Complex Hydride Compounds with Enhanced Hydrogen Storage Capacity

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2005 DOE Hydrogen Program Review
May 23-26, 2005
Arlington, VA
Project ID # ST6

This presentation does not contain proprietary or confidential information
Overview

• Timeline
  – 11/30/02 Start
  – 12/31/06 End
  – 40% Complete

• Budget
  – $2.9 M Total Program
    • $2.1M DoE
    • $0.8M (27%) UTC/ALB
  – $0.43M DoE FY’04
  – $0.68M DoE FY’05

• Barriers
  – Gravimetric Density: 2 kWh/kg
  – Volumetric Density: 1.5 kWh/l
  – Charging rate: 1.5 kgH₂/min.
  – Discharging rate: 4 gH₂/sec.
  – Safety: Meets or exceeds applicable standards
  – Durability: 1000 cycles

• Partners
  – SRNL
  – Albemarle
  – IFE
  – QuesTek LLC
Objectives

Total Program Objectives
To develop new complex hydride compounds that can:
- Reversibly store > 7.5 weight % capacity,
- Discharge H₂ at rates required for PEM fuel cell operation,
- Recharge for 1000 cycles with 100 % recovery.

First Year (2004) Objectives
- Implement and validate new atomic-thermodynamic predictive methods.
- Search out quaternary systems for high H capacity candidates formed from Na, Li, Ti, and/or Mg combined with Al and H, using multi-pronged approach:
  - Atomic-Thermodynamic Modeling
  - Solid State Processing (SSP)
  - Molten State Processing (MSP)
  - Solution Based Processing (SBP)
Approach
Virtual and Experimental Processing Methods

Discover reversible high H compounds, \( \text{Ak}_x\text{Ae}_y\text{M}^{+i}_z (\text{AlH}_4)_{(x+2y+iz)} \), formed between alkali (Ak) and alkaline earth (Ae) hydrides, metals (M), AlH\(_3\), and H\(_2\).

**Atomic-Thermodynamic Modeling (UTRC)**
- Survey broad compositional spaces
- Supplement thermodynamic data
- Generate descriptions of phase behavior

**Solid State Processing, SSP (UTRC)**
- Very rapid, low cost screening
- Limited conditions
- High cost for high volume production

**Molten State Processing, MSP (SRNL)**
- Rapid screening
- Wide range of T & P
- Includes metastable phases
- Expensive equipment

**Solution Based Processing, SBP (Albemarle)**
- Excellent control
- High purity products
- Expensive processing
- Cost-effective high volume production

Unique aspect of approach: utilize a wide range of modeling and synthesis methods to search out and discover new high H\(_2\) capacity systems.
Accomplishments: Established Atomic-Thermodynamic Flowpath

**INPUT:** High H candidate phases

- **Density Functional Theory (DFT)**
  - Ground state (0 K) structures & enthalpies

- **Direct Method Lattice Dynamics**
  - Finite temperature thermodynamic predictions

- **Favorable candidates $\Delta G_{\text{form}}^{\text{298 K}}$**

- **Computational Thermodynamics**
  - Assessment / database development

**OUTPUT:** Multi-order phase diagram & property predictions

Coupled methodologies provide the capability to discover and evaluate high H capacity candidates’ thermodynamic phase behavior, prior to experimentation.
Accomplishments:
Validation of First Principles (FP) Predictions

Validation with experiment: lattice dynamic predictions in excellent agreement with thermodynamic assessment of experimental Na alanate dissociation data.

