First-Principles Computational Search for Reversible Room-Temperature Hydrides

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Project ID #: STP44
Overview

Timeline

• Start Date: 5/1/2004
• End date: 4/30/2007
• % complete: 67

Budget

• Total project funding
  – DOE: $2,000,000
  – UOP: $2,910,618
  – Ford: $75,000
• DOE FY05: $604,423
• DOE FY06: $525,032

Barriers

• Barriers addressed
  – Useable H₂ density
    • 2.0 kWh/kg & 1.5 kWh/L
  – H₂ Delivery Temperature Range
    • -40 to +85 °C
  – Cycle life (thermodynamic modeling)

Partners

• UOP LLC
• Ford
• Hawaii Hydrogen Carriers
• Striatus
Objectives

✓ Using first-principles computational modeling, identify new H₂ storage materials that can enable the DOE 2010 targets in storage density (weight and volumetric) and operating temperatures

✓ Provide accurate reaction enthalpies for combinatorial material optimization at UOP LLC

✓ Provide leads for experimental testing/refinement using high-throughput combinatorial setup at UOP LLC
Approach

Use *first-principles density functional calculations* to obtain electronic, structural and crystal bonding properties of complex hydrides.

- **Known complex hydrides:**
  - Input:
    - Chemical composition
    - Crystal structure type & symmetry
  - Results of calculations:
    - Structural properties (e.g., volumetric densities)
    - Thermodynamic & vibrational properties
    - Reaction enthalpies $\Delta H$ and entropies $\Delta S$

- **New (unknown) complex hydrides:**
  - Develop and apply methods for determining crystal structure
  - Calculate thermodynamics properties ($\Delta H$ and $\Delta S$)
  - Screen for materials with enthalpies in the 20-50 kJ/mol-H$_2$ range
Overview of Progress

1st YEAR

Validated approach on known hydrides
- Refinement of technical methods
- Literature search
- Calculations for all known materials with >6 wt% H₂
- Large database of reaction enthalpies
- Initial screen for new mixtures of materials

COMPLETED WORK:
- Mixtures of alanates:
  - Stable compounds not found
  - Not promising
- Mixtures of alanates and borohydrides $X_nY_m(BH_4)_p(AlH_4)_{n+m-p}$, where X and Y are monovalent cations (Li, Na, K):
  - Formation enthalpies positive
  - Not promising

2nd YEAR

Expand to new materials with unknown crystal structures

CURRENT WORK:
- Expanded search to new material classes:
  - Identified materials with 10-15 wt.% H₂ (theoretical)
  - ΔH in the 30-40 kJ/mol-H₂ range
- Optimize these materials for lower ΔH and/or higher ΔS:
  - Mixing/Alloying
  - Destabilized reactions

FUTURE WORK:
- Complete material optimization
- Complete searching of phase space

3rd YEAR

Not promising

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6
Highlights

- First-Principles provides accurate predictions of decomposition enthalpies for known compounds. This provides confidence in predictions of thermodynamics for unknown compounds.

- In FY 2004, constructed a large database of first-principles calculated structural and thermodynamic properties of known alanates, borohydrides and amides. It is being used to screen for new reactions and materials.

\[ MH_x \rightarrow M + \frac{x}{2} H_2 \]

Wolverton, Ozolins, and Asta, 2004
Highlights

First-principles can steer us away from certain regions:
✓ Investigated mixtures of alanates and borohydrides (LiAlH$_4$-XBH$_4$, where X=Li, Na, K). All studied compounds had positive formation enthalpies, indicating that mixed alanates and borohydride-alanate compounds will decompose into constituent hydrides exothermically.

First-principles can guide us toward promising reaction classes:
✓ We have predicted novel materials/reactions with targeted thermodynamics (material-only, theoretical)*:
  ✓ 7-15 wt.%
  ✓ ~120 g/L volumetric H$_2$ densities
  ✓ 30-40 kJ/mol-H$_2$, including vibrational contributions

*Theoretical first-principles work done in collaboration with Ford
Structural Energies

✓ Ordered compounds are constructed from the known crystal structures of alanates and borohydrides
✓ Which ones to pick?
✓ Answer: Use $\Delta E_x(Y)$, the excess energy of compound $X$ (e.g., LiAlH$_4$) in the crystal structure $Y$ (e.g., of NaAlH$_4$). Energies given in kJ/mol:

<table>
<thead>
<tr>
<th>Compounds</th>
<th>LiAlH$_4$</th>
<th>NaAlH$_4$</th>
<th>KAlH$_4$</th>
<th>LiBH$_4$</th>
<th>NaBH$_4$</th>
<th>KBH$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiAlH$_4$</td>
<td>0.0</td>
<td>4.0</td>
<td>12.2</td>
<td>8.3</td>
<td>21.0</td>
<td>7.3</td>
</tr>
<tr>
<td>NaAlH$_4$</td>
<td>6.1</td>
<td>0.0</td>
<td>8.7</td>
<td>13.8</td>
<td>10.3</td>
<td>10.2</td>
</tr>
<tr>
<td>KAlH$_4$</td>
<td>8.1</td>
<td>2.4</td>
<td>0.0</td>
<td>24.2</td>
<td>11.9</td>
<td>12.0</td>
</tr>
<tr>
<td>LiBH$_4$</td>
<td>4.9</td>
<td>10.0</td>
<td>4.2</td>
<td>0.0</td>
<td>18.8</td>
<td>4.6</td>
</tr>
<tr>
<td>NaBH$_4$</td>
<td>10.2</td>
<td>0.0</td>
<td>0.9</td>
<td>2.7</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>KBH$_4$</td>
<td>10.7</td>
<td>18.3</td>
<td>0.8</td>
<td>13.9</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Pick trial crystal structures with low values of $\Delta E_x(Y)$ for all end-compounds!
Mixed Alanates-Borohydrides

