Fundamental Studies of Advanced, High-Capacity Reversible Metal Hydrides

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Overview

Timeline
• Start Date: March 2005
• End Date: September 2010
• 73% complete

Budget
• Total project funding: $2,945,058
  – DOE share: $2,235,173
  – Contractor share: $609,885
• Funding received in FY08: $477,587
• Funding for FY09: $357,587

Barriers
A. System Weight and Volume
E. Charging/Discharging Rates
F. Thermal management
P. Lack of understanding of hydrogen chemisorption and physisorption

Partners
• E. Akiba, K. Sakaki; AIST
• R. Bowman; Jet Propulsion Laboratory
• R. Cantelli; University of Rome
• B. Hauback, M. Sorby; Institute for Energy Technology
• H. Hagmann, R. Cerny; University of Geneva
• S-J. Hwang, C. Ahn; California Institute of Technology
• L. Knight, G. Lewis, J. Low, A. Sachtler; UOP, LLC
• R. Kuboto; KEK
• R. Kumar; University of Nevada at Las Vegas
• S. McGrady; University of New Brunswick
• S. Orimo, Y. Nakamori; Tohoku University
• I. Robertson; University of Illinois
• E. Ronnebro; Sandia National Laboratory
• T. Udovic; NIST
• J. Reilly, J. Graetz; Brookhaven National Laboratory
• S. Srinivasan; University of South Florida
• J. Vajo, P. Liu; HRL
Objectives and Relevance

Development of a new class of reversible complexes that have the potential to meet the DOE 2010 kinetic and system gravimetric storage capacity targets.

Current investigations include:

• Al and Mg nano-confined carbon aerogels
• Borohydrides that can be reversibly dehydrogenated at low temperatures
• Development of a method for the hydrogenation of Al to alane, AlH₃ and/or LiH/Al to LiAlH₄ at moderate pressures in unconventional solvents.
Nano-confined Al and Mg in Carbon Aerogels

- Low temperature homogenous organometallic approach to incorporation of Al and Mg into carbon aerogels results in high loadings of clean surface, MgH$_2$ without degradation of nano-porous scaffold.

- Determine the effects of nano-confinement on the kinetics and thermodynamics of the dehydrogenation of MgH$_2$.
Group I and II Salts of Anionic Transition Metal Borohydride Complexes

> Several potential improvements over neutral complexes:
  - Higher (9-13 wt %) hydrogen content than neutral TM borohydrides.
  - Ionic character reduces volatility and increases stability.
  - Very low levels of diborane are evolved during the dehydrogenation of some ionic complexes such as Na₂Zr(BH₄)₆.
> Altered thermodynamic stability might allow reversibility.

Catalytically Enhanced Mg(BH₄)₂

> Mg(BH₄)₂ evolves 14 wt % H₂ upon dehydrogenation.
> Ball-milled mixtures of MgB₂ and the catalytic additive undergoes full hydrogenation to Mg(BH₄)₂ at 400 °C and 900 atm.
Hydrogenation of Alane in Non-conventional Solvents

> Dehydrogenation of AlH₃ to Al gives 10 wt % H₂
> Controllable dehydrogenation at acceptable rates below 100 °C with additives.
> Low (< 10 kJ/mol H₂) ΔH_{dehy} mandates very high pressures for charging at ambient or higher temperatures.
> Supercritical fluids (SCFs) have different physical properties than gases and liquids and no phase boundary between liquid and gas phases, ⇒ reduce the requisite pressures hydrogenations (ie hydrogenations of organic molecules and NaH/Al to NaAlH₄).
> Explore hydrogenation of Al to AlH₃; Al/MgH₂ to Mg(AlH₄)₂; and LiH/Al to LiAlH₄ in SCFs.
> Explore hydrogenation of Al to AlH₃; Al/MgH₂ to Mg(AlH₄)₂; and LiH/Al to LiAlH₄ in liquefied gases such as dimethyl ether which can form adducts during synthesis but are easily eliminated due to their high volatility.
Technical Accomplishments and Progress
Nano-Confined Mg in Carbon Aerogels

> Previous Results - High, (9-16 wt %) MgH₂ loadings of carbon aerogel without host degradation are obtained using the organometallic method.
> TEM imaging, EDS, and XRD confirmed MgH₂ incorporation in aerogel.
> Higher MgH₂ loadings can be obtained with materials that have larger pore sizes.

