Fundamental Studies of Advanced High-Capacity, Reversible Metal Hydrides

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Objectives
Technical Barriers and Targets
Budget

I. Characterization of the Active Titanium Species in Ti Doped $NaAlH_4$ and related materials.

II. Development of a model of the mechanism of action of the dopants in the dehydrogenation and re-hydrogenation processes in $NaAlH_4$ and related materials.

III. Determine if the thermodynamics of the reversible dehydrogenation of alanates and related materials are altered upon doping.

IV. Prepare "thermodynamically tuned" binary hydrides with improved hydrogen cycling kinetics with the potential to meet the DOE 2010 system gravimetric storage capacity target.

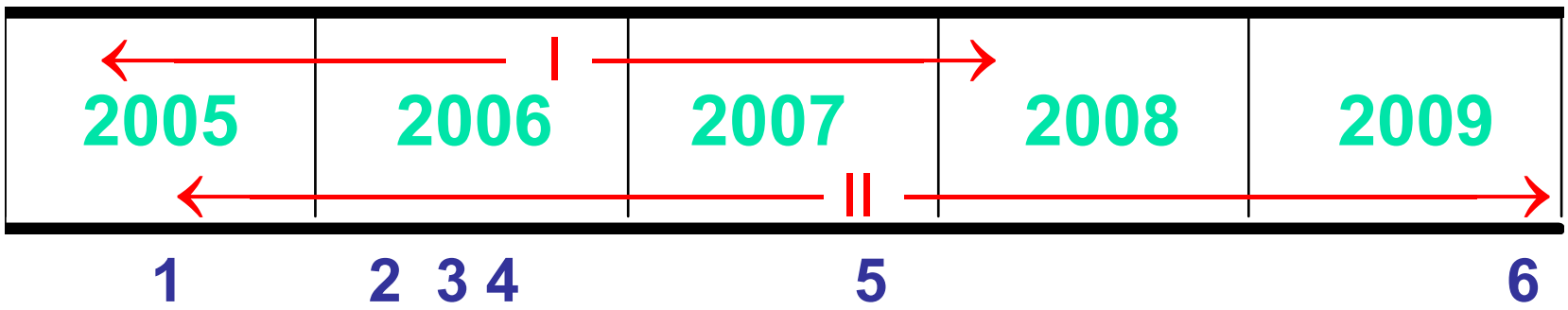
Property	Units	Target
Hydrogen Density (gravimetric)	wt.% H	6
Energy Efficiency	%	97
Energy Density (volumetric)	W-h/L	1100
Hydrogen Density (volumetric)	kg H_2/m^3	33
Specific Energy	W-h/kg	2000
Cost	$/kW-h	5
	($/kg H_2)	(167)
Operating Temperature	˚C	-40 - +50
Start-Up Time to Full Flow	sec	15
Hydrogen Loss	scc/hr/L	1.0
Cycle Life	cycles	500
Refueling Time	min	<5
Recoverable Usable Amount	%	90

FY05 Funding

DOE:	250,000
UH Cost Share:	62,500
Total:	$312,500

(UH - US DOE agreement in place as of 4/20/05)

Project Timeline



I. Fundamental Studies of Advanced High-Capacity, Reversible Complex Metal Hydrides

1. Complete studies of titanium in doped $NaAlH_4$.
2. Complete investigation of thermodynamic effects of mechanical doping.
3. Complete characterization of “mobile” hydrogen in Ti-doped $NaAlH_4$.
5. Complete fundamental studies of doped complex hydrides, amides and related materials.

II. Kinetically Enhanced, ”thermodynamically tuned” binary hydrides

4. Development of a method doping ”thermodynamically tuned” binary hydrides that induces hydrogen cycling kinetics meeting DOE targets.
6. Preparation of kinetically optimized, ”thermodynamically tuned” binary hydrides.

