Solid-State Hydriding and Dehydriding of LiBH₄ + MgH₂ Enabled via Mechanical Activation and Nano-Engineering

Leon L. Shaw, Tippawan Markmaitree, William Osborn, Xuefei Wan, Kyle Crosby
University of Connecticut

Z. Gary Yang, Jianzhi Hu, Ja Hu Kwak
Pacific Northwest National Laboratory

May 18 – 22, 2009
2009 DOE Hydrogen Program Review

Project ID: stp_44_shaw
Overview

Timeline:
- Project start date: December 2004
- Project end date: December 2009
- Percent complete: 85%

Budget:
- Total project funding:
  - DOE share: $1.35 mil
  - Contractor share: $0.4 mil
- Funding received in FY08: $250,000 for UConn; $80,000 for PNNL
- Funding for FY09: $200,000 for UConn; $70,000 for PNNL

Partners/Collaborators:
- Pacific Northwest National Laboratory – NMR analysis
- Universidad de Extremadura, Badajoz, Spain – X-ray analysis
- HRL Laboratories – Ball milling of LiBH₄ + MgH₂ at liquid N₂ temperature
- University of Pittsburgh – Information exchange

Barriers
A. System weight and volume: 2 kWh/kg & 1.5 kWh/L
E. Charging/discharging rates: 3 min for 5 kg
Technical Objectives – Relevance

Objective in FY 08:

- Establishing solid-state hydriding and dehydriding kinetics of LiBH₄ + MgH₂ systems
- Enhancing solid-state hydriding and dehydriding kinetics of LiBH₄ + MgH₂ via doping of transition metals such as Mn and V
- Enhancing solid-state hydriding and dehydriding kinetics of LiBH₄ + MgH₂ via milling additives such as graphite

Objective in FY 09:

- Further improving the solid-state hydriding/dehydriding properties of LiBH₄ + MgH₂ via ball milling at liquid nitrogen temperature with the addition of transition metals and milling additives such as boron nitride
- Investigating the hydriding and dehydriding reversibility of carbon aerogel confined LiBH₄ and increasing its storage capacity
- Demonstrating hydrogen uptake and release of LiBH₄ + MgH₂ systems with a storage capacity of ~ 10 wt% H₂ at 200°C
Technical Impacts – Relevance

- Demonstrated hydriding and dehydriding reactions of LiBH$_4$ + MgH$_2$ systems at the solid state, i.e., below the melting point of LiBH$_4$ ($T_m = 280^\circ$C) with 9.3 wt% H$_2$ uptake and 4.5 wt% H$_2$ release;

- Established a two-step ball milling procedure to improve the solid-state hydriding and dehydriding kinetics of LiBH$_4$ + MgH$_2$ systems;

- Identified the solid-state hydriding and dehydriding mechanisms and established a partial ion exchange model to guide the improvement of the diffusion-controlled hydriding dehydriding reaction; and

- Demonstrated the release of H$_2$ from LiBH$_4$ at 80°C and the completion of H$_2$ release at 275°C via nano-engineering with carbon aerogel confinement.
Technical Methods – Approach

- Identifying the mechanism and rate-controlling step of solid-state hydriding and dehydriding reactions of LiBH$_4$ + MgH$_2$ systems.

- Liquid nitrogen temperature ball milling combined with doping of transition metals and milling additives to enhance the solid-state hydriding and dehydriding kinetics.

- Developing the mechanistic understanding of the effect of mechanical activation and nano-engineering on hydriding and dehydriding properties.

