Metal Hydride Center of Excellence

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http://www.ca.sandia.gov/MHCoE/

ID# ST29

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Overview

Timeline

- Project started in March '05
- Project end ~ 2010
- Percent complete 60%

Barriers

A. System Weight and Volume
C. Efficiency
E. Charging/Discharging Rates

Budget

Lead Lab Mngmt. Funding:

- $445K in FY07
  (5.2% of total MHCoE funding)

- $450K in FY08

MHCoE Total Funding:

- $8.6M Center-wide FY07
- $8.6M Center-wide FY08 (planned)

MHCoE Partners

National Labs: SNL, Brookhaven, JPL, NIST, SRNL, ORNL

Universities: UIUC, Pitt, CMU, U. Utah, Stanford, Caltech, UNR, UNB, Hawaii

Industry: Intematix, GE, UTRC, HRL

Pending: OSU, LLNL, GT

MHCoE Objectives

Research, develop and validate reversible on-board metal hydride storage materials and systems that meet the 2010 DOE system targets for hydrogen storage, with a credible path forward for meeting the 2015 DOE storage targets

Approach to Technical Targets

H Capacity: 2010 System Targets: 6 wt. %, 45gH_2/L vol. density

- **Synthesize and characterize hydride materials with high hydrogen capacity and favorable thermodynamics. Use state-of-the-art theory to guide materials discovery effort.**

Charge/Discharge Rates: 2010 Sys. Target: 3 min. system fill (5kg)

- **Develop materials that are fully reversible, catalysts that aid reversibility, assess nanoengineering promotion of kinetics, and investigate role of contamination on reaction rates**

Hydrogen Purity (from Storage) : 2010 Target: 99.99% pure

- **Assess release of NH_3, B_2H_6 and other volatile species from metal hydrides during desorption and cycling**

Cycle Life: 2010 Target: 1000 Desorption/Adsorption Cycles

- **Investigate durability of materials, cycling behavior, effects of contaminants, structural stability, release of volatiles**

MHCoE Project Structure

DOE

Coordinating Council (2007-2008)

Bruce Clemens (Stanford, POC A), Ewa Rönnebro (SNL, POC B), Zak Fang (Utah, POC C), Jim Wegrzyn (BNL, POC D), Don Anton (SRNL, POC E), Craig Jensen (UH), Jay Keller (SNL) and Lennie Klebanoff (SNL)

Project Groups

A

Destabilized Hydrides

- **Stanford (POC)**
- Caltech
- JPL
- UIUC
- U. Hawaii
- U. Pitt/CMU
- HRL
- U. Utah
- Intematix
- NIST

B

Complex Anionic Materials

- **SNL(POC)**
- GE
- U. Hawaii
- UIUC
- JPL
- ORNL
- NIST
- UNR
- Utah
- UTRC

C

Amides/ Imides (M-N-H)

- **Utah (POC)**
- GE
- UNR
- ORNL
- U. Hawaii
- JPL
- Caltech
- SRNL

D

Alane (AlH_3)

- **BNL(POC)**
- SRNL
- U. Hawaii
- SNL
- UIUC
- UNB
- JPL

E

Engineering Analysis & Design

- **SRNL(POC)**
- NIST
- JPL
- GE
- SNL

Project E to be dissolved, with materials engineering studies moved to Projects A-D as appropriate

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Comings and Goings

Welcome New Partners: (current total 19)

- UTRC (Dan Mosher, Sarah Arsenault, Susanne Opalka, and Xia Tang ---Project B)
- University of New Brunswick (Sean McGrady, Proj. D)
- The Ohio State University (J.-C. Zhao, Project B)
- Georgia Tech (David Sholl, Theory Group)
- Lawrence Livermore Lab (Ted Baumann, Project A)

} pending

Goodbye Former Partners, and thank you!

