Catalytically Enhanced Hydrogen Storage Systems

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Project ID: # ST3

This presentation does not contain any proprietary or confidential information
Objectives
Technical Barriers and Targets
Budget

I. Determination of the chemical nature and mechanism of action of the species that is responsible for the enhanced kinetics of Ti-doped NaAlH₄.

II. Apply insights gained from fundamental studies of Ti-doped NaAlH₄ to the design and synthesis of hydrogen storage materials that will meet DOE hydrogen storage system targets.

<table>
<thead>
<tr>
<th>Property</th>
<th>Units</th>
<th>Target</th>
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</thead>
<tbody>
<tr>
<td>Hydrogen Density (gravimetric)</td>
<td>wt.% H</td>
<td>6</td>
</tr>
<tr>
<td>Energy Efficiency</td>
<td>%</td>
<td>97</td>
</tr>
<tr>
<td>Energy Density (volumetric)</td>
<td>W-h/L</td>
<td>1100</td>
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<tr>
<td>Hydrogen Density (volumetric)</td>
<td>kg H₂/m³</td>
<td>33</td>
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<tr>
<td>Specific Energy</td>
<td>W-h/kg</td>
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<tr>
<td>Cost</td>
<td>$/kW-h</td>
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<tr>
<td></td>
<td>($/kg H₂)</td>
<td>(167)</td>
</tr>
<tr>
<td>Operating Temperature</td>
<td>°C</td>
<td>-40 - +50</td>
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<tr>
<td>Start-Up Time to Full Flow</td>
<td>sec</td>
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<tr>
<td>Hydrogen Loss</td>
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<tr>
<td>Cycle Life</td>
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<tr>
<td>Refueling Time</td>
<td>min</td>
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<tr>
<td>Recoverable Usable Amount</td>
<td>%</td>
<td>90</td>
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Total Funding 5/00 - 4/05
DOE: 1,022,837
UH Cost Share: 238,000
Total: $1,283,000

FY04 Funding: $271,962
FY05 Funding: 0
Project Timeline

I. Maximization of hydrogen cycling performance of Ti-doped NaAlH₄
   1) Mechanically doped NaAlH₄ first prepared by Zidan and Jensen in 1998.
   2) DE-FC36-00GO10537 initiated.
   3) Demonstration of hydrogen flow of 1.8 wt/h @ 100 °C against 1 atm H₂ pressure.
   4) Demonstration of >4 wt % hydriding of NaH/Al in <4 min
   5) 100 cycle, > 3 wt % capacity test completed.

II. Determination of the fundamental basis of enhanced hydrogen cycling performance
   6) XRD studies of structural and compositional effects of doping and cycling completed.
   7) Electron paramagnetic resonance studies of dopant completed.
   8) Conclusions of EPR and XRD studies verified through electron microscopy and XAFS studies.
   9) Anelastic spectroscopic studies reveal dynamics of point defects involving hydrogen that are generated as a result of doping.
Collaborations

- Dr. Hendrik Brinks, Prof. Bjorn Hauback, Dr. Arnulf Maeland - Institute for Energy Technology, Norway.
- 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.
- Prof. Sandra Eaton - University of Denver.
- Dr. Carmen Andrei, Prof. Randi Holmestad - Norwegian University of Science and Technology.
- Dr. Job Rijssenbeek, Dr. Yan Gao - G.E. Global Research Center.
- Prof. Rosario Cantelli - University of Rome.
- Dr. Kristin Kumashiro, Dr. Walter Niemczura - Department of Chemistry, University of Hawaii.
- Dr. Terry Udovic - National Institute of Standards and Technology.
Consulting for Other DOE EERE Projects

- UOP - “Discovery of Novel Complex Metal Hydrides for Hydrogen Storage through Molecular Modeling and Combinatorial Methods

- United Technologies - “On-Board Hydrogen Storage Demonstration”
Approach

I. Maximization of hydrogen cycling performance of Ti-doped NaAlH$_4$

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

- **Synchrotron X-ray and Neutron Diffraction Studies**  Influence of doping on structure and composition.
- **Determination of Equilibrium Hydrogen Plateau Pressures**  Influence of doping on thermodynamic properties.
- **Kinetic measurements and modeling**  Mechanism of hydrogen cycling process.
- **Electron Paramagnetic Resonance (EPR) Studies**  Direct characterization of Ti dopants.
Approach

Infrared Spectroscopy, Inelastic Neutron Scattering, and Anelastic Spectroscopy Direct probes of the effects of doping on hydrogen.