Collaborations

- Prof. Sandra Eaton - University of Denver.
- Dr. Job Rijssenbeek, Dr. Yan Gao - GE Global Research
- Prof. Rosario Cantelli - University of Rome
- Dr. Kristin Kumashiro, Dr. Walter Niemczura - University of Hawaii
- Dr. Etsuo Akiba - AIST, Tskuba, Japan
- Dr. Terry Udovic - National Institute of Standards and Technology.
- Dr. Lee Sefanakos - University of South Florida
- Dr. John Vajo - HRL
- Dr. Robert Bowman - Jet Propulsion Laboratory
- Dr. Channing Ahn - California Institute of Technology
- Prof. Bruce Clemens - Stanford University
- Dr. James Riely, Dr. Jason Graetz - Brookhaven National Laboratory
- Dr. Ragaiy Zidan - Savanah River National Laboratory
- Dr. Hendrik Brinks, Prof. Bjorn Hauback - Institute for Energy Technology, Norway
- Dr. Nancy Yang - Sandia National Laboratory

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

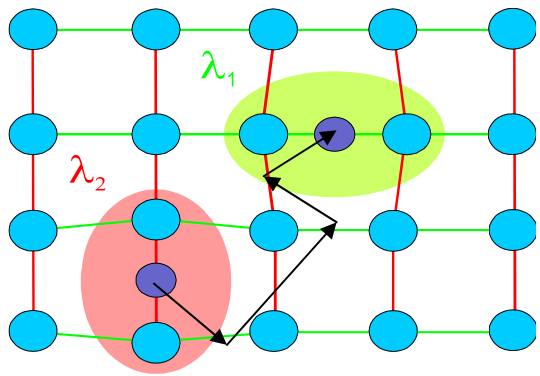
FY05 Work Plan

Task 1. Characterization of Active Ti species

- Complete EPR studies of Ti-doped $NaAlH_4$ (collaboration with University of Denver).
- Complete XAFS studies of Ti-doped $NaAlH_4$ (collaboration with GE Global Research).

Task 2. Elucidation of mechanism of action in dopants

- Anelastic spectroscopy on Ti-doped: $NaAlD_4$ and Na_3AlH_6; Group I and II amides; and $LiBH_4/MgH_2$ (collaboration with University of Rome).
- Position annihilation studies of Ti-doped (collaboration with AIST, Tskuba,Japan).
- NMR studies of Ti-doped revisited.



Approach

FY05 Work Plan

Task 3. Thermodynamic effects of dopants?

- Differential scanning calorimetry on Ti-doped $NaAlH_4$ (collaboration with University of South Florida).

