Reversible Hydrogen Storage Materials – Structure, Chemistry and Electronic Structure

Ian Robertson and Duane Johnson
University of Illinois

A Participant in the DOE Metal Hydride Center of Excellence

**Overview**

<table>
<thead>
<tr>
<th><strong>Timeline</strong></th>
<th><strong>Barriers addressed</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Start date: FY 05</td>
<td>Optimization of absorption /desorption kinetics of solid-state storage systems.</td>
</tr>
<tr>
<td>End Date: FY 09</td>
<td>Theoretical modeling to guide material development</td>
</tr>
<tr>
<td>Percent Complete: 15%</td>
<td>Improve understanding of fundamental processes impacting alloy development that surpass targets.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Budget</strong></th>
<th><strong>Partners</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Total project funding</td>
<td>Participants in the <strong>DOE Metal Hydride Center of Excellence, specifically Sandia National Laboratory, HRL, University of Hawaii, University of Pittsburgh, General Electric.</strong></td>
</tr>
<tr>
<td>$1,566,746</td>
<td></td>
</tr>
<tr>
<td>DOE Share: $1,253,396</td>
<td></td>
</tr>
<tr>
<td>UIUC Share: $313,350</td>
<td></td>
</tr>
<tr>
<td>Funding for FY05: $150,000</td>
<td></td>
</tr>
<tr>
<td>Funding for FY 06: $175,000</td>
<td></td>
</tr>
</tbody>
</table>
## Objectives

<table>
<thead>
<tr>
<th>Overall</th>
<th>Support and guide development of complex metal hydrides to meet systems requirements by</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>• provide center partners with structural and chemical insight of candidate systems.</td>
</tr>
<tr>
<td></td>
<td>• provide experimentally based and validated theoretical modeling.</td>
</tr>
<tr>
<td>2006</td>
<td>• to determine degradation during transfer to analytical instruments and conduct structural and chemical analysis of systems of interest to partners.</td>
</tr>
<tr>
<td></td>
<td>• developed structural database for information sharing with partners.</td>
</tr>
<tr>
<td>2007</td>
<td>• to provide theoretical modeling to guide materials development.</td>
</tr>
<tr>
<td></td>
<td>• to provide understanding of role of catalysts and to determine nature, state and effect of surface contaminants on uptake and release.</td>
</tr>
</tbody>
</table>
Our approach combines use of advanced characterization capabilities with first principles electronic and thermodynamic calculations.

**Structural/chemical information**
- TEM structure
- And crystallography
- EDS and EELS
- Chemical and bonding information

**First principles calculations of thermodynamic properties**
- Provides needed information
- Aids interpretation
- MgH₂

**Outcome:** Provides guidance for new alloys with improved properties
The structural database. Data sharing

All VASP structures (xyx), energies ($\Delta H$), ... are stored into electronic Structural Database (http://data.mse.uiuc.edu)


ORACLE® type database.

All MHCoE collaborators (and others) access, download, and contribute by upload via scripts. No unnecessary repetition!
This deviation is simply due to melting and should not be included in the analysis.
Using the correct physics we can construct van’t Hoff plot!

Can calculate the enthalpy change or latent heat and Gibbs Free Energy by including Electronic + vibrational (harmonic) + librational energies.

Debate about stable high temperature phase – get wrong answer if you do not include rotational energies

**Hexagonal Unit Cell**

 Libreational mode is approximated by a free rotation and we obtain Free Energy per LiBH$_4$ analytically

\[ F_r = -k_B T \left( \frac{\ln T}{2} + \ln \frac{\sqrt{2\pi k_B l^3}}{3\hbar} \right) \]

*All other vibrational modes are obtained via VASP/PHONON code, but no imaginary frequency. Therefore, the hexagonal phase is not inherently unstable as predicted in previous models.*

H atoms undistinguishable after $2\pi/3$ rotation 5+5kJ barrier
van’t Hoff plot  
DFT Theory and Experiment

Experimental Data (HRL)
Vajo, Skeith, and Mertens,  
*J. Phys. Chem. B 109, 3719 (2005).*

Theory using DFT*

\[
\ln P = -\frac{\Delta G_{\text{elec}} + \Delta G_{\text{vibr}}}{k_B T} + \left(\frac{7}{2} - \frac{1}{4}\right) \ln T + E
\]

This has the proper well-known general form of

\[
\ln P = \frac{A}{T} + B \ln T + CT + DT^2 + E
\]

* DFT was shifted by a constant $\Delta E$ arising from nuclear degrees of freedom, which is not included

**2LiBH$_4$ + MgH$_2$ $\leftrightarrow$ 2LiH + MgB$_2$ + 4H$_2$**

How do we compare Latent Heat determined from theory and measured experimentally?
But, experimentally, $\Delta H(T)$ is extracted assuming 
$$\ln P \approx \frac{A}{T} + E$$
that is van’t Hoff slope is a constant $\Delta H \sim A$

Comparison of DFT $\Delta H(T)$, $\Delta H \approx A$, and $\Delta H$ from experiment.