### Table

<table>
<thead>
<tr>
<th>Scaffold</th>
<th>Activated Carbon</th>
<th>13 nm Aerogel</th>
<th>25 nm Aerogel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Pore Size (nm)</td>
<td>&lt; 2</td>
<td>13</td>
<td>25</td>
</tr>
<tr>
<td>Pore Volume (cm³/g)</td>
<td>0.58</td>
<td>0.80</td>
<td>1.38</td>
</tr>
<tr>
<td>MgH₂ Loading (wt%)</td>
<td>4.2</td>
<td>17</td>
<td>23</td>
</tr>
</tbody>
</table>
Kinetic Studies
> The rate of dehydrogenation at 252 °C is >5 times faster than the initial rate found for ball milled MgH₂ and comparable to those found for nano-confined MgH₂ in carbon aerogels by alternative methods at HRL.
> The rate of dehydrogenation remains approximately the same over 4 cycles of dehydrogenation/rehydrogenation.
Technical Accomplishments and Progress
Nano-Confined Mg in Carbon Aerogels

> Equilibrium pressure of MgH$_2$ nano-confined in 13 nm aerogel at 250 °C agrees with database value for bulk MgH$_2$.
⇒ no change in thermodynamics.
Technical Accomplishments and Progress
Anionic Borohydrides

\[
\begin{align*}
X \ MH_x + Y \ M'B_x & \rightarrow \text{No Reaction} \\
MgB_2 + Y \ M'B_x & \rightarrow Mg(BH_4)_2 + Y \ M'B_x \\
MgB_2 & \rightarrow Mg(BH_4)_2
\end{align*}
\]

M = Group I or II metal, M’ = Transition metal

Rönnebro, Jensen, and Severa US patent application 61/093,937
Technical Accomplishments and Progress
Anionic Borohydrides

Infrared spectrum of MgB$_2$ + 2 mol % additive hydrogenated under 950 bar at 400 °C

Absorptions for B-H stretching and bending modes at characteristic frequencies indicate formation of Mg(BH$_4$)$_2$
Technical Accomplishments and Progress
Anionic Borohydrides

MAS $^{11}$B NMR

> XRD not generally used due the highly amorphous nature of boranes and bororhydrides.
> MAS $^{11}$B NMR spectroscopy allows detection and differentiation of all the boron containing species that are present.

> Full Hydrogenation of MgB$_2$ beyond MgB$_{12}$H$_{12}$ to Mg(BH$_4$)$_2$
> One major boron containing product is observed.
> Chemical shift of -41 ppm: Mg(BH$_4$)$_2$.
> Minor signal observed for MgB$_{12}$H$_{12}$, at -24 ppm, represents < 5% of product mixture.
> Not clear if the catalyzed reaction pathway is the same as the uncatalyzed pathway.

MAS $^{11}$B NMR MgB$_2$ + 2 mol % additive hydrogenated under 950 bar at 400 °C
Previous studies headed by researchers at GE within the MHCoE showed Mg(BH$_4$)$_2$ undergoes stepwise dehydrogenation to give MgB$_2$ while releasing 14.8 wt% H$_2$.

$$6 \text{Mg(BH}_4\text{)}_2 \rightarrow 5 \text{MgH}_2 + \text{Mg(B}_1\text{2H}_1\text{2)} + 13 \text{H}_2 \uparrow \quad (1)$$

$$5 \text{MgH}_2 + \text{Mg(B}_1\text{2H}_1\text{2)} \rightarrow 5 \text{Mg} + 5 \text{H}_2 \uparrow + \text{Mg(B}_1\text{2H}_1\text{2)} \quad (2)$$

$$5 \text{Mg} + \text{Mg(B}_1\text{2H}_1\text{2)} \rightarrow 6 \text{MgB}_2 + 6 \text{H}_2 \uparrow \quad (3)$$

The $\Delta$H$_\text{dehyd}$ of 42 kJ/mole suggests that it should be possible to hydrogenate MgB$_2$ to Mg(BH$_4$)$_2$ at moderate temperatures and pressures. Experimentally it has not proven possible to reverse the processes in equations 2 and 3 at temperatures lower than 500 ºC.

It has been suggested that this is due to the high kinetic stabilization of MgB$_{12}$H$_{12}$.

Does the catalytic pathway circumvent the MgB$_{12}$H$_{12}$ “sink”?
Hydrogenation in alternative SCFs, catalysts, and/or activation of Al have yet to produce higher yields of alane than the ~5% obtained in Me₂O/H₂ that was reported last year.