- GE (J.-C. Zhao moved to OSU)
- Carnegie Mellon University (David Sholl moved to GT)
- Intematix (Jonathan Melman, Darshan Kundaliya), leaving 6/2008

Materials Down-select Criteria

The MHCoE is focusing on 5 primary performance criteria on which Go/No-Go materials decisions were based:

1) **The material's hydrogen storage gravimetric density should be at least 5 weight percent, with a clear potential for much more**
2) **The material should be at least 50% reversible after 3 cycles**
3) **The material should release its H_2 at temperatures below 350 °C**
4) **The material's non-H_2 volatilization products should not exceed 1000 ppm for a single thermal cycle**
5) **The material should release and reabsorb H_2 in less than 24 hrs**

These criteria were used as guidelines in determining if specific material systems had sufficiently promising characteristics to warrant further work. They were not applied with absolute rigidity, nor do they substitute for the full DOE system targets for on-board hydrogen storage.

Materials Down-select Report

- 51 materials systems have been investigated in the MHCoE. Of these 51 materials, 24 were down-selected removing them from further study. 27 have satisfied the 5 performance metrics and are being studied further.

Some Materials No Longer Being Pursued:

MgH_2/Si: not reversible **X**

$2LiNH_2 + MgH_2$: wt. % limited to ~5% **X**

$Li_2Zn(BH_4)_4$: B_2H_6/H_2 ratio of 0.3 **X**

Some Materials Still Being Pursued:

$Ca(BH_4)_2$ ✓

$LiBH_4/MgH_2$ in aerogels ✓

LiMgN, $Li_3AlH_6/3LiNH_2$ ✓

AlH_3 , and 22 other systems ✓

In fulfillment of the end of FY2007 Materials Down-select Milestone

Materials Go/No-Go Decisions Made Within the Department of Energy Metal Hydride Center of Excellence (MHCoE)

In fulfillment of the end of Fiscal Year 2007 Project Milestone on Materials Down-selection

Lennie Klebanoff, Director
Sandia National Laboratories
Livermore, CA 94551

September/October 2007

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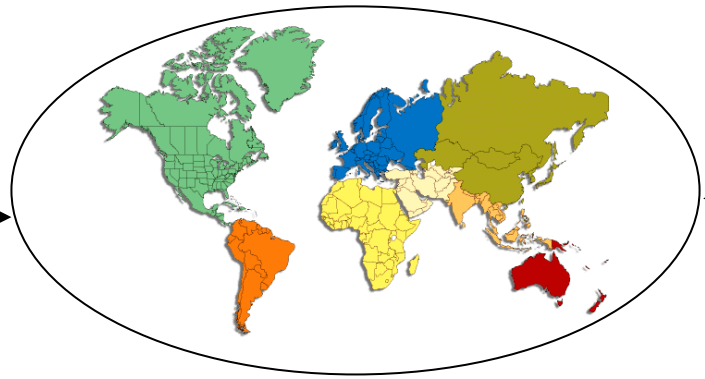
--available at:

http://www.hydrogen.energy.gov/

Flow of Materials Ideas and Studies in the MHCoE



U.S. and international collaborations

Theory Group Ideas

Experimentalists' Ideas

Feedback to TG

MHCoE Project A,B,C,D
Formulate Collaborations
Measure ΔH, structure, H_2 des./abs. kinetics

X

No/Go

Down-select Criteria

✓

Go

Improve Material: dopants, nanoengineering

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By The Numbers….

From 3/2007 to 3/2008:

60 -- **MHCoE Publications (Published, Accepted, Submitted)***

25 -- **Collaborative Publications (between partners)**
(42% joint publications)

97 -- **MHCoE Talks**

4 -- **Patents filed based on MHCoE work**

***Published in:**

Phys. Rev. Lett. (4)	**J. Inorg. Chem.**
Phys. Rev. B	**J. Alloys and Comp.**
J. Amer. Chem. Soc.	**J. Appl. Phys.**
J. Phys. Chem. B, C	**Scripta Materialia**

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Critical Issues Addressed Today:

Kinetics:

The adsorption/desorption kinetics of metal hydrides are typically too slow. Progress will be reported in the use of nanoconfinement (**HRL, Caltech, UTRC, NIST**) and catalysts (**SNL, Intematix**) to increase kinetic performance, and gaining a deeper understanding of the influence of morphology on kinetics (**Stanford**).

