DOE Review, May 16, 2007

Metal Hydride Center of Excellence

Lennie Klebanoff, Director (presenting)
Jay Keller, Sandia H₂ Program Manager

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

(This presentation does not contain any proprietary information)
MHCoE Overview Outline

- Overall MHCoE Structure, Participants
- Coordinating Council, Management Costs
- Center-wide, Project Milestone Tracking
- Projects A – E, Technical Highlights
- By The Numbers (summary of MHCoE pubs, talks, patents)
- Working Together
- Connections with Other Groups
- MHCoE Materials Relative to DOE Targets
- Closing the Gaps
- Overall MHCoE Future Direction
MHCoE Project Structure

Coordinating Council (2006-2007)

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

Project Groups

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

B
Complex Anionic Materials
- SNL(POC)
  - GE
  - U. Hawaii
  - UIUC
  - JPL
  - ORNL
  - NIST
  - Intematix
  - UNR
  - Utah

C
Amides/Imides (M-N-H)
- Utah (POC)
  - GE
  - UNR
  - ORNL
  - U. Hawaii
  - JPL

D
Alanes (AlH₃)
- BNL(POC)
  - SRNL
  - JPL
  - U. Hawaii
  - SNL

E
Engineering Analysis & Design
- SRNL(POC)
  - NIST
  - JPL
  - GE
  - SNL

Planned MHCoE Budget: $8.2M FY’07
Coordinating Council

Purpose: Provide overall discussion/guidance to DOE on technical and programmatic directions, go/no-go decisions, center-wide issues

Current Activities:

- Evaluating/Renewing Partner Phase I/Phase II Contracts
- Formulating Materials Down-Select Process for 9/2007 Milestone
- Improving Intellectual Property Procedures for the MHCoE

The Council convenes many times per year, both telecons, face-face

Klebanoff, Keller are permanent members, with other positions evaluated yearly. Project POC’s are also C.C. members
MHCoE Mgmt. FY’07 Estimated Costs

Lead-Lab Center Mgmt. Cost: $445K total
– DOE Interactions $26.2K/partner (17 partners)
– Coordinating Council 5.4% of MHCoE Budget
– MHCoE Milestones Tracking
– Center Meetings
– Partner Coordination
– Collaborations with Other Groups

Lead-Lab + Partners Mgmt. Cost: $625K total
– All of the above, plus..... $36.8K/partner
– Project Meetings 7.6% of MHCoE Budget
– Developing/Tracking Project Milestones
– Coordinating Council
– Project-Project MHCoE Collaborations

Management and coordination of a large center is being provided at very reasonable cost
As a Center we are organizationally tied to the MYRDDP Milestones

### MHCoE Milestone Spreadsheet
-- Center-Wide Milestones --

**As a Center we are organizationally tied to the MYRDDP Milestones**

<table>
<thead>
<tr>
<th>Milestone Level: MYRDDP, Center, or Project</th>
<th>Timeline begins FY05 (10/1/2004) and ends FY15 (9/30/2015). Each cell has a 6 month duration and starts on the day indicated.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organization</td>
<td>Task Description</td>
</tr>
<tr>
<td>CTR Mat Workshop for partners to present materials and show the council how their material or class of materials will meet the 2010 technical targets. (AUG 2007)</td>
<td>M UPDATE</td>
</tr>
<tr>
<td>CTR Mat Prepare material classes for down selection &amp; recommendations to DOE for redirection of resources to the top 50% (9/15/07)</td>
<td>R UPDATE</td>
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<tr>
<td>DOE 7 Down-select on-board reversible metal hydride materials (4Q 2007)</td>
<td>M UPDATE: moved back from 4Q FY09</td>
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<tr>
<td>CTR Sys Workshop for partners to present design engineering concepts and show the council how their concepts will meet the 2010 targets. (2Q 2009)</td>
<td>M UPDATE</td>
</tr>
<tr>
<td>CTR Sys Prepare 2010 target based design concepts for down selection &amp; recommendations to DOE for redirection of resources to the top 50%. (3Q 2009)</td>
<td>R UPDATE</td>
</tr>
<tr>
<td>CTR Sys Complete proof of concept for a complex hydride integrated system meeting 2010 targets. (4Q 2010)</td>
<td>M UPDATE</td>
</tr>
<tr>
<td>DOE 10 Go/No-Go: Decision on continuation of on-board reversible metal hydride R&amp;D (4Q 2010)</td>
<td>D UPDATE: moved back from 4Q FY12</td>
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### A. Destabilized Hydrides

