Doped Sodium Aluminum Hydride: Fundamental Studies and Development of Related Hydrogen Storage Materials

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This presentation does not contain any proprietary or confidential information
Objectives

I. Determination of the chemical nature and mechanism of action of the species that is responsible for the enhanced kinetics of Ti-doped NaAlH$_4$.

II. Apply insights gained from fundamental studies of Ti-doped NaAlH$_4$ to the design and synthesis of hydrogen storage materials that will meet DOE hydrogen storage system targets.
Budget

Total Funding FY00 - FY04
- DOE: $4 \times 250K = 1,000K$
- UH Cost Share: $283K$
  
  $1,283K$

FY04 Funding
- Received from DOE: $110K$
- Committed by DOE: $140K$
- UH Cost Share: $70K$
  
  $320K$
2010 DOE Targets

- **Usable H₂ Densities**
  - Volumetric: 4.5 kg H₂/L
  - Gravimetric: 0.06 kg H₂/kg

- **Delivery temperature range** -30 to 100°C

- **Delivery pressure** 2.5 atm

- **Minimum H₂ Flow Rate** (0.027g/sec)kW

- **Refueling Rate** 1.5 kg H₂/min

- **Cycle Life Stability** 90 capacity for 1000 cycles
I. Maximization of hydrogen cycling performance of Ti-doped NaAlH$_4$
   1) Mechanically doped NaAlH$_4$ first prepared by Zidan and Jensen in 1998.
   2) Current project initiated.
   3) Demonstration of hydrogen flow of 1.8 wt/h @ 100 °C against 1 atm H$_2$ pressure.
   5) Demonstration of >4 wt % hydriding of NaH/Al in <4 min
   6) 100 cycle, > 3 wt % capacity test completed.

II. Determination of the fundamental basis of enhanced hydrogen cycling performance
   4) X-ray diffraction indicates dopants are substituted into the bulk of the hydride.
   7) EPR studies show dopant is initially a Ti(III) species.

III. Design, synthesis, and evaluation of advanced complex hydrides
   8) Method developed for the extraction of doping by products.
   9) Advanced complex hydrides synthesized.
Approach

I. Determination of the fundamental basis of enhanced hydrogen cycling performance

- **Electron Paramagnetic Resonance (EPR) Studies** Direct characterization of Ti dopants
- **Infrared Spectroscopy and Inelastic Neutron Scattering** Direct probes of the effects of doping on hydrogen
- **Determination of Equilibrium Hydrogen Plateau Pressures** Influence of doping on bulk hydride thermodynamic properties
- **Kinetic measurements and modeling** Mechanism of hydrogen cycling process
- **Synchrotron X-ray and Neutron Diffraction Studies** Influence of doping on structure and detection of minor phases
Approach

II. Design, synthesis, and evaluation of advanced complex hydrides

- Synthesis and Evaluation of “Sodium-Titanium” Alanate
  Evaluation of purified “bulk substituted” materials.
- Synthesis and Evaluation of Novel Complex Hydride Systems
  Evaluation of “guided design” materials with theoretical hydrogen storage capacity of >7 wt %.
Methods for the handling, storing, and disposing of all hazardous materials connected with this project are in compliance with EPA and Hawaii Department of Health regulations.

PI has completed the Hazardous Materials Waste Generator Training course and annual refresher courses of the University of Hawaii Environmental Health and Safety Office.

Unblemished safety record in the preparation of over 100 samples of alanate materials since US DOE funded studies of these materials were initiated in our laboratories in 1997.
In situ, Synchrotron XRD Study Of Cycling of Ti-doped NaAlH₄

NaAlH₄ $\rightleftharpoons \frac{1}{3} \text{Na}_3\text{AlH}_6 + \frac{2}{3} \text{Al} + \text{H}_2 \rightleftharpoons \text{NaH} + \text{Al} + \frac{3}{2} \text{H}_2$

Collaboration with Dr. J. Rijsenbeek and Dr. Y. Gao - GE Global Research Center and Brookhaven National Lab
Redox vs. Substitution Models of Ti-doped NaAlH₄

Issue must be resolved to assess the possibility of developing improved alanates.