- Applying the fundamental understanding of mechanical activation and the established reaction mechanism and rate-controlling step to enhancing the solid-state hydriding and dehydriding properties of LiBH$_4$ + MgH$_2$ systems.
# Milestones – Approach

<table>
<thead>
<tr>
<th>Month/Year</th>
<th>Milestone or Go/No-Go Decision</th>
</tr>
</thead>
</table>
| **Nov-08** | **Milestone:** Establish the atomic level understanding of the mechanism and kinetics of solid-state hydriding/dehydriding reactions of mechanically activated, nano-engineered LiBH$_4$ + MgH$_2$ systems;  
(ii) Demonstrate hydriding and dehydriding reactions of LiBH$_4$ + MgH$_2$ systems at the solid state, i.e., below the melting point of LiBH$_4$ ($T_m$ = 280°C);  
(iii) Demonstrate hydrogen uptake and release of (LiBH$_4$ + MgH$_2$) systems with a storage capacity of ~ 10 wt% H$_2$ at 200°C. |
| **Dec-08** | **Go/No-Go Decision:** Demonstrate hydrogen uptake and release of (LiBH$_4$ + MgH$_2$) systems with a storage capacity of ~ 10 wt% H$_2$ at 200°C.  
(a) Milestones (i) and (ii) were met; however, milestone (iii) was not.  
(b) A no-go decision was made because milestone (iii) was not met.  
(c) This project with the original end date of December 2010 will be terminated in December 2009. |
| **Dec-09** | **Milestone:** Demonstrate hydrogen uptake and release of (LiBH$_4$ + MgH$_2$) systems with a storage capacity of ~ 10 wt% H$_2$ at 200°C. |
Solid-State Hydriding and Dehydriding of the LiBH$_4$+MgH$_2$ Storage System

- LiBH$_4$ + $\frac{1}{2}$MgH$_2$ $\leftrightarrow$ LiH + $\frac{1}{2}$MgB$_2$ + 2H$_2$
- 11.6 wt% H$_2$
- $\Delta$H = 44 kJ·mol$^{-1}$ H$_2$
- $T_m$(LiBH$_4$) = 280 °C
- $T$ = 265 °C $\Rightarrow$ Solid State Operation

- Milled in the dehydrogenated state
- Milling duration greatly effects properties
- Solid-state hydriding and dehydriding accomplished by long-term ball milling – nano-particle formation & high crystal defects (high diffusion rates)
Technical Accomplishments and Progress (FY09)

Enhancing Hydriding & Dehydriding Properties via Milling Additives

- Include graphite in ball milling of LiH+MgB\(_2\) to improve milling efficiency and uniformity
- Normalized composition to exclude 15 vol% C
- Simply adding graphite reduces absorption by 40%
- LiH and C are reactive – Two-step milling to address this issue (e.g., 120h without C + 1h with C)
Technical Accomplishments and Progress (FY09)

Solid-State Hydrogen Release of LiBH$_4$+MgH$_2$ Storage System

- 120 hr milling with C does improve release kinetics
- *Two-step milling*, i.e., 120+3 and 120+1 further enhances performance
- 120+1 milling is better than 120+3 milling because of the limited reaction between LiH and C
- Release of 4.5 wt% H$_2$ at 265°C accomplished.
Technical Accomplishments and Progress (FY09)

Further Enhancing the Solid-State Hydrogen Uptake/Release Kinetics via Milling at Liquid Nitrogen Temperature

- 120hr RT milling for LiH and MgB\(_2\), followed by Liq. N\(_2\) milling – *Two-step milling at Liq. N\(_2\)*
- Liq. N\(_2\) milling provides the best improvement because of the limited reaction between LiH and C
- 9.3 wt% H\(_2\) uptake at 265°C accomplished
- Anomalous absorption during the temp ramp
Further Enhancing the Solid-State Hydrogen Uptake/Release Kinetics via Milling at Liquid Nitrogen Temperature (Cont.)

- Samples milled in the dehydrogenated state are exposed to 5+ hours at 265 °C (97% $T_m$) → Growth
- 4.2 wt% H$_2$ release at 265 °C
- LN$_2$ milling does not offer large improvements in hydrogen release over RT milling, suggesting that hydriding & dehydriding kinetics are controlled by different mechanisms.
265 °C allows solid-state, but is still too warm

Diffusion rate is thermally activated

\[ D = D_0 \exp\left(-\frac{Q}{RT}\right) \]