<table>
<thead>
<tr>
<th>A. Destabilized Hydrides</th>
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### B. Complex Anionic Materials (Borohydrides & Alanates)

<table>
<thead>
<tr>
<th>B. Complex Anionic Materials (Borohydrides &amp; Alanates)</th>
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### C. Amide/Imides (M-N-H Systems)

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<th>C. Amide/Imides (M-N-H Systems)</th>
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MHCoE Milestone Spreadsheet
-- Project B Milestones --

Progress checked against milestones quarterly, aids planning, tracks technical risk, Rolls up to MYRDDP Milestones

<table>
<thead>
<tr>
<th>Timeline Level: MYRDDP, Center, or Project</th>
<th>Organization</th>
<th>Task Description</th>
<th>FY05</th>
<th>FY06</th>
<th>FY07</th>
<th>FY08</th>
<th>FY09</th>
<th>FY10</th>
<th>FY11</th>
<th>FY12</th>
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</thead>
<tbody>
<tr>
<td>B. Complex Anionic Materials (Borohydrides &amp; Alanates)</td>
<td>SNL-CA</td>
<td>Development of alanates</td>
<td>D</td>
<td>D</td>
<td>D</td>
<td>D</td>
<td>D</td>
<td>D</td>
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<tr>
<td></td>
<td>1.1</td>
<td>Accomplish synthesis, characterization and measuring of sorption properties of a new bialkali alanate K2LiAlH6. Published in the Journal of Physical Chemistry B.</td>
<td>R</td>
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<td></td>
<td>U. Hawaii</td>
<td>Complete fundamental studies of the alanates. (Task completed)</td>
<td>R</td>
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<tr>
<td></td>
<td>SNL-CA &amp; U</td>
<td>Synthesis and characterization of borohydrides</td>
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<tr>
<td></td>
<td>1.2.1</td>
<td>Synthesize high-capacity borohydrides in the solid state guided by the modeling efforts</td>
<td>D</td>
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<tr>
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<td>1.2.2</td>
<td>Go/no-go for formation of Ca(BH4)2 and Mg(BH4)2. Go for Ca, no-go for Mg.</td>
<td>D</td>
<td>D</td>
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Planned Portfolio Reallocation Decision Point (Project bars)

No Go decision / Resources reallocated to other materials

Go decision established

Milestone (Subtask bars)

Output (Task bars)
Project A – Destabilized Hydrides

Develop strategies for reducing H₂ storage thermal requirements, improve hydride kinetics

New Project Lead: Ian Robertson, UIUC

Project A Technical Highlight: Nickel wetting layer enables incorporation of Mg into carbon aerogel

--- See talk by: Ping Liu (HRL)

Posters by:
- Caltech
- JPL
- Stanford
- Intematix
- NIST
Project B - Complex Anionic Materials

Predict, synthesize and evaluate promising new complex hydride materials

Project Lead: Ewa Ronnebro, Sandia

Project B Technical Highlight: Theory-predicted Ca(BH₄)₂ is reversible

\[ \text{CaB}_6 + 2\text{CaH}_2 + 10 \text{H}_2 \leftrightarrow 3\text{Ca(BH}_4\text{)}_2 \text{ re-hydrided at 700bar, 400C} \]

--- See Talk by: Ewa Ronnebro (SNL)
Other talks by: J.-C. Zhao (GE) Craig Jensen (UH) Karl Johnson (Pitt.)

Posters by: UIUC, JPL ORNL, NIST Intematix UNR, Utah
Project C - Amides/Imides

Assess viability of amides, imides for on-board H₂ storage

New Project Lead: Zak Fang, U. Utah

Project C Technical Highlight:

\( \text{Li}_3\text{AlH}_6/\text{Mg(NH}_2\text{)}_2 \) can reversibly store \( \sim 6 \text{ wt}\% \text{ H}_2 \) at \( T < 300 \degree \text{C} \). Reversibility confirmed by \( ^{27}\text{Al NMR} \)

\[
\begin{align*}
2/3 \text{Li}_3\text{AlH}_6 + \text{Mg(NH}_2\text{)}_2 & \rightarrow 2/3 \text{Al} + \text{Li}_2\text{Mg(NH)}_2 + 3\text{H}_2 \\
\text{(Dehydrogenated)} & \quad \text{Dehydrogenated} \\
\text{Hydrogenated}
\end{align*}
\]
Project D - Alane (AlH₃)

Understand desorption and regeneration properties of AlH₃ for H₂ storage

Project Lead: Jim Wegrzyn, BNL

Project D Technical Highlight: Electrochem. Regeneration of Al $\rightarrow$ AlH₃