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

Synthesis and Evaluation of Novel Complex Hydride Systems
Evaluation of “guided design” materials with theoretical hydrogen storage capacity of $>7$ wt %.
Maximization of hydrogen cycling performance of Ti-doped NaAlH₄

Dehydrogenation:
Rate of 1.8 wt % per hour observed at 100 °C for 2 mol % Ti doped NaAlH₄ to Na₃AlH₆ is adequate to meet the demands of an onboard PEM fuel cell.

Re-hydrogenation

Cycling Tests of 2 mol % Ti-doped Na/Al

Determination of the Fundamental Basis of Enhanced Hydrogen Cycling Performance Neutron and X-ray diffraction

Rietveld analysis of X-ray diffraction peak broadening indicates that mechanical milling of the hydride results in distortion of the lattice primarily in the c direction.

☑ mechanical milling distorts microstructure.

Determination of the Fundamental Basis of Enhanced Hydrogen Cycling Performance
Synchrotron X-ray Diffraction Studies

In situ dehydrogenation/re-hydrogenation

J. Rijsenbeek, Y. Gao C.M. Jensen, S.S. Srinivasan

Rietveld refinements indicate that the shoulders correspond to a solid solution of Ti in Al of composition Al\textsubscript{0.93}Ti\textsubscript{0.07}.

Determination of the Fundamental Basis of Enhanced Hydrogen Cycling Performance Kinetic Studies

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.

Current Year Results
Electron Paramagnetic Resonance

Collaboration with Prof. S. Eaton, University of Denver

**NaAlH₄** doped with 2.0 mol % of TiF₃

Upon doping, the spectrum of NaAlH₄ is dominated by sharp signal with \( g = 1.976 \) and \( \Delta B_{pp} \approx 90 \) G that is characteristic of spin isolated Ti(III).

After 5 cycles, instead of the signal with \( \Delta B_{pp} \approx 90 \) G or \( \Delta B_{pp} \approx 1500 \) G, the spectrum is dominated by a signal with \( \Delta B_{pp} \approx 650 \) G. There is also a signal near zero-field.

After 10 cycles, only the Ti(0) signal near zero-field has largely disappeared and only the Ti(0) signal at \( \Delta B_{pp} \approx 650 \) G.

**NaAlH₄** doped with 2.0 mol % of TiCl₃

Upon doping, the spectrum is dominated by a strong signal near zero-field. There is also a small signal with \( g \approx 1.97 \) that is quite similar to the Ti(III) signal that is observed in the TiF₃ doped sample.

After 5 cycles, there is now a signal with \( g = 2.01 \) and \( \Delta B_{pp} \approx 650 \) G plus a signal near zero-field that is quite different from the original one. This spectrum is very similar to TiF₃ doped sample after 5 cycles.

After 10 cycles, only the Ti(0) signal near zero-field has largely disappeared and only the Ti(0) signal at \( \Delta B_{pp} \approx 650 \) G.

Dominant Ti species changes dramatically on cycling but kinetics do not ⇒ minority Ti species responsible for enhanced kinetics.
Current Year Results

X-ray Absorption Spectroscopy
Collaboration with Dr. J. Rijssenbeek and Dr. Gao, GE Global Research

Comparison of Ti K-edge XANES for samples doped with 2 mol % TiF₃ and a 3 cycle sample doped with 2 mol % TiCl₃ (green). These three samples have identical near-edge features, indicating the same Ti oxidation state.

XAFS controversy


“Ti(0) species are formed immediately on doping and state is nearly invariant during hydrogen cycling with TiCl₃. The formation of an alloy with Al or TiH₂ is not supported by EXAFS data.” - A. Leon, O. Kircher, J. Rothe, M. Fichtner, *J. Phys. Chem.* 2004 16372.