✓ Excellent agreement between theory and experiment when assessed from van’t Hoff plot using a constant slope.
Finding the location of the elusive catalyst particles
(Univ. of Hawaii)

Chemical map of 2 mol % TiCl₃ doped NaAlH₄, 10x cycle

- Acquisition of Gatan transfer stage prevents excess oxidation during transfer.
- EDS elemental maps show distribution after ten cycles – Ti still highly localized and associated with Cl.
- Growth of Na-bearing crystals may alter composition of storage material – Both heat and electron beam stimulated growth.

Na crystal growth in different crystal of Ti doped NaAlH₄, ~ 70 °C

No longer a Center material, presented to show capability as current effort not yet cleared for presentation.
Location of the Ti.
Electron energy loss spectroscopy

Ti-doped NaAlH₄ (hydrided form), 10 cycle

Ti L edge @ 450 eV

Orthorhombic Al₃Ti

O K edge @ 540 eV

Cubic Al₃Ti

Confirmed presence of Ti and peak shapes show it is NOT oxidized
Post Ti shapes confirm Al₃Ti and possibly show orthorhombic form

Sub-doublets appear only in TiO₂

From this can determine density of states – compare with theory.
MgH$_2$ + ½ Si – Oxidation

collaboration with HRL

- Direct imaging of oxide and its thickness using energy-filtered TEM
- Oxide is present prior to microscopy

How much does oxide thickness on Mg and Si slow H penetration into lattice?

Does this affect H uptake?

MgH$_2$ + ½ Si + 0.05 Nb$_2$O$_5$, previously dehydrided EFTEM at 100 eV, 20 eV slit
Shows oxide on outside of Si particle.
Dynamic studies not showing elemental segregation – need higher nominal temperatures. Nb not well distributed after ball milling. Need to verify effectiveness of “dilution milling.”
Element redistribution during discharge cycle (Collaboration with HRL)

- Above 240 °C, Nb-doped Mg/Si does form the intermetallic (sub-grain size ~ 250 nm)

- Average composition over scan axis:
  - 10 at % O
  - 62 at % Mg
  - 29 at % Si
  - Nb near detector limit

- Removing O → 68 at % Mg, 35 at % Si (ideal 66/33)

- Very close to Mg$_2$Si as expected and reported via XRD
Future experiments and theory

Continued search and assessment of candidate metal-hydrides, as well as determining “best practice” for comparison to experiment and rapid design.

Focus efforts on most likely candidate systems with the goal of elucidating which defects and contaminants impact kinetics.

FY 06.
• Complete van’t Hoff analysis for BH₄ systems. (with HRL, U.Pitt, CMU)
• Continue study of Ca 2CaH₂/CaB₆ (with SNL)
• Continue to assess effectiveness of ball milling strategies for Li/Mg/destabilized systems (with SNL)
• Maintain database of candidate systems and reactions. Expand use, scope, and vetting reliability. (with all partners)

FY 07
• Determine chemical and structural change occur during (de)hydriding cycles? (with SNL, HRL, U Hawaii)
• Structure and energy of combined magnesium / boro-hydrides. (with GE)
• Complete study of CaH₂/CaB₆ (with SNL)
• Structure and chemistry of contaminant layers on (de)hydriding cycle (U. Nevada)
Talks, papers and Collaborations

Theoretical Tutorial to MHCoE: Capabilities and background of first-principles modeling to the experimentalists (Aug. 17, 2005).

Collaborative Visits/Talks:
  – Duane Johnson (UIUC) talked at Pittsburgh (Nov. 16-17, 2005).
  – S. Alapati (CMU) and R. Stumpf (SNLL): (Dec. 12-13, 2005)
  – Craig Jensen 18-19 October 2005

Papers.
  – Calculating enthalpies of hydrogen storage complex-metal hydrides - Hydrogen Meeting, Hawaii 2006
Summary

• Demonstrated how theory can interface with experiment and improve understanding of assessed properties.
• Used experiment to improve understanding of and to assess processing strategies and reliability.