Complex Hydride Compounds with Enhanced Hydrogen Storage Capacity

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Overview

- **Timeline**
  - 11/30/02 Start
  - 8/31/07 End
  - 95% Complete

- **Budget**
  - $2.9M Total Program
    - $2.1M DOE
    - $0.8M UTC & Alb.
  - $0.59M DOE FY06
  - $0.38M DOE FY07

- **Barriers/Targets Addressed**
  - System Gravimetric Capacity: 1.5 kWh/kg
  - System Volumetric Capacity: 1.2 kWh/L
  - Discharging Rate: 0.02 g/s/kW

- **Partners**
  - Albemarle Corporation
  - Savannah River National Laboratory
  - Institute For Energy - Norway
  - QuesTek, LLC
Objectives

Overall

- Develop new complex hydride compounds capable of reversibly storing \( \text{H}_2 \) with capacities \( \geq 7.5 \text{ wt \%} \) to meet DOE system \textit{gravimetric} goals.

\[ \text{2007 Target} \quad 4.5 \text{ wt\% System} \]

- Assess potential \textit{volumetric} capacity of new materials.

\[ \text{2007 Target} \quad 36 \text{ kg H}_2 / \text{m}^3 \]

2006 – 2007

- Deploy integrated methods to design and optimize high \( \text{H}_2 \) capacity \textit{mixed metal borohydrides} with and without ligand stabilization.
## Approach

<table>
<thead>
<tr>
<th>Task Phase</th>
<th>First Principles Modeling</th>
<th>Solid-State Processing</th>
<th>Solution-Based Processing</th>
<th>Molten-State Processing</th>
<th>Thermo-dynamic Modeling</th>
</tr>
</thead>
<tbody>
<tr>
<td>2006 Novel Borohydrides</td>
<td>Refine phase structure &amp; thermo. predictions.</td>
<td>Synthesize high capacity borohydrides containing alkaline earths, transition metals and/or stabilized with ligands.</td>
<td></td>
<td></td>
<td>Design high capacity reactions.</td>
</tr>
</tbody>
</table>

Iterative design and synthesis of high H₂ capacity systems.
# Program Scope

<table>
<thead>
<tr>
<th>System</th>
<th>Compositions</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alanates</td>
<td>Na-Li-Al-H</td>
<td>FPM, SSP, MSP</td>
</tr>
<tr>
<td></td>
<td>Na-Tm-Al-H</td>
<td>FPM, SSP, SBP, MSP</td>
</tr>
<tr>
<td></td>
<td>Li-Tm-Al-H</td>
<td>FPM, SSP, SBP, MSP</td>
</tr>
<tr>
<td></td>
<td>Na-Mg-Al-H</td>
<td>FPM, SSP, SBP, MSP</td>
</tr>
<tr>
<td></td>
<td><strong>Li-Mg-Al-H</strong></td>
<td>FPM, SSP, SBP</td>
</tr>
<tr>
<td></td>
<td>Li-Na-Mg-(Ti,V,Cr,Mn,Ni,Co,Fe)-H</td>
<td>SSP, MSP</td>
</tr>
<tr>
<td>Borohydrides</td>
<td><strong>Tm-B-H w/ ligands &amp; coreactants</strong></td>
<td>SBP</td>
</tr>
<tr>
<td></td>
<td><strong>Mg-B-H w/ &amp; w/o ligands or coreactants</strong></td>
<td>FPM, SSP, SBP, MSP</td>
</tr>
<tr>
<td></td>
<td><strong>Ak-Tm-B-H w/ &amp; w/o ligands</strong></td>
<td>FPM, SSP, SBP</td>
</tr>
</tbody>
</table>

UTRC/FPM – First Principles Modeling, UTRC/SSP – Solid State Processing, Albemarle/SBP – Solution-Based Processing, SRNL/MSP – Molten State Processing,
Ak = alkali, Tm = transition metal

Broad range of compositions surveyed and approaches used. Ak-Tm-B-H systems are the most promising.
Characterization Methods

**XRD**
- Crystalline structure & phase

**DSC**
- Assess reversibility potential

**TGA-MS**
- Desorption temperature & species

**DRIFTS**
- Amorphous & crystalline bond identification

**PCI / Sievert’s**
- Kinetics & reversibility evaluation

**ND - IFE**
- Crystal / hydrogen structure
New Borohydrides – 6/2006 to Date

**Ligand-Stabilized Mg(BH$_4$)$_2$:**
- SBP Mg(BH$_4$)$_2$*2NH$_3$ with up to 16 wt% H$_2$ capacity.
- SSP Mg(BH$_4$)$_2$*3THF complexes also synthesized.
- Ligand complexation alters decomposition mechanism and significantly lowers dehydrogenation onset T.
- Varying complex stability observed by experiment and predicted by FPM.