⇒ EPR data indicates both maybe correct.
Current Year Results

Tunneling and Scanning Electron Microscopy

Collaboration with Dr. C. Andrei and Prof. R. Holmstad, Norwegian University of Science and Technology

SEM image taken with backscattered electrons (BSE).

Energy Dispersive X-ray spectrum of a particle observed in uncycled NaAlH₄ doped with 2 mol % TiF₃ shows strong Ti and F peaks.

Small Angle Diffraction pattern of a Ti, F rich particle matches TiF₃.

TEM bright field image of a Ti, F rich particle observed in uncycled sample of NaAlH₄ doped with 2 mol % TiF₃.

High resolution image of TiF₃ grain. Indicated lattice planes were indexed as TiF₃.
Current Year Results
Tunneling and Scanning Electron Microscopy

- No correlation between Al and Ti seen in the EDS maps directly after ball milling but correlation, suggesting Al-Ti bonding, seen after 15 cycles.

Agrees with findings from synchrotron X-ray, EPR, and XAFS studies

Current Year Results
Doping with Cubic Al₃Ti

Hydrogenation profiles of NaH/Al + 3 mol % Al₃Ti powder mechanically milled for 30 min and charge under 100 atm H₂ at 120 °C.

Dehydrogenation profile at 160 °C for NaH/Al + 3 mol % Al₃Ti powder mechanically milled for 30 min and charge under 100 atm H₂ for 10 h at 120 °C.

Only Minor Kinetic Enhancement of Hydrogen Cycling
⇒ Al₃Ti is not the active Ti species
Current Year Results
Doping with Off-the-Shelf Ti Powder

First dehydrogenation profiles at 150 °C for samples of NaH/Al + 4 mol % Ti powder mechanically milled for different periods.

Comparison of the dehydrogenation profiles of NaH/Al + 4 mol % Ti powder and NaAlH4 + 4 mol % Ti both mechanically milled for 10h.

⇒ Ti precursors differ only in the length of milling time required to produce the active Ti species.

Determining the Fundamental Basis of Enhanced Hydrogen Cycling Performance

**Solid State $^1$H NMR and Infrared Spectroscopy**

**IR SPECTROSCOPY**

Al-H stretching frequency shifts

$\Rightarrow$ Al bonding is perturbed.


$^1$H NMR SPECTROSCOPY

Narrow Spectral Components: residual solvent, free $H_2$ and mobile species arising upon doping.


$\Rightarrow$ Ti-doping perturbs Al-H bonding and induces a population of highly mobile hydrogen
Anelastic Relaxation

Long range component of the strain due to defects
Elastic dipoles $\lambda$ (hopping with time $\tau$)
Anelastic strain $\varepsilon^a = \lambda_1 n_1 + \lambda_2 n_2$
Stress $\sigma$: $dE_i = -\lambda_i \sigma$
Boltzmann distribution:
$$n_i = \exp \left(-\frac{E_i}{kT}\right)$$

Relaxation strength:
$$\Delta = \frac{\varepsilon^a}{\varepsilon^e} \sim \left(\Delta \lambda \right)^2/T$$
Anelastic Relaxation
Prof. R. Cantelli, University of Rome

Flexural vibrations

Prismatic Sample suspended on two nodal lines by thin wires

Electrode: alternating stress

Extensional, torsional vibrations

C

C'
Relaxation process

- Elastic energy dissipation coeff.: $Q^{-1} = M'/M''$ from the decay of the vibration amplitude or from width of resonance curve.
- The maximum of the elastic energy loss occurs when the angular vibration frequency is equal to the relaxation rate of the mobile species.

$$d_\Lambda = \ln \left[ \frac{A(t)}{A(t+T)} \right]$$

logarithmic decrement

$$Q^{-1} = \frac{Mv_0(\lambda_1 - \lambda_2)^2n_1n_2}{T} \frac{1}{(\omega \tau)^\alpha + (\omega \tau)^{-\alpha}}$$
Current Year Results
Anelastic Spectroscopy

Temperature dependence of elastic energy loss and frequency during thermal cycles of NaAlH$_4$ Doped with 2 mol % TiF$_3$.