- Electrochemical charging under elevated hydrogen pressure
- 500 psi H₂
- 60°C
- 10 V
- 2 hr

--- for more results, see MHCoE Poster by Ragaiy Zidan (SRNL)

Also see talks by:
Jason Graetz (BNL)
Craig Jensen (UH)
Provide engineering, analysis and design supporting DOE system performance goals. Provide engineering-based materials targets

**Project Lead: Don Anton, SRNL**

**Project E Technical Highlight:** MH/High Pressure Hybrid Tank Analyzed

*Comparison of 316ss with Graphite Reinforced Composite, GREC*

*Hybrid Tank System Gravimetric Densities*

--- Analysis reveals the effects of storage tank construction material, operating pressure, media gravimetric density and void fraction on system gravimetric and volumetric storage densities…

-- For more results, see poster by: Don Anton, SRNL
By The Numbers....

From 5/2006 to 4/2007:

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

20 -- Collaborative Publications (between partners)

87 -- MHCoE Talks

10 -- Patents filed based on MHCoE work

*Published in:
Working Together in the MHCoE

Teaming is occurring naturally due to organization in “project” space, see presentations

2010 System
Theory Guides the MHCoE Materials Discovery Efforts

MHCoE Theory Group
Mark Allendorf (SNL, Coordinator), Duane Johnson (UIUC), Karl Johnson (Pitt.), Dave Sholl (CMU), Eric Majzoub (SNL), Ursula Kattner (NIST)

(Examples)
ScH₂ + 2LiBH₄
ΔH ~ 34kJ/mol H₂

Ahn (Caltech)
Sc hydrogenation
ScH₂/2LiBH₄ prep.
H₂ desorption
⁴⁵Sc, ¹¹B, ⁷Li, ¹H MAS-NMR

Bowman (JPL)
(Project A)

Fang (Utah)
Hydrogenation @
138 bar/ 240°C,
⁶Li, ¹H MAS NMR

LiMgN

Bowman (JPL)
(Project C)
Working Together in Project A

**New Destabilized Systems**
- HRL (LiBH₄-based systems)
- Pitt/CMU/UIUC (Theory/modeling)
- Caltech/JPL (Ca alanate systems, ScH₂ + 2(LiBH₄))
- Hawaii (Work w/ UOP)
- Utah (Li-Al-N syst.–mainly in Proj. C)

**Theory**
- CMU/U.Pitt/UIUC (Thermo.)
- NIST (Phase diagrams)

**Advanced Characterization**
- NIST (Neutron methods)
- JPL/Caltech (NMR, TEM)
- Stanford (Synchrotron XRD)
- UIUC (In situ TEM)
- SNL (High-P Sieverts system)

**Kinetics**
- HRL (Nanostruct. materials, scaffolds)
- Stanford (Thin-film model systems)
- Intematix (Combinatorial – catalysts; nanoparticle synthesis)
- Utah (High energy milling, CVS)
- JPL/Caltech (T-ramp, RGA)
- Hawaii (Novel catalysts)

“*The MHCoE brought additional synthesis, characterization and modeling capabilities to the initial destabilization team, thereby accelerating this effort.*”

-- Ian Robertson, UIUC (Proj. A POC)
Working Together in Project B

Theory, Modeling

SNL (MC, DFT)
UIUC (DFT)
Pitt (Kinetics)

Advanced Characterization

SNL (XRD, Raman, DSC, TGA)
JPL/LLNL (NMR)
NIST (Neutron diffraction)
SIUC (TEM)
U. Nevada (In-situ XRD)
Intematix (Catalyst screening)
GE (Synchrotron in-situ XRD)

New Materials Synthesis

SNL (Ca(BH₄)₂, X-Ge-H, H.P. sintering, solvent, rapid screening)
GE (Mg(BH₄)₂, ball milling)
Hawaii (TM Borohydrides)
Utah (Mg mat., Reactive milling)
ORNL (Al(BH₄)₃, Liq. Phase methods)

“The MHCoE enables metal hydride researchers to join forces towards finding new high-performance hydrogen storage materials”

-- Ewa Ronnebro, SNL (POC Project B)
Working Together in Project C

**Theory, Modeling**
- U.Pitt/CMU (DFT theory)
- SNL (MC theory)

**Advanced Characterization**
- JPL (NMR, TEM)
- GE (Synchrotron XRD)
- UNR (PCT, cycling)
- Hawaii (anelastic spect.)
- SNL (High-P Sieverts system)