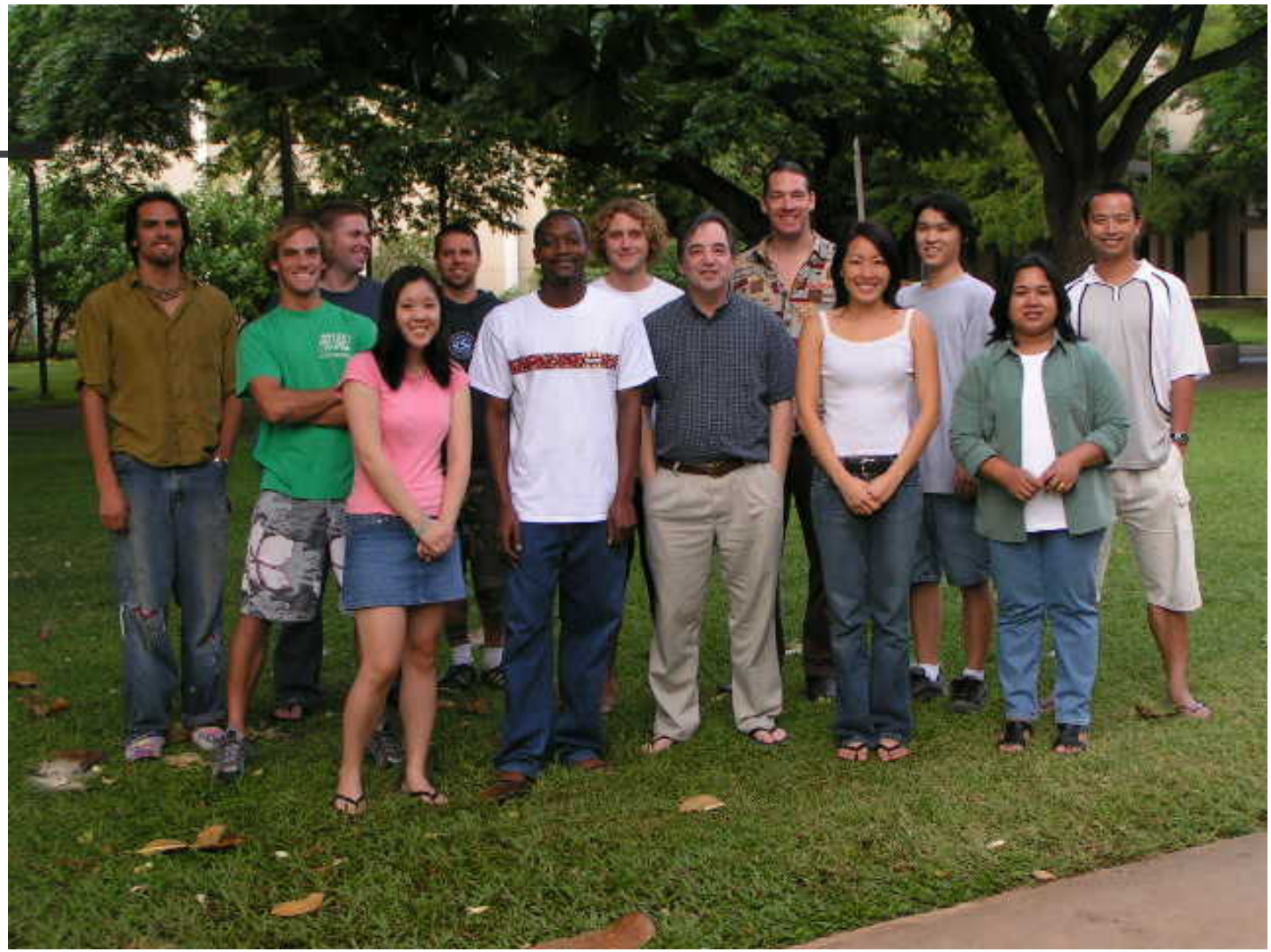
Task 4 High Capacity, Thermodynamically Tuned Binary Metal Hydrides

- 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. $LiBH_4/MgH_2$. (collaboration with HRL, JPL, CalTech, and Stanford University).
- Elucidation of the structural differences of the different phases of AlH_3 through X-ray and neutron diffraction studies. (collaborations with Brookhaven National Laboratory and Institute for Energy Research, Norway).

Approach

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

Synchrotron X-ray and Neutron Diffraction Studies of $NaAlH_4$ Containing Ti Additives. H.W. Brinks, C. M. Jensen, S.S. Srinivasan, B.C. Hauback, D. Blanchard, and K. Murphy; *J. Alloys Compd.*2004, *376*, 215.

Structure and Hydrogen Dynamics of Pure and Ti-doped Sodium Alanate. Jorge Iniguez,T. Yildirim, T.J. Udovic, M. Sulic, and C. M. Jensen; *Phys. Rev. B.* 2004 *65,* 235433.

Long Term Cycling Behavior of Titanium Doped $NaAlH_4$ Prepared through Solvent Mediated Milling of NaH and Al with Titanium Dopant Precursors. Sesha S. Srinivasan, Hendrik W. Brinks, Bjorn C. Hauback, Dalin Sun and Craig M. Jensen; *J. Alloys and Compd.* 2004 377, 283.

Method for Preparing Ti-doped $NaAlH_4$ using Ti powder: Observation of Unusual Reversible Dehydrogenation Behavior. Ping Wang and Craig M. Jensen; *J. Alloys and Compd.* 2004 *379*, 99.

Rehydrogenation and Cycling Studies of Dehydrogenated $NaAlH_4$. Dalin Sun, Sesha S.Srinivasan, Guorong Chen and Craig M. Jensen; *J. Alloys and Compd.* 2004, *373*, 265.

Dehydrogenation of Alkanes Catalyzed by an Iridium-Phosphinito PCP Pincer Complex, David Morales-Morales, Rocío Redón, Cathleen Yung, and Craig M. Jensen; *Inorg. Chim. Acta* 2004 *357*, 2953. (invited contribution for topical volume on Rhodium and Iridium Chemistry).