**Experimental Data**
- Dymova 1974
  - △ undoped NaAlH₄(liquid)
  - □ undoped Na₃AlH₆
- Thomas 1999
  - ◈ Ti-doped NaAlH₄
  - ★ Ti-doped Na₃AlH₆
- Gross 2002
  - ◇ Ti-doped NaAlH₄
- Bogdanovic 1997: PCI
  - × Ti-doped NaAlH₄
  - ☆ Na₃AlH₆ from Ti-doped Na₃AlH₆
- Bogdanovic 2000: PCI
  - ● Ti-doped NaAlH₄
  - ○ Na₃AlH₆ from Ti-doped Na₃AlH₆
- Bogdanovic 2000: dissociation
  - + Ti-doped NaAlH₄
  - ♦ Ti-doped Na₃AlH₆
Accomplishments:

Integrated Experimental & FP Predicted Data

Potential diagram 100°C

Predictions extend computational thermodynamics beyond experimental realm. Phase diagrams calculated from integrated assessment of experimental data and predictions used to evaluate candidate phase stability over a wide range of T & P.
Accomplishments:

Virtually Surveyed Multiple Quaternary Spaces

Year II Quaternary Systems:
To Date:
Na-Mg-Al-H
Li-Mg-Al-H
Surveyed >40 Phases to date
Identified Numerous Candidates!

Year I Quaternary Systems:
Na-Ti-Al-H
Li-Ti-Al-H
Na-Li-Al-H
Surveyed >170 Phases
No Candidates Found!

Phases Simulated:
Complex hydrides
Competing phases
Lower order phases
Hypothetical End-Members

High Capacity Media Criteria:
- 7.5 wt% retrievable H capacity
- Stability $\Delta G_{\text{formation}} << 0$
- $\Delta G_{\text{dehydrogenation}} \rightarrow 0$

FP atomic-thermodynamic methodologies used to accelerate survey of broad compositional phase spaces, reducing and focusing experimental effort.
**Accomplishments:**

**Integrated Predictions and Experiments**

Predicted and experimental (Fossdal et. al, J. Alloys Compd., in press.) dissociation P are in excellent agreement.

First two reactions correspond to a 2-step 5.2 w/o H₂ reversible system.

1st, 3rd & 4th reactions for synthesis.

Successfully employed FP predictions to evaluate Na₂LiAlH₆ structure and phase behavior. Explained observed synthesis and disproportionation reactions.
Accomplishments:
Identification of High Capacity Candidates

**LiMgAlH₆ Candidate**

Many mixed alkali/alkaline earth alanate candidates predicted to have $\Delta H_{\text{form}}$ (0 K) $>-8$ kJ/mol*atom

Numerous possible disproportionation products are currently being evaluated. Actual reversible H₂ content dependent upon identification of most favorable dehydrogenation end products.

Combined predictive methodologies are effective in identifying and evaluating new candidate hydrides, yielding recommendations for experimental evaluation.
Accomplishments

New High H Capacity Material Search Strategy

A method of predicting destabilized alanate compounds with *in-situ* rechargeability can be described thermodynamically as:

\[ M_1(AlH_4)_y + M_2H_x \rightleftharpoons M_1M_2Hi + Al + \frac{(4y+x-i)}{2}H_2 \]

where:

\[ \Delta G \approx 0 \approx G_f^0 M_1M_2Hi + G_f^0 Al + RT\ln(P_{H_2}) - G_f^0 M_1(AlH_4)y - G_f^0 M_2Hx \]

at 70<T<120°C & 1<P<100 bar and M₁ & M₂ are metal ions.

Systematic Approach:

- Comprehensively search databases to select candidates from known phases.
- Identify candidate phase chemical reactions, prioritize according to H₂ storage capacity.
- Where thermodynamic data is unavailable, predict thermochemical properties.
- Conduct thermodynamic assessments combining both experimental and predicted data to evaluate *in-situ* reversibility for hydrogen storage.

New modeling tools used to select candidates for focused synthetic evaluation.
Accomplishments

New Hydrogen Storage Opportunities

• All in-situ rechargeable systems have $\Delta H_f \approx 40 \text{ kJ/mole H}_2$.
• $\Delta H_f \approx 0 \text{ kJ/mole H}_2$ reactions can only be achieved at $\sim 10^6 \text{ bar}$.
• This results from $\Delta S_f$ for $\text{MH}_x$ approximately constant.