Focus turned to LiAlH₄

**BACKGROUND**

- Like sodium alanate, stepwise dehydrogenation, BUT first step is exothermic
  
  **Step 1:** \(3\text{LiAlH}_4 \rightarrow \text{Li}_3\text{AlH}_6 + 2\text{Al} + 3\text{H}_2\) \(\Delta H = -30\text{ kJ}\)
  
  **Step 2:** \(\text{Li}_3\text{AlH}_6 \rightarrow 3\text{LiH} + \text{Al} + 1.5\text{H}_2\) \(\Delta H = 38\text{ kJ}\)

- Together steps 1 and 2 provide ~7.9 wt %H

- Ashby (1963) – thermodynamics altered by adduct formation, reversible in THF (high T and P)

- Ritter (2007) – reversible in THF (high energy milling) with Ti catalyst. Requires material to be ball milled prior to each hydrogenation half-cycle

- Graetz (2008) – reversible in THF (low T and P) with Ti catalyst

- THF removal requires heating to 60 °C for 6 h. Incompatible with Ti catalyst since dehydrogenation occurs at the temperature required for removal of THF.
Using liquid dimethyl ether as solvent eliminates adduct removal issues

\[
\text{LiH} + \text{Al[Ti]} \xrightarrow{\text{Me}_2\text{O/H}_2 \text{ (100 bar)}} \text{LiAlH}_4[\text{Ti}] \quad \text{r.t.; 24 h}
\]

- Solvent vents immediately with H\(_2\)
- Fully charged Ti-doped LiAlH\(_4\) obtained
- Very low levels of Ti can be used (~500 ppm)

G.S. McGrady and C.M. Jensen  
U.S. Patent Application 60/945,650.

XRD patterns of LiAlH\(_4\) samples: (a) ICDD ref; (b) ball milled (2.0 mol% TiCl\(_3\)); (c) fully de-H (0.2 mol% TiCl\(_3\)); (d) re-H (2.0 mol% TiCl\(_3\)); (e) re-H (0.2 mol% TiCl\(_3\)).
H₂ Desorption from Ti-Doped LiAlH₄

- 0.5-0.2 mol% Ti optimal
- ~7 wt% H at 80-180 °C
- Excellent kinetics

TPD plots for LiAlH₄ samples: (a) as-received; (b) milled with 2.0 mol% TiCl₃; (c) re-H (2.0 mol% TiCl₃); (d) re-H (1.0 mol% TiCl₃); (e) re-H (0.5 mol% TiCl₃); and (f) re-H (0.2 mol% TiCl₃).

Why does dimethyl ether work so well?
• $\text{Me}_2\text{O}$ is both more polar and more volatile than $\text{Et}_2\text{O}$
• Forms strong complex with $\text{Li}^+$
• Evaporates quickly at r.t.

What is Wells-to-Wheels efficiency of a hydrogen storage system based on re-hydrogenation in liquid $\text{Me}_2\text{O}$?
• Energy for compression of $\text{Me}_2\text{O}$ and $\text{H}_2$ is $\sim 1/5$ that of $\text{H}_2$ production.
• High $\sim 5\text{M}$ solubility of $\text{LiAlH}_4$ in $\text{Me}_2\text{O}$ pushes the WWT to 60%.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>b.p./°C</th>
<th>D/debye</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Me}_2\text{O}$</td>
<td>-24</td>
<td>1.30</td>
</tr>
<tr>
<td>$\text{Et}_2\text{O}$</td>
<td>+35</td>
<td>1.15</td>
</tr>
<tr>
<td>THF</td>
<td>+66</td>
<td>1.63</td>
</tr>
</tbody>
</table>

Primary Energy and WTT Efficiency

![Diagram showing energy and WTT efficiency relationship]
Technical Accomplishments and Progress
Hydrogenation in Non-conventional Solvents

Cycling Studies
Material shows a drop in capacity over several cycles due to formation of $\text{Ti}_x\text{Al}_{1-x}$ phase.

TEM-EDAX patterns of $\text{LiAlH}_4/0.5$ mol\% Ti: (a) after first de-H; (b) after second de-H indicates Ti clustering and formation of $\text{Ti}_x\text{Al}_{1-x}$ phases.

Cycle performance of hydrogenated $\text{LiH/Al/TiCl}_3$ (1:1:0.005). (a) Cycle-1; (b) Cycle-2; (c) Cycle-3.
Future Work

Nano-confined Mg in Carbon Aerogels
• Determine dehydrogenation and re-hydrogenation kinetics of aerogels loaded with both MgH₂ and Ti-catalyst.
• Preparation of nano-confined MgH₂ from the hydrogenation of dimethyl magnesium intercalated aerogels to increase loadings.
• Determine PCT isotherms to determine effect of nano-confinement on the ΔH_{dehyd} of MgH₂.

Anionic Borohydrides
• Explore variations in reactions conditions to improve yield of lower pressure hydrogenation of MgB₂ to Mg(BH₄)₂.
• Continue the studies of the catalyzed and un-catalyzed hydrogenation of MgB₂ utilizing MAS ^{11}B NMR to determine mechanism in order to improve kinetics.