Diffraction Studies of Alanates. H. W. Brinks, B. C. Hauback, D. Blanchard, C. M. Jensen, M. Fichtner, and H. Fjellvåg; *Advanced Materials for Energy Conversion II*, 2004, 153.

Dehydrogenation Process of Titanium and Zirconium Doped Alanates, T. Kiyobayashi, Akita, S.S. Srinivasan, D. Sun, S. Sangawa, C.M. Jensen and N. Kuriyama; *Advanced Materials for Energy Conversion II*, 2004, 157.

2004-05 Publications

Preparation of Ti-doped Sodium Aluminum Hydride from Mechanical Milling of NaH/Al with Off-the-Shelf Ti Power. P. Wang and C.M. Jensen; *J. Phys. Chem. B.* **2004** *108*, 15829.

Point Defect Dynamics and Evolution of Chemical Reactions in Alanates by Anelastic Spectroscopy. Oriele Palumbo, Rosario Cantelli, Annalisa Paolone, Sesha S. Srinivasan, and Craig M. Jensen; *J. Phys. Chem. B.* **2005,** *109*, 1168.

Electron Microscopy Studies of $NaAlH_4$ Doped with TiF_3: Hydrogen Cycling Effects. C.M. Andrei, J. Walmsley, H.W. Brinks, R. Homestad, C.M. Jensen, B.C. Hauback; *Appl. Phys. A*.**2005**, *80*, 709.

Effects of Milling, Doping and Cycling of $NaAlH_4$ Studied by Vibration Spectroscopy and X-ray Diffraction. S. Gomes, G. Renaudin, H. Hagemann, K. Yvon, M.P. Sulic, and C.M. Jensen, *J. Alloys and Compd.* **2005** *390*, 305.

Synthesis and Crystal Structure of Na_2LiAlD_6. H.W. Brinks, B.C. Hauback, C.M. Jensen, and R. Zidan; *J. Alloys and Compd* **2005** in press.

2004 Invited Presentations

3/14/04 "Doped Sodium Aluminum Hydride: Development and Fundamental Studies of a Promising New Hydrogen Storage Material", Symposium on the Fundamentals of Advanced Materials for Energy Conversion II, 2004 meeting of the Minerals, Metals, and Materials Society, Charlotte, North Carolina.

3/22/04 "Doped Sodium Aluminum Hydride: Development and Fundamental Studies of a Promising New Hydrogen Storage Material", Session on Perspectives on Hydrogen Storage, annual meeting of the American Physical Soceity, Montreal, Canada.

5/10/04 "Characterization and Mechanistic Studies of the Active Titanium Species in the Reversible Dehydrogenation of Ti-Doped Sodium Aluminum Hydride" Symposium on Hydrogen Storage Materials , 205th meeting of the Electrochemical Society, San Antonio, Texas.

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.

9/15/04 "PCP Pincer Complexes as Catalysts for Novel Organic Transformations", Utrecht 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

11/3/04 "Characterization and Mechanistic Studies of the Active Titanium Species in the Reversible Dehydrogenation of Ti-Doped Sodium Aluminum Hydride Symposium on Hydrogen Absorbing Materials, Fifth Pacific Rim International Conference on Advanced Materials and Processes (PRICM-5), Bejing, China.

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.

11/30/04 "Doped Sodium Aluminum Hydride: Development and Fundamental Studies of a Promising New Hydrogen Storage Material", Cornell University.

12/1/04 "Characterization and Mechanistic Studies of the Active Titanium Species in the Reversible Dehydrogenation of Ti-Doped Sodium Aluminum Hydride", Symposium on Hydrogen Storage, 2004 Materials Research Society fall meeting, Boston, Massachusetts.

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.

3/23/05 "Anelastic spectrosopic Studies of Point Defect dynamics and Evolution of Chemical Reactions in Alanates. Focus session on Hydrogen Storage: Measurements, American Physical society , Los Angeles, California.

5/29/05 "X-ray and Neutron Diffraction Studies of Ti-doped Sodium Aluminum Hydride, a Promising New Hydrogen Storage Material", Session on "Crystalline Hydrogen Storage Materials",