Thermodynamic assessments of in-situ reversible hydrogen storage reactions.
Accomplishments

Solid State Processing (SSP) System Surveys

Am/Ae/Tm

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Processing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na:Ti:Al</td>
<td>Hand Mix ⇒ XRD</td>
</tr>
<tr>
<td>Na:Li:Al</td>
<td>SPEX Mill 3 hr. ⇒ XRD</td>
</tr>
<tr>
<td>Na:Mg:Al</td>
<td>200barH₂/60°C/20 hr ⇒ XRD</td>
</tr>
<tr>
<td>Na:Ti:Li:Al</td>
<td>200barH₂/80°C/20 hr ⇒ XRD</td>
</tr>
<tr>
<td>Na:Ti:Mg:Al</td>
<td>200barH₂/100°C/20 hr ⇒ XRD</td>
</tr>
<tr>
<td>Li:Mg:Al</td>
<td>200barH₂/120°C/20 hr ⇒ XRD</td>
</tr>
</tbody>
</table>

Analysis

Semi-quantitative analysis using: MDI Corp. Jade 7.0
utilizing data bases:
ICDD/PDF-2 Release 2002
ICSD Release 2004/2.

High throughput SSP screening of 7 quaternary/quinary systems completed.
Accomplishments
Development of SSP NaH:TiH₂:AlH₃ Method

Cations introduced via chloride additions led to far too much MClₓ to be effective.

NaH:Ti:Al

NaH+Ti+Al+5/₂H₂ => NaAlH₄+TiHₓ

Primary metal additions were only an effective method of synthesizing NaₓAlHₙ at temperatures > 100°C.

No previously unidentified phases found in the Na-Li-Ti-Al-H systems.
**Accomplishments**

**SSP NaH-LiH:MgH₂:TiH₂:AlH₃ System Survey**

**NaH:MgH₂:TiH₂:AlH₃**

- **NaH + MgH₂ + TiH₂ + AlH₃** ⇌ **MgH₂ + TiH₂ + NaAlH₄**
- **NaH + MgH₂ + TiH₂ + AlH₃** ⇌ **1/3MgH₂ + 1/2NaAlH₄ + 1/4NaMgH₃ + 1/2Al**

**NaAlH₄ + MgH₂** ⇌ **NaMgH₃ + Al + 3/2H₂ 3.7 w/o**

**LiH:TiH₂:LiH:AlH₃**

- **LiH + MgH₂ + TiH₂ + AlH₃** ⇌ **3/4MgH₂ + 1/8LiNa₂AlH₆ + 1/4NaAlH₄ + 1/4NaMgH₃ + 3/8Al**

**LiH** absorbed

- **4NaAlH₄ + LiH + 2MgH₂** ⇌ **Na₂LiAlH₆ + 2NaMgH₃ + 3Al + 9/2H₂ 3.3 w/o**

**NaAlH₄** and **MgH₂**

- **4NaAlH₄ + LiH + 2MgH₂** ⇌ **LiNa₂AlH₆ + 2NaMgH₃ + 3Al + 9/2H₂ 3.3 w/o**

**NaAlH₄** and **MgH₂**

- **4NaAlH₄ + LiH + 2MgH₂** ⇌ **LiNa₂AlH₆ + 2NaMgH₃ + 3Al + 9/2H₂ 3.3 w/o**

Numerous mixed compound systems identified having H₂ capacities ranging from 2.6-5.6 w/o, and which are rechargeable ≤ 200 bar at T<120°C.
Accomplishments
SSP 2005 Approach Going Forward

CY ‘04:
Hand Mix, Ball Mill
60, 80, 100 & 120°C /200bar/20 hrs

CY ‘05:
Hand Mix, Ball Mill
100°C/200bar/20 hrs

- Moving on to transition metal substituted systems.
- Maximize compositional ranges covered by using fewer thermal treatments.
Accomplishments

Molten State Processing (MSP) Proof of Concept

\[ \text{NaH} + \text{LiH} + \text{NaAlH}_4 \rightarrow \text{Na}_2\text{LiAlH}_6 \]

Range of Processing Conditions
- RT-600°C
- 200 bar
- 8 hr dwell time
- Quiescent or agitated
- 1 liter ~600g capacity

Processing Conditions
- 190°C, 200 bar, 15 min. dwell time, agitated

Demonstrated MSP advantages: Solvent- and anion-free processing produces high yields of clean complex hydrides. One liter pressure vessel scaleable to meet system demonstration requirements.
Accomplishments

MSP Compositional System Surveys

**NaAlH₄+LiH+KH=>**

LiNa₂AlH₆+KAIH₄+NaH+KH+Na₃AlH₆+ ?