T = 235 °C & 6.1 wt% H₂ uptake
$^{11}$B MAS NMR spectra:
a) Bulk LiBH$_4$
b) Bulk MgB$_2$
c) LiH + MgB$_2$ with 3hr ball milling
d) LiH + MgB$_2$ with 120hr ball milling

- The similar $^{11}$B MAS centerband peak positions of the 3hr and 120hr ball milled LiH+MgB$_2$ as that of pure MgB$_2$ indicates that the layered boron structure is unchanged during ball milling.
- The substantially increased centerband linewidth for the 120hr milled sample suggests that the MgB$_2$ particle size is dramatically decreased by ball milling.
The 2.76ppm $^6$Li peak is assigned to LiH, while the 0.06ppm $^6$Li peak is an intermediate in an ionic state. The quantity of the intermediate increases with the milling time.

Long-term ball milling (120 h) leads to the formation of amorphous MgH$_2$ and the particle size refinement of MgB$_2$.

Approximately 50% of MgB$_2$ is converted to MgH$_2$ during 120h ball milling.
Long-term ball milling results in the partial exchange of the Mg\(^{2+}\) ions in the MgB\(_2\) crystal by the Li\(^{+}\) ions from the LiH crystal.

This partial ion exchange results in the formation of a compound with a composition of \((\text{Mg}_{1-x}\text{Li}_{2x})\text{B}_2\) where \(x\) is a variable changing from 0 to less than 1.

Each expelled magnesium combines with two protons from LiH to form MgH\(_2\).

Formation of \((\text{Mg}_{1-x}\text{Li}_{2x})\text{B}_2\) enhances the hydriding reaction because Mg needs to be expelled to form LiBH\(_4\).
During hydrogenation LiH continues to react with MgB$_2$ to form the intermediate (Mg$_{1-x}$Li$_{2x}$)B$_2$ which is subsequently hydrided to form LiBH$_4$, as shown by $^6$Li MAS spectra.

During hydrogenation MgB$_2$ continues to decreases while LiBH$_4$ increases, as shown by $^{11}$B MAS spectra.

During hydrogenation MgB$_2$ continues to decrease while MgH$_2$ increases, not shown here because of the space limitation.
Solid-state hydriding and dehydriding of the LiBH₄ + MgH₂ system are diffusion-controlled.

The diffusion control phenomenon is in good accordance with the partial ion exchange model identified.

Thus, to enhance the hydriding and dehydriding kinetics of LiBH₄ + MgH₂, one needs nano-particles and fast diffusion rates.

Analysis of the hydrogenation curves of the 120hr, 24hr, and 3hr ball-milled mixtures, based on the diffusion-controlled core/shell model.
Mn enhances hydrogenation because it dissolves in MgB$_2$. However, it does not improve dehydrogenation.

V does not enhance hydrogenation because it does not dissolve in MgB$_2$. However, it improves dehydrogenation because V forms VH$_{0.81}$ during hydrogenation and VH$_{0.81}$ behaves like a hydrogen pump during dehydrogenation to induce decomposition of MgH$_2$. 

Comparisons of 24h ball milled LiH+MgB$_2$ mixture with and without Mn or V
Pore size distributions of CAs from 4 to 12 nm

Confining LiBH$_4$ to CA pores eliminates long range microstructural growth

Solvent infiltration provides good control of the size of LiBH$_4$

Low concentrations for LiBH$_4$ in THF (0.5 M)
Technical Accomplishments and Progress (FY09)

Improving Kinetics and Thermodynamics via Nanoengineering – Carbon Aerogel Confinement (Cont.)

As Received CA

THF Solvent

THF infiltrated CA

No H₂ Released by CA or THF
Improving Kinetics and Thermodynamics via Nanoengineering – Carbon Aerogel Confinement (Cont.)

- 0.5 M LiBH₄ in THF
- Evacuate CA
- Submerge in solution
- Pressurize
- Drain and vacuum dry (RT)
- 0.5 M in a 5 nm pore
  → <1 nm LiBH₄ particle
- LiBH₄ released H₂ at 80°C!
- Completed H₂ release at 275°C!
- Change the thermodynamic properties?