Thermodynamics:

Metal hydrides typically require desorption temperatures in excess of PEM fuel cell operating temperatures. Progress will be reported today in predicting new reaction schemes with favorable ΔH_{rxn} (**Pitt/GT**), increasing the accuracy of such calculations (**UIUC**), realizing those predicted materials (**Utah**), and studies of low-temperature reactions (**Hawai'i**).

Reversibility:

Many thermodynamically-promising metal hydride systems are either not reversible, or reversible only under impractical conditions. Work will be reported today on regenerating AlH_3 from Al (**BNL, SRNL, UNB, UH**), improving $Ca(BH_4)_2$ reversibility (**SNL**), and probing reversibility and general reaction mechanisms with NMR (**JPL, Caltech**).

… in addition to cycle life, H_2 capacity, hydrogen purity….

Summary of Key MHCoE Accomplishments 3/07 – 3/08

1. Quantitatively demonstrated the kinetic benefits of confinement in aerogels
2. Discovered $B_{12}H_{12}$ as an important intermediate species in hydrogen desorption of $Mg(BH_4)_2$ and possibly other borohydrides
3. Showed $Ca(BH_4)_2$ to be partially reversible at significantly lower pressures and higher capacities than achieved previously
4. Experimentally realized the predicted LiMgN system, found to be reversible with at least 6.6 wt. % capacity.
5. Characterized NH_3 and B_2H_6 release from selected amides and borohydrides
6. DFT models used to screened 16 million compositions to identify single and multi-step hydrogen desorption reactions with favorable wt.% and ΔH values
7. Developed a new approach for more quantitative predictions of reaction enthalpies using first-principles DFT free-energy estimates with bond counting
8. Predicted a new low-energy structure for $Mg(BH_4)_2$, suggesting metastability
9. Demonstrated a liquid-phase system for Al hydrogenation at RT and 35 bar
10. Completed thermal model for tube/fin heat exchanger metal hydride hydrogen storage system

Summary of Selected MHCoE Materials Properties

Properties	MgH_2/ Ni^{nano}	$NaAlH_4$	**$LiBH_4$ /MgH_2**	**$Ca(BH_4)_2$**	**$Na_2Zr(BH_4)_6$**	**AlH_3**	**AlH_3-TEDA (in solution)**	**Li_3AlH_6 /$3LiNH_2$**	**LiMgN**
Theoretical reversible wt% H_2 (without catalyst)	7.6	5.6	**11.6**	**9.6**	**10.7**	**10.1**	**2.1**	**7.3**	**8.2**
Volumetric density (g/L) (without catalyst)	112	92	**95**	**TBD**	**TBD**	**149**	**TBD**	**99**	**107 (estimated)**
Demonstrated reversible wt% H_2 (with catalyst)	6.5	~5	**8 - 10**	**4.5**	**TBD**	**0**	**2.1**	**4.9 (PCT)**	**6.6 (PCT)**
Desorption Temp (°C) (with catalyst)	150-250 (low P)	100-160	**400**	**350**	**100**	**< 100**	**< 100**	**160-300**	**160-240**
Adsorption Temp (°C) (with catalyst)	150	120	**300**	**350**	**TBD**	**NA**	**< 100**	**200-300**	**160-300**
Isothermal Plateau Pressure, with catalyst, (Bar) (temp °C)	1 (280)	1st step 1(~40) 10 (~90)	**8 (360) Est 1(225)**	**TBD**	**TBD**	**28 kbar (300)**	**2 bar (88)**	**1 (255°C) 60 (375°C)**	**1, and 20 (240 °C)**
Kinetics (with catalyst)	moderate	Good	**Slow**	**Good for des, slow for abs**	**Good for desorption**	**good**	**good**	**TBD**	**TBD**

MgH_2/Ni nano:
N. Hanada, T. Ichikawa, H. Fujii, *J. Phys. Chem. B*, 109, 7188 (**2005**).

$NaAlH_4$:
B. Bogdanovic, M. Schwickardi, *J. Alloys. Compd. 253-254 1* (**1997**).
B. Bogdanovic, et. al. *J. Alloys. Compd. 302, 36* (**2000**).