Multiple unidentified peaks identified

Processing Conditions
190°C, 200 bar, 15 min. dwell time, agitated

Four quaternary/quinary composition systems investigated to date:
- Na-Li-Al-H
- Na-Ti-Al-H
- Na-K-Li-Al-H
- Na-Mg-Al-H

**NaAlH₄+MgH₂=>** Al+NaMgH₃+Mg

Multiple unidentified peaks observed in Na:Li:K:Al:H system provided evidence for formation of new compounds.

Processing Conditions
190°C, 200 bar, 15 min. dwell time, agitated

United Technologies Research Center
**Accomplishments**

**MSP Produced Highly Active NaAlH₄**

**Before Fusion**
Solid-state processed NaAlH₄ + 4%TiH₂

**After Fusion**
At 200 bar, 190°C, 15 min.

TPD discharge experiments showed MSP hydrides to be more active than conventionally ball milled hydrides. This material is being kinetically examined for possible use in CCHSS#2.

**United Technologies Research Center**
Accomplishments
Solution Based Processing (SBP) Ti/Na Alanates

\[
\text{TiCl}_4(\text{THF})_2 + \text{Al}(i-\text{Bu})_3 \rightarrow \text{TiCl}_3(\text{THF})_3
\]
\[
\text{NaAlH}_4 + x\text{TiCl}_3(\text{THF})_3 \rightarrow \text{NaTi}_{x}\text{Al}_{1-x}\text{H}_4 + \ldots
\]

- Complete solution doping reaction at 25°C.
- Disproportionation to Al$_3$Ti.
- New ordered phases observed in related systems.

Demonstrated SBP synthesis route to homogeneous Ti$^{+3}$ doped alanates. This material is being kinetically examined for possible use in CCHSS#2.

Hydrogen Evolution as a Function of Time and Temperature

<table>
<thead>
<tr>
<th>Mole ratio</th>
<th>Ti:Al</th>
<th>2:100</th>
<th>4:100</th>
<th>10:100</th>
<th>33:100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mole ratio</td>
<td>H$_2$:Ti</td>
<td>7.7</td>
<td>6.7</td>
<td>6.4</td>
<td>5.7</td>
</tr>
</tbody>
</table>

United Technologies Research Center
**Future Work**

**Discovery of High H Capacity Hydrides**
- **FP Modeling**
  - New Phase Simulations
  - Thermodynamic Predictions
  - FY’05 Ak/Ae with Al, B & TM

**Thermodynamics**
- Survey of Compositional Space
- Phase Behavior Predictions
- FY’05 Designed Endproducts

**Experimentation**
- Synthesis, Characterization, Performance Evaluation
- New phase properties
- Validate predictions
- Refine compositions
- Recommend syntheses
- ID systems with competitive stability

**Solid State Processing**
- New Phases from Mechanochemical Mixing
  - FY’05 Ak/Ae with Ni, Co, Fe

**Molten State Processing**
- New Phases from High T & P Fusion
  - FY’05 Ak/Ae with V, Cr, Mn

**Solution Based Processing**
- New Phases from Chemical Design and Synthesis
  - FY’05 Ak/Ae with Al, B & TM

**Parallel Search Strategies**

**Discovery of High H Coupled Reactions**

**FY’05** Deploy integrated methods to search and discover high capacity systems.

**FY’06** Refine new system compositions. Catalyze improved kinetic performance.

Ak = alkali
Ae = alkaline earth
TM = transition metals
Responses to Previous Year
Reviewers’ Comments

• Comment
  “Consider broadening to include non-alanate materials?”
  By adding other complexing elements such as B, Ga ... vastly increases the scope of investigation, thus limiting empirical investigations into all possible combinations. Additions of these elements will be investigated atomistically and empirically where modeling indicates high hydrogen capacity materials are stable.