![Graph showing temperature, weight loss, and intensity over time.](image)

- Temperature
- Weight loss
- H₂ @ 80°C
- 165°C
- 275°C

![Graph showing mass loss over time.](image)

- Mass [%]
- Time [min]
Properties of Carbon Aerogels (CAs) before and after LiBH$_4$ infiltration and evaporation of the solvent under vacuum

<table>
<thead>
<tr>
<th></th>
<th>Mass of the material (g)</th>
<th>Mass increase (%)</th>
<th>Specific surface area (m$^2$/g)</th>
<th>Pore volume (cm$^3$/g)</th>
<th>Peak pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CA before infiltration and drying*</td>
<td>0.0464</td>
<td>-</td>
<td>558.3</td>
<td>1.46</td>
<td>10.03</td>
</tr>
<tr>
<td>CA after infiltration and drying</td>
<td>0.0543</td>
<td>17 wt%</td>
<td>376.2</td>
<td>1.17</td>
<td>8.52</td>
</tr>
</tbody>
</table>

Infiltration of LiBH$_4$ into CAs results in a 17% weight gain and simultaneous decreases in the specific surface area, pore volume and peak pore diameter. Based on the peak pore diameter change, the thickness of LiBH$_4$ film or the particle diameter is ~ 0.75 nm.
**Collaborations**

- Pacific Northwest National Laboratory (Drs. Z. Gary Yang, Jianzhi Hu, and Ja-Hu Kwak within the DOE H₂ Program) – Extensive NMR analysis of hydrogen storage properties with the following joint publications.

Collaborations (Cont.)

• HRL Laboratories (Dr. John Vajo within the DOE H₂ Program) – Ball milling of LiBH₄ + MgH₂ at both RT and liquid N₂ temperature to investigate whether MgB₂ can be formed below the melting temperature of LiBH₄.

• Universidad de Extremadura, Badajoz, Spain (Prof. Angel L. Ortiz outside the DOE H₂ Program) – Detailed XRD analysis of hydrogen storage properties with the following joint publications.

• University of Pittsburgh (Prof. Karl Johnson within the DOE H₂ Program) – Information exchange on the prediction of the first-principles calculations.
Proposed Future Work

- Quantify the storage capacity of carbon aerogel-confined LiBH₄ and investigate its hydriding and dehydriding reversibility.

- Increase the storage capacity of carbon aerogel-confined LiBH₄ through high loading of LiBH₄ in carbon aerogels and study the relationship between the LiBH₄ loading and the kinetics of hydriding and dehydriding processes.

- Investigate the effect of Sc and Al addition to ball milled LiH + MgB₂ mixtures on their hydriding and dehydriding properties.

- Enhance the hydriding and dehydriding properties of ball milled LiH + MgB₂ mixtures through boron nitride addition.

- Liquid N₂ temperature ball milling of LiBH₄ + MgH₂ to promote hydrogen release at low temperatures.
**Project Summary**

**Relevance:** Explore fundamental mechanisms related to mechanical activation and nano-engineering necessary for improving kinetics of reversible hydrogen storage materials.

**Approach:** Investigate hydriding/dehydriding properties of LiBH₄+MgH₂ materials with different degrees of mechanical activation and nano-engineering; Enhance the storage performance based on the understanding developed.

**Technical Accomplishments:** (i) Demonstrated hydriding and dehydriding reactions of LiBH₄ + MgH₂ systems at the solid state, i.e., below the melting point of LiBH₄ (Tₘ = 280°C) with 9.3 wt% H₂ uptake and 4.5 wt% H₂ release; (ii) Enhanced hydriding and dehydriding kinetics via milling additives and doping of transition metals; (iii) Further improvement via liquid nitrogen temperature ball milling; (iv) Identify the solid-state hydriding and dehydriding mechanisms and established a partial ion exchange model to guide the improvement of the diffusion-controlled hydriding dehydriding reaction; and (v) Demonstrated the release of H₂ from LiBH₄ at 80°C and the completion of H₂ release at 275°C via nano-engineering with carbon aerogel confinement.