-- MHCoE Materials in blue

Closing The Gaps---Future Plans

Kinetics (Charge/Discharge Rates):

-- *Nanoconfinement is one of the ways to improve kinetics*

Work by Vajo et al. (**HRL**) shows that the kinetics of hydrogen release can be improved via incorporation into aerogels. In the next year we aim to:

1) improve the degree of incorporation into aerogels/scaffolds
2) demonstrate incorporation of a destabilized system ($LiBH_4/MgH_2$)
3) improve the aerogels with regard to pore size and volume to aid practicality
4) expand R&D into inorganic scaffolds

-- *Catalysis is another way to improve kinetics*

There have been prior catalytic studies in the MHCoE, but we need more for our current materials. We will be expanding our catalysis studies in:

- Nanoconfined Materials
- Bulk Borohydrides, Amides ($Ca(BH_4)_2$, LiMgN,…)
- AlH_3 Regeneration (liquid, electrochemical, SCF)

Improving kinetics with catalysts and additives will be a high priority, Eric Majzoub will lead a coordinated MHCoE-wide catalyst screening program.

Closing The Gaps---Future Plans

Thermodynamics and Hydrogen Capacity:

-- Continue to predict (ΔH, structure) and experimentally assess thermodynamically favorable destabilized reactions with high wt.%

Work by Sholl et al. (**GT**) shows that promising theoretical reactions can be realized experimentally (LiMgN, $Ca(BH_4)_2$, …). New reactions to be explored:

$LiBH_4 + C \rightarrow LiBC + 2\ H_2$ (12.0 wt.%, ΔU_0 = 44 kJ/mol)

$CaH_2 + 6\ LiBH_4 \rightarrow CaB_6 + 6\ LiH + 10\ H_2$ (11.7 wt.%, ΔU_0 = 63 kJ/mol)

$TiH_2 + 2\ LiBH_4 \rightarrow TiB_2 + 2\ LiH + 4\ H_2$ (8.6 wt.%, ΔU_0 = 22 kJ/mol)

$Mg_2Ni/LiBH_4$ system (potential for 7 wt. %)

-- Emphasize lower-temperature materials to avoid BOP penalties

Work by Jensen et al. (**Hawai'i**) reveals that some anionic transition metal borohydrides release H_2 at low temperatures (40 -110 ˚C) with undetectable diborane release. The high weight % anionic transition metal borohydrides will be emphasized more.

-- Assess if nanoconfinement improves thermodynamics

Closing The Gaps---Future Plans

Reversibility:

-- Focus on high weight percent materials and improve their reversibility.

- Rönnebro and colleagues (**SNL**) show that additives dramatically affect reversibility of $Ca(BH_4)_2$. We will examine the affect of additives on the reversibility of anionic transition metal borohydrides, other borohydrides and amides to improve their reversiblility.

- Work by Graetz and coworkers (**BNL**) demonstrates the importance of catalysts in Al rehydrogenation to AlH_3. The catalyst effort will be expanded in efforts to rehydrogenate Al by organometallic (**BNL**), electrochemical (**SRNL**) and supercritical fluid (**UH, UNB**) means.