• Comment
  “DOE should consider how this project relates to or coordinates with the Sandia Metal Hydride Center of Excellence?”
  UTRC has always maintained a high degree of communication with SNL and many of its CoE partners through DoE sponsored meetings, IEA meetings, and laboratory visits. This communication will continue.

• Comment
  – “Need validation that the modeling is predicting properties correctly.”
  – “Need to insure that the modeling efforts are not independent of experiment.”
  As shown in the progress to date, modeling and empirical results have shown very good agreement. We have a very high confidence level in modeling predictions when phonon approach is incorporated. The modeling & empirical efforts are designed to be interdependent with each other, and are closely coordinated with monthly meetings used to exchange data, ideas, and concepts.
Backup Slides
**Publications**


**Presentations**


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Multiple collaborations foster H₂ storage research progress and communication.
**Safety**

**Risk Identification**

**Burn Rate Test**
- Partially Discharged CCH00-33
  - 13.11
  - 20.01
  - 24.20
  - 31.06

**Water Immersion Test**
- Partially Discharged CCH00-33
  - 4.12
  - 4.24
  - 4.27

**Water Injection**
- Partially Discharged CCH00-33
  - 31.06
  - 31.23
  - 101.09

**Dust Explosion Testing**

<table>
<thead>
<tr>
<th>Test Materials</th>
<th>Weight Class</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tc (°C)</td>
<td>MIE (mJ)</td>
</tr>
<tr>
<td>----------</td>
<td>----------</td>
</tr>
<tr>
<td>St-1</td>
<td>320</td>
</tr>
<tr>
<td>St-3</td>
<td>124</td>
</tr>
</tbody>
</table>

- Dust explosion: class St-3, Highly Explosive when finely divided and dispersed.

**Fire risk quantitatively assessed**

**Explosion risks quantitatively assessed**

Comprehensive risk assessment performed on all major operations quantitatively describing both impact and probability of occurrence.

**Appendix V: UTRC Risk Assessment Form**

<table>
<thead>
<tr>
<th>Process, Task or Step</th>
<th>Potential Hazard</th>
<th>Controls in Place</th>
<th>Likelihood Occurrence</th>
<th>Potential Impact</th>
<th>Risk Rank</th>
<th>Controls Required</th>
<th>To reduce risk further/Name/Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixing Powder</td>
<td>Fire, Explosion</td>
<td>Glovebox filled with nitrogen</td>
<td>High</td>
<td>85%</td>
<td>6</td>
<td>Gloves inspected every day</td>
<td>Nitrogen pressure checked every day</td>
</tr>
<tr>
<td>Hydrogen Storage</td>
<td>Failure of High Pressure Systems</td>
<td>Restricted use</td>
<td>Moderate</td>
<td>50%</td>
<td>3</td>
<td>Pressure rated components</td>
<td>Local rules and procedures</td>
</tr>
<tr>
<td>Hydrogen Storage</td>
<td>Explosion</td>
<td>Sparkless</td>
<td>Moderate</td>
<td>75%</td>
<td>2</td>
<td>Redundant valves</td>
<td>Detailed procedures; Employee training</td>
</tr>
<tr>
<td>Working in glovebox</td>
<td>Ergonomic Pain</td>
<td>Limited time in glovebox to 45 minutes max.</td>
<td>Low</td>
<td>25%</td>
<td>6</td>
<td>Set up to avoid awkward reaching</td>
<td></td>
</tr>
<tr>
<td>Lifting, transporting</td>
<td>Ergonomics Training, procedures</td>
<td>Weight kept to &lt; 30 pounds</td>
<td>Low</td>
<td>25%</td>
<td>6</td>
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Safety

Risk Mitigation

- Material handled under inert gas
- Incoming material stored in fire cabinet
- Materials tested in commercial equipment installed in a glove box
- Media stored under inert gas

All risks reduced to low impact or negligible probability.