Current Year Results
Anelastic Spectroscopy

Low Temperature Dependence of Elastic Energy Loss

⇒ A point-defect is formed during the dehydrogenation of the Ti-doped hydride that gives rise to a thermally activated relaxation process.

Current Year Results
Anelastic Spectroscopy

Experimental curve is much broader than predicted for a single Debye process

\[ \Rightarrow \text{At 70 K, the relaxing entities (very likely hydrogen) are strongly interacting and/or highly mobile, performing about } 5 \times 10^3 \text{ jumps/s (corresponding to an activation energy of 0.126 eV).} \]

Conclusions

- The rate of dehydrogenation of 2 mol % Ti doped NaAlH₄ to Na₃AlH₆ at 100 °C (1.8 wt % per hour) is adequate to meet the demands of an onboard PEM fuel cell.
- Ti-doped NaH/Al has rapid hydrogenation kinetics (4.0 wt % absorbed in <30 min at 100 °C and 100 atm H₂ pressure.
- 2 mol % Ti doped NaAlH₄ has a highly stable hydrogen cycling capacity of 3.0 wt % at 120 °C within 3h and 4.0 wt % at 150 °C within 3h.
- The kinetic effects resulting from variation in Ti dopant precursor arise from variation in the length of milling time required to produce and position the active Ti species.
- Hydrogen cycling kinetics in Ti-doped NaAlH₄ are limited by processes long range atomic transport phenomenon and location of dopants.
Conclusions

- High valent Ti dopant precursors are transformed Ti(0) species during the first few cycles dehydrogenation-rehydrogenation.
- The observation that only a relative minor change in the hydrogen cycling kinetics occurs whether the majority of titanium is transformed from Ti(III) to Ti(0) during early cycles of dehydrogenation/rehydrogenation strongly suggests that the enhanced hydrogen cycling kinetics are due to a minority Ti species and that the majority of the Ti is in a resting state.
- Mechanical milling of NaAlH$_4$ not only reduces particle size but also results in distortions microstructure and perturbs Al-H bonding.
- Ti-doping perturbs Al-H bonding and induces a population of highly mobile hydrogen.
- Ti-doping of NaAlH$_4$ induces a thermally activated process the generates point-defects. These entities very likely involve hydrogen and are highly mobile, performing about 5x10$^3$ jumps/s at 70K.
FY04 Review’s Comments

Over 100 comments!  ~50/50 positive and negative. 90% of criticism related to 3 questions.

Q1. Why continue to study the alanates?

Q2. Why is the understanding of the fundamental processes involved in hydrogen cycling in the doped alanates so slow in emerging?

Q3. Why weren’t any details given about the 7 wt % material that was mentioned in the presentation?
A1. A better understanding of the fundamental basis of the phenomenal enhanced hydrogen cyclic kinetics in Ti-doped alanates would be a great aid to efforts to develop improved hydrogen storage materials based on any complex hydride or related material. The statement is supported by recent reports the Ti-doping enhances the hydrogen cycling kinetics of metal amides and LiBH$_4$/MgH$_2$.

A2. The complete decomposition and reformation of compounds with strong covalent bonding in the solid state at moderate temperatures was unknown until the discovery of the “Bogdanovic effect” of active Ti species on the reversible NaAlH$_4$ to NaH, Al, and H$_2$. The establishment of the fundamental basis this phenomenon has required the develop revolutionary fundamental models and wide variety of measurements. This was no small chore. In our efforts alone, we have recruited 15 top scientist from 6 countries (mostly at no additional cost to the DOE) to work on this problem. In the past year comprehensive model in agreement with all the experimental results is beginning to emerge.