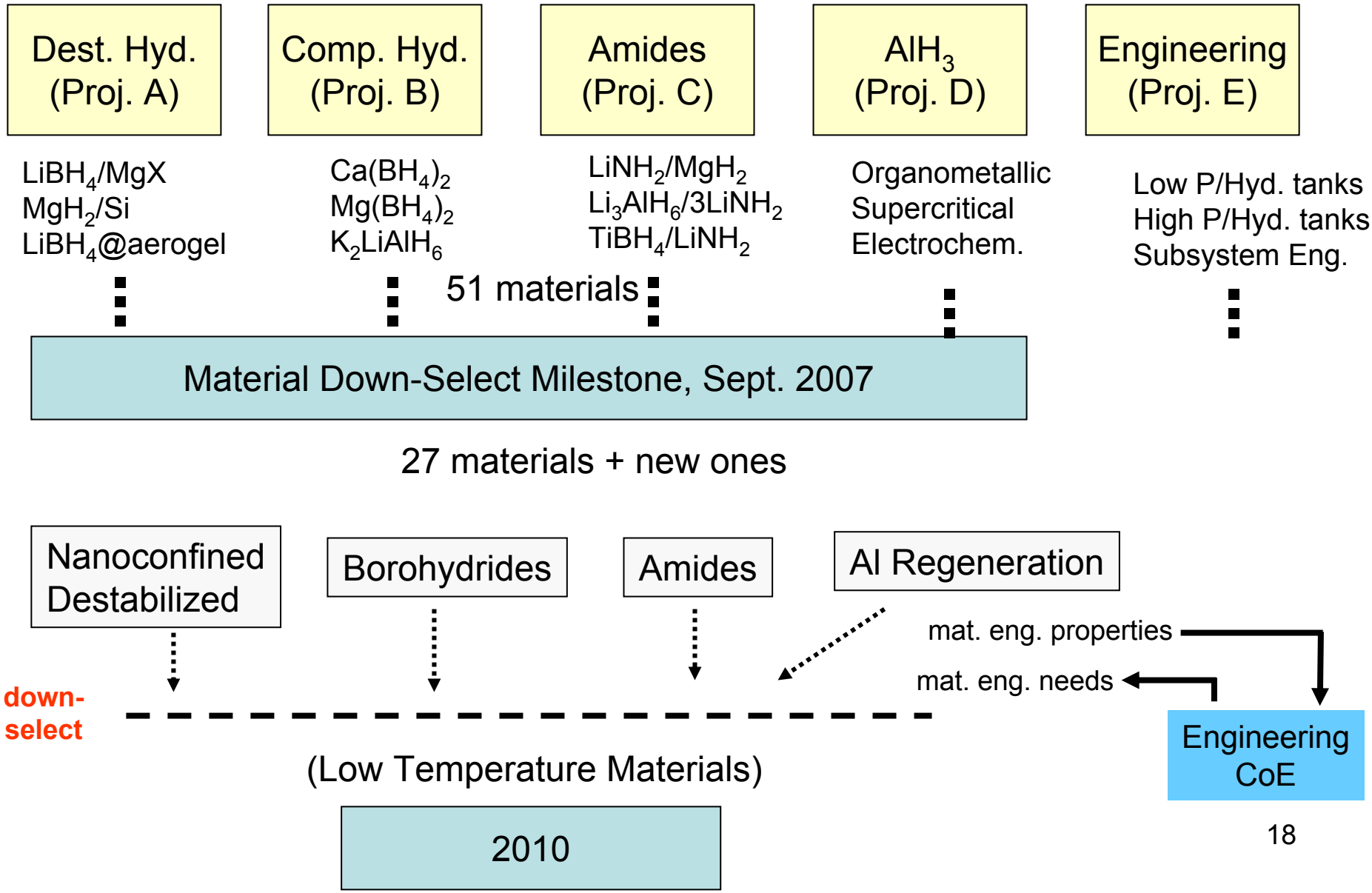
Closing The Gaps---Future Plans

Cycle Life:

-- Focus on determining the degree of material volatilization via release of ammonia and diborane, causes of material degradation

- Work by Jensen et al (**Hawai'i**) shows that diborane can be detected, and that it's release varies greatly with material. In the next year, there will be increased study of diborane emission from promising borohydrides such as $Ca(BH_4)_2$, anionic transition metal borohydrides and Mg-based borohydrides.
- Work by Fang (**Utah**) shows that ammonia release from amides depends on heating rates, a finding of considerable practical importance. This phenomenon needs more study and the influence of additives on ammonia release will be examined.
- Cycling work by Chandra et al (**UNR**) demonstrates that amides have good long-term cycling behavior, with stability against contaminants. Cycling work will continue on selected promising materials, with studies of their resistance to contamination.

MHCoE Path Forward



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MHCoE Face-to-Face Meeting
Sandia-CA, Livermore CA, December 11-12, 2007