Redox Model
NaAlH₄ + x TiCl₃ → 1-3x NaAlH₄ + x 3 NaCl + TiAl₃
⇒ Surface isolated, catalytic TiAl alloy formed upon doping
⇒ No change in bulk thermodynamic properties
⇒ Theoretical hydrogen capacity is <5.4 wt %
⇒ Fine “thermodynamic tuning” through low level substitution is not possible.
Substitution model of Ti-doped NaAlH$_4$

NaAlH$_4$ + x TiCl$_3$ $\rightarrow$ Ti$_x$Na$_{1-3x}$AlH$_4$ + x NaCl

- Changes in bulk thermodynamic properties.
- Hydrogen capacity increases (and kinetics enhanced) upon increased doping if Na by-product is removed.
- Thermodynamic properties of complex hydrides can be fine tuned through partial substitution.

Kinetic Studies

Collaboration with Dr. T. Kiyobayashi, Institute for Advanced Science and Technology, Osaka Japan

At 150 °C dehydrogenation of Na$_3$AlH$_6$ is much slower than NaAlH$_4$ starting with Ti-doped NaAlH$_4$
Kinetic Studies

Dehydrogenation profiles at 110°C of:
A) Ti-doped NaAlH$_4$
B) Ti-doped Na$_3$AlH$_6$
C) Zr doped NaAlH$_4$
D) Zr doped Na$_3$AlH$_6$

Directly Ti doped Na$_3$AlH$_6$ undergoes dehydrogenation at rates equal to that of Ti doped NaAlH$_4$!!
⇒ Dehydrogenation kinetics are not controlled by relative strengths Al-H bonds.
⇒ Kinetics are limited by processes long range atomic transport phenomenon and location of dopants.

Synchrotron XRD

Collaboration with Dr, H. Brinks and Prof. B. Hauback
Institute for Energy Research, Kjeller, Norway.

<table>
<thead>
<tr>
<th></th>
<th>a (Å)</th>
<th>c (Å)</th>
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<tbody>
<tr>
<td>NaAlH₄ Pure</td>
<td>5.0232(1)</td>
<td>11.3483(2)</td>
</tr>
<tr>
<td>6% TiCl₃</td>
<td>5.0231(1)</td>
<td>11.3481(2)</td>
</tr>
<tr>
<td>6% TiCl₄</td>
<td>5.0234(1)</td>
<td>11.3493(2)</td>
</tr>
<tr>
<td>6% TiF₃</td>
<td>5.0234(1)</td>
<td>11.3493(2)</td>
</tr>
<tr>
<td>NaH+Al+2% Ti(OBu)₄ 7 cycles</td>
<td>5.0233(1)</td>
<td>11.3498(2)</td>
</tr>
</tbody>
</table>

- No changes of unit cell.
- No extra phases in uncycled samples.
Cycling 1:1 NaH/Al doped with 2 mol % Ti(OBu)$_4$ results shoulders on the Al-peaks. Accounts for ~1/3 of Ti introduced into the hydride.

H.W. Brinks, C.M. Jensen, S.S. Srinivasan, B.C. Hauback, D. Blanchard, K. Murphy

*J. Alloys Compd.* 2004, in press
Rietveld Analysis of XRD Peak Broadening

Collaboration with Prof. K. Yvon, University of Geneva

Degree of cell expansion tracks milling time **not** doping level.
Rietveld Analysis of XRD Peak Broadening

Distortion is primarily in the direction of the c axis.
Al-H stretching frequency shifts upon mechanical milling both with and without dopant precursor. ⇒ Al-H bonding and alanate structure is perturbed by mechanical milling.
Electron Paramagnetic Resonance
Collaboration with Prof. S. Eaton, University of Denver

Upon doping, the spectrum of NaAlH$_4$ doped with 1.5 mol % of TiCl$_3$ is dominated by a signal that is characteristic of spin isolated Ti(III).