A3. Exact compositional detail were withheld to protect priority information. Experimental details were withheld to further emphasize that the results were preliminary and prevent data from being “published” on the web.
Future Directions

Member of the Metal Hydride Center of Excellence

New Project  Fundamental Studies of Advanced High-Capacity, Reversible Metal Hydrides

FY05 Budget: $250,000 (UH - US DOE agreement in place as of 4/20/05)

Objectives

• Characterization of the Active Titanium Species in Ti Doped NaAlH₄ and related materials.
• Development of a model of the mechanism of action of the dopants in the dehydrogenation and re-hydrogenation processes in NaAlH₄ and related materials.
• Determine if the thermodynamics of the reversible dehydrogenation of alanates and related materials are altered upon doping.
• Prepare “thermodynamically tuned” binary hydrides with improved hydrogen cycling kinetics with the potential to meet the DOE 2010 system gravimetric storage capacity target.
Future Directions

FY05 Work Plan

Task 1. Characterization of Active Ti species
- Complete EPR studies of Ti-doped NaAlH₄ (collaboration with University of Denver).
- Complete XAFS studies of Ti-doped NaAlH₄ (collaboration with GE Global Research).

Task 2. Elucidation of mechanism of action in dopants
- Anelastic spectroscopy on Ti-doped: NaAlD₄ and Na₃AlH₆; Group I and II amides; and LiBH₄/MgH₂ (collaboration with University of Rome).
- Position annihilation studies of Ti-doped (collaboration with AIST, Tscuba, Japan).
- NMR studies of Ti-doped revisited.

Task 3. Thermodynamic effects of dopants?
- Differential scanning calorimetry on Ti-doped NaAlH₄ (collaboration with University of South Florida).
Future Directions

FY05 Work Plan

Task 4 High Capacity, Thermodynamically Tuned Binary Metal Hydrides

- Determine the effects of doping on the hydrogen cycling kinetics of “thermodynamically tuned” binary hydrides with the potential to meet the DOE 2010 system gravimetric storage capacity target, i.e. LiBH₄/MgH₂. (collaboration with HRL, JPL, CalTech, and Stanford University).

- Elucidation of the structural differences of the different phases of AlH₃ through X-ray and neutron diffraction studies. (collaborations with Brookhaven National Laboratory and Institute for Energy Research, Norway).
Future Directions

Beyond FY05

- Apply methods developed for the study and evaluation of doped alanates for the development of advanced complex hydrides and related materials with the potential application in a system that meets the DOE 2010 system storage targets.
- Preparation of advanced complex hydrides and related materials with the potential application in a system that meets the DOE 2010 system storage targets.
2004 Publications


2004-05 Publications


2004 Invited Presentations


9/4/04   “Mechanistic Studies of the Active Titanium Species in the Reversible Dehydrogenation of Ti Doped Sodium Aluminum Hydride” International Symposium on Metal Hydrogen Systems, Crakow, Poland.

9/14/04  “ Characterization and Mechanistic Studies of the Active Titanium Species in the Reversible Dehydrogenation of Ti-Doped Sodium Aluminum Hydride”, Leiden University, The Netherlands.


10/18/04 “ Characterization and Mechanistic Studies of the Active Titanium Species in the Reversible Dehydrogenation of Ti-Doped Sodium Aluminum Hydride”, Symposium on the Hydrogen Economy , meeting of the American Society for Materials, Columbus, Ohio.
2004-05 Invited Presentations


11/5/04  “Hydrogen Storage Materials Research in the USA: Update and Prospectus”, Nankai University, Tainjin, China.

11/8/04  “Hydrogen Storage Materials Research in the USA: Update and Prospectus”, Fudan University, Shanghai, China.


1/12/05  “Characterization and Mechanistic Studies of the Active Titanium Species in the Reversible Dehydrogenation of Ti-Doped Sodium Aluminum Hydride Gordon Research Conference on Hydrocarbon Resources, Ventura, California.


Hydrogen Safety

The most significant hydrogen hazard associated with this project is: that some of the compounds and mixtures have pyrophoric and/or react violently with water.
Hydrogen Safety

Our approach to deal with this hazard is:

- 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.
- All students and postdocs receive intensive training in the safe handling and manipulation of air and moisture sensitive compounds.