**Ak-Tm-B-H (Ak = alkali, Tm = transition metal):**
- Partially reversible SSP material with up to 11.7 wt% H$_2$ capacity.
- Ligand-stabilized SBP complexes with up to 7.3 wt% H$_2$ capacity.
- Metastable & stable Ak-M-B-H compositions identified by FPM.
- Continuing work with novel additives to improve Ak-Tm-B-H reversibility.

Identified multiple alkali/alkaline earth borohydrides with above target gravimetric capacities; all with issues that need resolution.
Mg(BH\textsubscript{4})\textsubscript{2} \cdot 2\text{NH}_3 System with Up to 9 –16 wt% H\textsubscript{2}

**Hydride-NH\textsubscript{3} dissociation: 9 wt% H\textsubscript{2}**

Large endotherm at 100-200 °C:

\[ \text{Mg}(\text{BH}_4)_2 \cdot 2\text{NH}_3 = \text{Mg}(\text{BH}_4)_2 + 2\text{NH}_3 \]

Small exotherm at 200-250 °C:

\[ \text{Mg}(\text{BH}_4)_2 = \text{MgH}_2 + 2\text{B} + 3\text{H}_2(\text{g}) \]

Small endotherm at 430-470 °C:

\[ \text{MgH}_2 = \text{Mg} + \text{H}_2 \]

**BH\textsubscript{3}NH\textsubscript{3}-like mechanism: 16 wt% H\textsubscript{2}**

Hydride H- reaction with acidic H\textsuperscript{+}

Exotherm at 150-280 °C:

\[ \text{Mg}(\text{BH}_4)_2 \cdot 2\text{NH}_3 = \text{MgH}_2 + 2\text{BN} + 6\text{H}_2 \]

Endotherm at 480-520 °C:

\[ \text{MgH}_2 = \text{Mg} + \text{H}_2 \]

**Coupled H\textsubscript{2} and ligand desorption reaction mechanisms change with processing conditions and thermal history.**
Models Show Evolving Mg(BH$_4$)$_2$∗2NH$_3$ Structures

Mg(BH$_4$)$_2$∗2NH$_3$ forms adducts of varying stability, exhibiting a range of decomposition reaction products and enthalpies.
Synthesis reaction: $\text{MgCl}_2 + 2\text{LiBH}_4 + 3\text{THF} \rightarrow \text{Mg(BH}_4)_2(\text{THF})_3 + 2\text{LiCl}$

Identified multiple chemical routes to stabilizing $\text{Mg(BH}_4)_2$. 
Mg Ligands Are a Route to Low T $H_2$ Release

Mg(BH$_4$)$_2$ from LiBH$_4$+MgCl$_2$

Mg(BH$_4$)$_2$*3THF

TGA / MS Analyses
All 10 °C/min

Mg(BH$_4$)$_2$ complexes release $H_2$ & ligands starting below 300°C.
New Aprotic Mg(BH$_4$)$_2$*Ligand Complex

Two-stage thermal-neutral weight losses. First stage H$_2$ discharge starts at 60 °C.

Complexing ligands have a significant impact on decomposition. New ligand eliminates possible irreversible BN formation.
New Quaternary Alkali-Tm-B-H Systems

Tm addition to alkali borohydrides by SSP:

- Some outgas during milling.
- Disappearance of alkali borohydride XRD peaks.
- Mostly amorphous structure.
- Some new XRD peak formation.

Transition metal addition disorders alkali borohydride structure.
Ak-Tm-B-H Have Up to 300°C Lower Discharge T

Multistep reactions significantly lower dehydrogenation onset T’s. Only trace B$_2$H$_6$/B$_3$H$_9$ detected in the outgas.
Ak-Tm-B-H have up to ~12 wt.% H₂ capacity. Most active composition recharged 3 wt.% H₂ at 250°C and 195 bar H₂. Reversibility limited by Tm reduction &/or boride formation.
First Principles Survey of Ak-M-B-H Systems

Quaternaries with max. theoretical 4.9 - 12.3 wt.% H₂.

Stability of M incorporation in quaternary complex hydride phase correlates well with M electronic properties.