Hydrogenation in Nonconventional Solvents
• Maximize the extended cycling capacity of Ti-doped LiAlH₄ through variation of the dopant concentration and recharging conditions in liquid Me₂O.
• Continue exploration of improving levels of hydrogenation of alane using alternative SCFs and variety of initiators/catalysts.
• Explore SCF synthesis of Mg(AlH₄)₂.
• Further evaluation of WTT efficiency of the DME/LiAlH₄ system to be examined in collaboration with Argonne National Lab.
Nano-confined Mg in Carbon Aerogels
• High, (9-16 wt %) MgH₂ loadings of carbon aerogel without host degradation are obtained using the organometallic method.
• Higher MgH₂ loadings obtained with materials that have larger pore sizes.
• Nano-confinement of MgH₂ improves kinetics but does not appear to effect ΔH_{dehyd}.

Anionic Borohydrides
• Full hydrogenation of MgB₂ to Mg(BH₄)₂ can be achieved in the presence of a catalyst at pressures as low as 120 atm.
• MAS ¹¹B NMR spectroscopy confirms that the product of the hydrogenation is Mg(BH₄)₂ and provides tool to probe the whether MgB₁₂H₁₂ is an intermediate in the catalyzed and uncatalyzed hydrogenation pathways.

Hydrogenation in Non-conventional Solvents
• Fully charged, Ti-doped LiAlH₄ can be obtained in major yields from the direct hydrogenation of Ti-doped LiH/Al in liquefied dimethyl ether at room temperature in 100 bar of Me₂O/H₂.
• WTT efficiency of a LiAlH₄ based hydrogen system utilizing liquid DME as a re-hydrogenation medium approaches the 60% target.
Collaborations

Nano-confined Mg in Carbon Aerogels
C. Ahn; California Institute of Technology (Academic): Characterization by TEM imaging.
J. Vajo, P. Liu; HRL (Industrial): Characterization by PCT.

Anionic Borohydrides and Complex Hydrides
E. Akiba, K. Sakaki; AIST, Tsukuba (Government): Characterization by positron annihilation.
T. Autrey; PNNL (Government): Synthesis.
R. Cantelli; University of Rome (Academic): Characterization by anelastic spectroscopy.
H. Hagmann, R. Cerny; University of Geneva (Academic): Characterization by IR and Raman Spectroscopy and XRD.
L. Knight, G. Lewis, J. Low, A. Sachtler; UOP, LLC (Industrial): Characterization by XRD and mass spectroscopy.
Collaborations

Anionic Borohydrides and Complex Hydrides
R. Kuboto; KEK, Tsukuba (Government): characterization by muon spin resonance.
S. Orimo; Tohoku University (Academic): Characterization by DSC and XRD. Synthesis.
I. Robertson; University of Illinois (Academic): Characterization by TEM.
E. Ronnebro; SNL (now with PNNL), Government: High pressure studies.
S. Srinivasan; University of South Florida (Academic): Characterization by DSC.
T. Udovic; NIST (Government) Characterization by Inelastic Neutron Scattering.

Hydrogenation in Non-conventional Solvents
S. McGrady; University of New Brunswick (Academic): SCF reaction system.
Supplemental Slides
Weak MgH$_2$ X-ray diffraction peaks indicate nanosized MgH$_2$ was incorporated in the 13 nm aerogel scaffold without contamination or graphite.
Carbon appears to have remained as 13 nm aerogel clusters. No Mg particles were observed, indicative of nanosized MgH$_2$ incorporation. EDS shows that the Mg concentration varied from 1.4 to 4.5 wt%, indicative of nanosized MgH$_2$ incorporation.
Hydrogenation of Al in Supercritical Media

Phase boundary between liquid and gas phases disappears in supercritical fluids (SCFs)....

7:1 mixture of liquid CO₂ and H₂ gas converts to a homogenous super critical fluid at 30°C and 10 atm

SCFs have different physical properties than gases and liquids.... as a result, the thermodynamics and kinetics of chemical processes can be modified when run in SCF solutions.
TITANIUM DOPED AL IN 2:1 SUPERCRITICAL CO$_2$-H$_2$

> Hydrogenation of titanium-doped aluminum in 2:1 supercritical CO$_2$-H$_2$.
  - Higher levels of hydrogenation.
  - Isothermal desorption at 110 °C indicates 3% of the Al was hydrogenated.
  - GC analysis: Hydrogen evolved only from the Al subjected to the SCF.
  - Low-level hydrogenation occurs on the surface of the powder.

> Confirmed by MAS $^{27}$Al NMR:

Clean Al peak prior to hydrogenation

After 4h in 2:1 supercritical CO$_2$-H$_2$ at 60 °C, an alane peak is revealed