After 5 cycles, the spectrum is dominated by the signal of a multi-spin Ti species. The Ti(III) signal is diminished to 30 % of its original intensity.

After 15 cycles, only the multi-spin Ti signal is observed and the Ti(III) signal disappears completely.
Inelastic Neutron Scattering

Collaboration with Dr. T. Udovic, Dr. J. Iniguez and T. Yildirim National Institute of Standards and Technology.

- Density function calculations by Iniguez and Yildirim show stabilization is achieved upon Ti@Na substitution.
- Spectral simulation requires inclusion of contributions from two-phonon processes.
- Features related to Ti@Na substitution are masked by strong two-phonon scattering.

Neutron Diffraction Structure Determinations

Collaboration with Prof. B. Hauback and Dr. H. Brinks, Institute for Energy Technology, Norway.
- No differences in Al-H bonding observed between doped and undoped.
- Studies of doped and undoped NaAlD$_4$ both carried out with mechanically milled material.

Collaboration with Prof. A. Albinati, U. Milan.
- Comparison of peak intensities of doped and undoped NaAlD$_4$ reveals differences that can be accounted for by Ti substitution of into Na sites!
Synthesis of Titanium-Sodium Alanate

- XRD studies confirm that the by-product from a selected dopant precursor can be removed from “Ti_{x/3}Na_{1-x}AlH_4” through a proprietary extraction method.
- By product free “Ti_{x/3}Na_{1-x}AlH_4” has been independently prepared through a proprietary method from NaH/Al.
- The hydrogen storage performance of both materials is currently under evaluation.
Proprietary formulation.

Preliminary data shows >7.0 wt % reversible H₂ capacity at relevant temperatures and reasonable kinetics.

The hydrogen storage performance of both materials is currently under evaluation.
Collaborations

- Dr. Hendrik Brinks, Prof. Bjorn Hauback, Dr. Arnulf Maeland - Institute for Energy Technology, Kjeller, Norway.

- Dr. Job Rijssenbeek, Dr. Yan Gao, G.E. Global Research Center and Brookhaven National Laboratory.

- Prof. Sandra Eaton - University of Denver.

- Prof. Alberto Albinati - University of Milan.

- Prof. Klaus Yvon, University of Geneva.

- Dr. Tetsu Kiyobayashi, Dr. Nobuhiro Kuriyama, Dr. Hiroyoyuki Takeshita - National Institute for Advanced Industrial Science and Technology, Osaka, Japan.

- Dr. Kristin Kumashiro, Dr. Walter Niemczura - Department of Chemistry, University of Hawaii.

- Dr. Terry Udovic, Dr. Jorge Inguez, Tander Yildirim - National Institute of Standards and Technology.
Responses FY03
Review’s Comments

**Lattice parameters**
- Specific recommendation to “get smaller error bars on lattice work.
- Accomplished through synchrotron X-ray studies in collaboration with the Institute for Energy Research and GE/Brookhaven and detailed Rietveld analysis of XRD peak broadening with U. Geneva.

**Can alanates meet the US DOE targets?**
- Bulk vs. surface doping issue must be resolved.
- Benefit of doping by-product removal will be determined by the end of FY04.
- Benefit of “substitution model” driven design of advanced complex hydrides with be determined by end of FY05.
Future Directions

**Remainder of 2004**
- Complete EPR studies of doped NaAlH$_4$ prepared from a Ti precursor that shows anomalous behavior.
- Neutron diffraction structure determination of unmilled NaAlD$_4$.
- Complete detailed comparison of date from neutron diffraction studies of doped and undoped NaAlD$_4$.
- Determine hydrogen storage capacity and hydrogen cycling kinetics of by-product free “Ti$_{x/3}$Na$_{1-x}$AlH$_4$” and advanced complex hydride system.

**Beyond**
- XAFS and TOM-SIMS depth profiling of Ti distribution in doped NaAlH$_4$(collaboration with GE Global Research).
- Preparation and evaluation of other advanced complex hydrides.