydrides. Amine complexes can reduce the desorption temperature (T\textsubscript{des}) when the borohydride T\textsubscript{des} is high, e.g. reduce the T\textsubscript{des} of Mg(BH\textsubscript{4})\textsubscript{2} from 290ºC to ~100ºC in Mg(BH\textsubscript{4})\textsubscript{2}(NH\textsubscript{3})\textsubscript{2}. Such complexes increase T\textsubscript{des} of several borohydrides when their T\textsubscript{des} is low (too unstable), e.g. increase the T\textsubscript{des} of Al(BH\textsubscript{4})\textsubscript{3} and Zn(BH\textsubscript{4})\textsubscript{2} to ~150-160ºC. 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 Mg(BH\textsubscript{4})\textsubscript{2}(NH\textsubscript{3})\textsubscript{2}, Figure 2. The reversibility clearly went well beyond the Mg to MgH\textsubscript{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 AlB\textsubscript{4}H\textsubscript{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 ~125ºC and ~5.5 wt% H was released at 200ºC. 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 Mg(BH\textsubscript{4})\textsubscript{2}. We have identified the intermediate amorphous phase as MgB\textsubscript{12}H\textsubscript{12} and have found that the formation of such M(B\textsubscript{12}H\textsubscript{12})\textsubscript{x} intermediates is a common phenomenon
in the decomposition process of borohydrides. Partial reversibility at the early stage of the decomposition process of Mg(BH₄)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 (Li,Na,Mg,K,Ca)₂B₁₂H₁₄ 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 Mg(BH₄)₂(NH₃)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 AlₓB₄H₁₁ which has high hydrogen capacity (13.5 wt%), low desorption temperature (~125°C), partial reversibility at 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

FY 2008 Publications/Presentations


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,


References