**New Materials Discovery**
- Utah (CVS, reactive milling)
- ORNL (Wet Chemistry)

**Kinetics**
- Intematix (Combinatorial – mainly catalysts; nanoparticle synthesis)
- Utah (Catalysts)
- Hawaii (Novel catalysts)

"The synergy, made possible by the Center, between materials discovery and fundamental studies, is critical to eventual success"

-- Zak Fang, U of Utah (Proj. C POC)
Working Together in Project D

Regeneration
BNL/ORNl (amide-alane mixtures)
SRNL (Electrochemical)
Hawaii (supercritical fluid approaches)

System Studies
BNL (Synthesis and kinetics)
SRNL (Proto-type tank studies)
SNL (Engineering properties)

Advanced Characterization
BNL (Synchrotron XRD, DSC, TEM, TPD)
JPL (NMR)
Hawaii/NIST (Neutron scattering)

Theory
MHCoE Theory Group
(first principle amine-alane models)

“The MHCoE approach covers all aspects of alane research from fundamental theory to tank design and testing.”

-- Jim Wegrzyn, BNL (Project D POC)
“The MHCoE has produced the collaboration, at a level of interaction not previously achieved, of a broadly-experienced team of hydrogen storage engineering experts”

--Don Anton, SRNL (Proj. E POC)
MHCoE Contacts with Other Groups

MHCoE/Carbon Center:
MHCoE Coordinating Council tours the Carbon Center on 7/18/2006, meets PI’s, discusses Carbon Center work

MHCoE/Chemical Center:
Initial meeting on 5/17/2007 to initiate contacts, discuss Al regeneration (Proj. D)

MHCoE/Berkeley H₂ Storage Group:
Two meetings on 7/21/06, 3/13/07 at LBNL
Examined nano approaches to improving kinetics, thermodynamics in AlH₃, destabilized systems

-- Agreed we should cooperate in developing metal hydride nanoparticle superlattices--
MHCoE Materials Relative to DOE Targets

DOE 2010 system goal
6 wt. % Reversible
(Box assumes a 50% balance of system penalty)

Red Materials—presented this year

(Material Storage Capacity [wt. % H₂])

Desorption Temperature [°C]

(Mg(BH₄)₂)

(Li₂AlH₆ + 3LiNH₂)

(Mg₂NiH₄)

(Reversible)

(LaNi₅H₆)

(AlH₃)

(Relief afforded by Proj. E)

(Mg(BH₄)₂)

(Ca(BH₄)₂)

(2LiBH₄ + MgH₂)

(Mg₂FeH₆)

(Original plot from GE)
The MHCoE collaborations are focussed on closing the gaps between the materials’ performance and the DOE 2010 goals.

**Weight Capacity:** Emphasizing high wt. % systems:
- 2007 Project B– Mg(BH\(_4\))\(_2\), Ca(BH\(_4\))\(_2\)
- 2007 Project E– reduced system penalty

**Reversibility:** Exploring effects of additives on reversibility:
- 2007 Project B– Ca(BH\(_4\))\(_2\) reversible with additive

**Thermodynamics:** Investigating destabilization, nanoconfinement:
- 2007 Project A– Sc predicted to lower ΔH for LiBH\(_4\)

**Kinetics:** Exploring additives, nanoconfinement to improve kinetics:
- 2007 Project C– LiNH\(_2\) lowers the E\(_a\) for LiAlH\(_4\), Li\(_3\)AlH\(_6\) to release hydrogen

*Combinatorial studies will be important in the materials discovery, guided by theory*
Overall Direction of the MHCoE

Dest. Hyd. (Proj. A)
LiBH₄/MgX/Aero MgH₂/Si nanoparticles
Ca(BH₄)₂
Mg(BH₄)₂
Mn(BH₄)₂

Comp. Hyd. (Proj. B)

Amides (Proj. C)
LiNH₂/MgH₂ Li₃AlH₆/3LiNH₂ TiBH₄/LiNH₂

AlH₃ (Proj. D)
Organometallic Supercritical Electrochem.

Engineering (Proj. E)
Low P/Hyd. tanks High P/Hyd. tanks Subsystem Eng.

Material Down-Select Milestone, Sept. 2007
More exploratory studies
Materials with engineering application (supporting targets)

Engineering Design Concept Down-Select Milestone, June 2009
Continue Exploratory Studies (Materials, Thermo., Kinetics)
Proof of Concept Tank, Sept. 2010
MHCoE Meeting, Livermore CA, October 30, 2006