Calculated $\Delta H$ (in kJ/mol H$_2$)

<table>
<thead>
<tr>
<th>Alkali Metal Alane</th>
<th>$\Delta H$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiBH$_4$</td>
<td>81.3</td>
</tr>
<tr>
<td>NaBH$_4$</td>
<td>106.8</td>
</tr>
<tr>
<td>KBH$_4$</td>
<td>133.0</td>
</tr>
<tr>
<td>LiAlH$_4$</td>
<td>11.3</td>
</tr>
<tr>
<td>NaAlH$_4$</td>
<td>36.8</td>
</tr>
<tr>
<td>KAlH$_4$</td>
<td>60.1</td>
</tr>
<tr>
<td>Mg(AlH$_4$)$_2$</td>
<td>0</td>
</tr>
<tr>
<td>Ca(AlH$_4$)$_2$</td>
<td>11.7</td>
</tr>
</tbody>
</table>

$\Delta H$ for LiAlH$_4$ is too low. Try mixing with NaBH$_4$ to increase $\Delta H$. Formation energy is strongly positive - NO MIXING!
Mixing Alanates: MgNa(AlH$_4$)$_3$

Initial structure from electrostatic considerations

Relaxed structure from DFT

\[ \text{Mg(AlH}_4\text{)}_2 + \text{NaAlH}_4 \rightarrow \text{MgNa(AlH}_4\text{)}_3 \quad \Delta E = +10.7 \text{ kJ/mol} \]

Conclusion: MgNa(AlH$_4$)$_3$ compounds will not form!
First-Principles results agree with experiments and virtual high-throughput screening (VHTS) results at UOP:
- Na-Li-Mg-Alanate phase diagram searched starting from hydrided side
- No stable mixtures found under these conditions.
Crystal Structure Determination

• **Problem:**
  – Crystal structure of material $X$ is often not known

• **Strategy:**
  – Identify compounds in crystallographic databases (e.g., ICSD) with the correct chemical formula and the correct ionic coordination
  – Obtain a set of $N$ structures ($N$ is usually from five to a few hundred)
  – Run first-principles DFT calculations for the material $X$ in all $N$ structures, relaxing all structural degrees of freedom
  – Pick the lowest energy structure to get an estimate of the crystal structure and hydriding enthalpy
Be(BH₄)₂ Energetics
93 Structures
875 eV, 4x4x4 k-points
Structures initially relaxed from 400eV 2x2x2 calcs
Relaxation constrained to symmetry of original structure

Tests of the method: Ground states of Be(BH₄)₂ and Ca(AlH₄)₂ predicted correctly!
New Material Predictions

ICSD Structures

Energies relative to the lowest found (in kJ/mol f.u.)

Material #1

Material #2
New First-Principles Predicted High Density Storage Reactions with $\Delta H \sim 30-40$ kJ

- These materials show several decomposition pathways.
- Good news: all $\text{H}_2$ should be released at one temperature!
- All reactions distinct from DFT predictions of the CoE (Alapati, Johnson, Scholl, 2006)
- All reactions involve experimentally-synthesized materials

Some Examples of Reactions:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta H$ (kJ/mol $\text{-H}_2$)</th>
<th>$\Delta S$ at 298 K $[\text{J/(K mol -H}_2)]$</th>
<th>$\text{H}_2$ Wt. % *</th>
<th>Volume density (g $\text{-H}_2$/L) *</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material #1</td>
<td>57</td>
<td>111</td>
<td>10</td>
<td>125</td>
</tr>
<tr>
<td>Material #2, Reaction #1</td>
<td>51</td>
<td>117</td>
<td>15</td>
<td>120</td>
</tr>
<tr>
<td>Material #2, Reaction #2</td>
<td>52</td>
<td>115</td>
<td>13</td>
<td>120</td>
</tr>
<tr>
<td>Material #2, Reaction #3</td>
<td>53</td>
<td>114</td>
<td>12</td>
<td>120</td>
</tr>
</tbody>
</table>

* theoretical, material-only
Future Work at UCLA/Ford

• Search for ways to lower reaction enthalpies of materials #1 and #2 using:
  – Alloying
  – Destabilization (Vajo et al, 2004)

• Continue search for new materials/reaction based on complex hydrides

• Study/Optimize reaction enthalpies in the LiBH$_4$-MgH$_2$-LiNH$_2$ system in collaboration with UOP and Ford
Summary

• First-Principles modeling steers away from regions of phase space - e.g., mixtures of alanates and borohydrides are not promising

• First-principles modeling has identified materials with 10-15 wt. % theoretical H\textsubscript{2} capacity and ΔH in the 30-40 kJ/mol-H\textsubscript{2} range