Reference Phases

<table>
<thead>
<tr>
<th>Ternary</th>
<th>Predicted ΔHₜₚ₉ₜₜformation (kJ/Mol*atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaBH₄</td>
<td>-33.03</td>
</tr>
<tr>
<td>LiBH₄</td>
<td>-34.69</td>
</tr>
<tr>
<td>Mg(BH₄)₂</td>
<td>-23.68</td>
</tr>
<tr>
<td>Al(BH₄)₃</td>
<td>-11.98</td>
</tr>
<tr>
<td>Ti(BH₄)₄</td>
<td>-14.46</td>
</tr>
</tbody>
</table>

Dopant M → M⁺ⁿ Redox Potential (V)

Predicted ΔH formation (kJ/mole*atom)

- Li-M-B-H
- Na-M-B-H
Ak-Tm-B-H* Ligand with Up to 7.3 wt% H₂ Endothermic

Fast kinetics, rapid H₂ desorption > 60 °C without catalyst. BₓHᵧ evolution below detection limit.

SBP Attributes:
High yield, low cost materials.
Partial H₂ discharge at 60°C and recharge at 20°C.
Compare to Ti-doped LiBH₄ which discharges at 350°C and recharges at 600°C (US pat. appl. 0046930, 2006).
DRIFTS analyses show evidence for partial rehydrogenation, probably limited by irreversible product formation.
Summary of Materials Discovery to Date

1) **Compositional surveys** of >9 quaternary systems

2) **Theoretical methods** - coupled complex reaction design.

3) **Synthesis & characterization** of high capacity materials with > 7.5 wt% H₂ & up to 0.04 kg H₂/L:
   \[
   \text{LiMg(AlH}_4\text{)}_3 \mid \text{Mg-B-H-Ligands} \mid \text{M-B-H-Ligand A} & \text{-Ligand B}
   \]

4) **Discovery** of low T, partially reversible, up to 11.7 wt% H₂ & up to 0.04 kg H₂/L capacity \(\text{Ak}_x\text{Tm(BH}_4\text{)}_y\) materials.
   * H₂ with only trace BₓHᵧ from SSP material.
   * Good kinetics for SBP material.

5) **Identification** of stable and metastable constituents for optimizing quaternary Ak-M-B-H capacity and reversibility.
Lessons Learned

Integration of FPM, syntheses and characterization is a successful paradigm for screening, testing and mechanistic understanding of new materials.

Syntheses often leads FPM in material discovery. Multiple synthesis methods maximize opportunities for material discovery. Unique FPM insights guide and focus experimentation for material design and optimization.

FPM yields greatest value when iteratively coupled with experiments for the:
- Determination of new material structures and properties and
- Investigation of experimentally observed material behavior, and for surveying hypothetical, lesser known or unstable material properties.

Future Work

- Complete evaluation of hydrogen release mechanisms from Mg(BH₄)₂*ligand complexes.
- Complete optimization of reversibility of Ak-Tm-B-H system.
- Final contract reporting and publications.
## Summary Table

### Progress Toward Hydrogen Storage System Targets*

<table>
<thead>
<tr>
<th>Target</th>
<th>Units</th>
<th>2007 System Targets</th>
<th>’05 to ’06 Best Alanate LiMg(AlH₄)₃ / System</th>
<th>’06 to ’07 Best Borohydride Mg(BH₄)₂*2NH₃ / System</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravimetric Capacity</td>
<td>kWh/kg (kg H₂/kg)</td>
<td>1.5 (0.045)</td>
<td>2.1 / 1.3 (0.070 / 0.042)</td>
<td>3.0 / 1.8 (0.091 / 0.055)</td>
</tr>
<tr>
<td>Volumetric Capacity</td>
<td>kWh/L (kg H₂/L)</td>
<td>1.2 (0.036)</td>
<td>0.5 / 0.38*** (0.015 / 0.011)</td>
<td>1.5 / 1.1 (0.044 / 0.033)</td>
</tr>
<tr>
<td>Desorption Rate** &amp; T</td>
<td>g/s/kW °C</td>
<td>0.02 (&lt;100)</td>
<td>0.019 165</td>
<td>0.037 100-300</td>
</tr>
</tbody>
</table>

* For system design with material 60% of system mass & 75% of system volume.

** Calculated results based on 5 kg storage for 75 kW fuel cell.

*** LiMg(AlH₄)₃ in as received condition – ball milling could improve densification.

Gravimetric & volumetric targets are feasible, but reversibility is a challenge.