DOE Hydrogen Program Annual Merit Review,
Arlington, VA May 19, 2009

Metal Hydride Center of Excellence

Lennie Klebanoff, Director (presenting)

Jay Keller, Sandia Hydrogen Program Manager

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

(This presentation does not contain any proprietary information)

Project ID: ST_01_Klebanoff

Overview

Timeline

- Project started in March ‘05
- Project end ~ 2010
- Percent complete 80%

Barriers

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

Budget

Lead Lab Mgmt. Funding:

- $485K in FY08
  (5.2% of total MHCoE funding)
- $490K in FY09

MHCoE Total Funding:

- $9.3M Center-wide FY08
- $9.5M Center-wide FY09 (planned)

MHCoE Partners

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

Universities: UIUC, PITT, GT, Utah, Stanford, Caltech, UNR, UNB, Hawaii, OSU

Industry: UTRC, HRL

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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 ($15 < \Delta H < 75$ kJ/mol H_2) as guided by theory

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

- Develop materials that are fully reversible, assess nanoengineering and catalysts as means for promoting kinetics

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

- Assess release of NH_3, B_2H_6 and other volatile species, extend theory to account for these species during rxn

Cycle Life: 2010 Target: 1000 Desorption/Adsorption Cycles

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

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Approach to R&D- Center Structure

DOE

Coordinating Council (2008-2009)

Bruce Clemens (Stanford, POC A), Craig Jensen (UH, POC B), Zak Fang (Utah, POC C), Jim Wegrzyn (BNL, POC D), Don Anton (SRNL), J.-C. Zhao (OSU) Jay Keller (SNL) and Lennie Klebanoff (SNL)

Project Groups

A

Destabilized Hydrides

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

B

Complex Anionic Materials

- **UH (POC)**
- SNL
- OSU
- UIUC
- JPL
- ORNL
- NIST
- UNR
- Utah
- UTRC

C

Amides/ Imides (M-N-H)

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

D

Alane (AlH_3)

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

Note: Original Project E (Eng.) discontinued with HSECoE

Approach To R&D - Participants

Welcome New Partners: (current total 18)

- The Ohio State University (J.-C. Zhao, Project B)
- Georgia Tech (David Sholl, Theory Group)

Goodbye Former Partners, and Thank You!

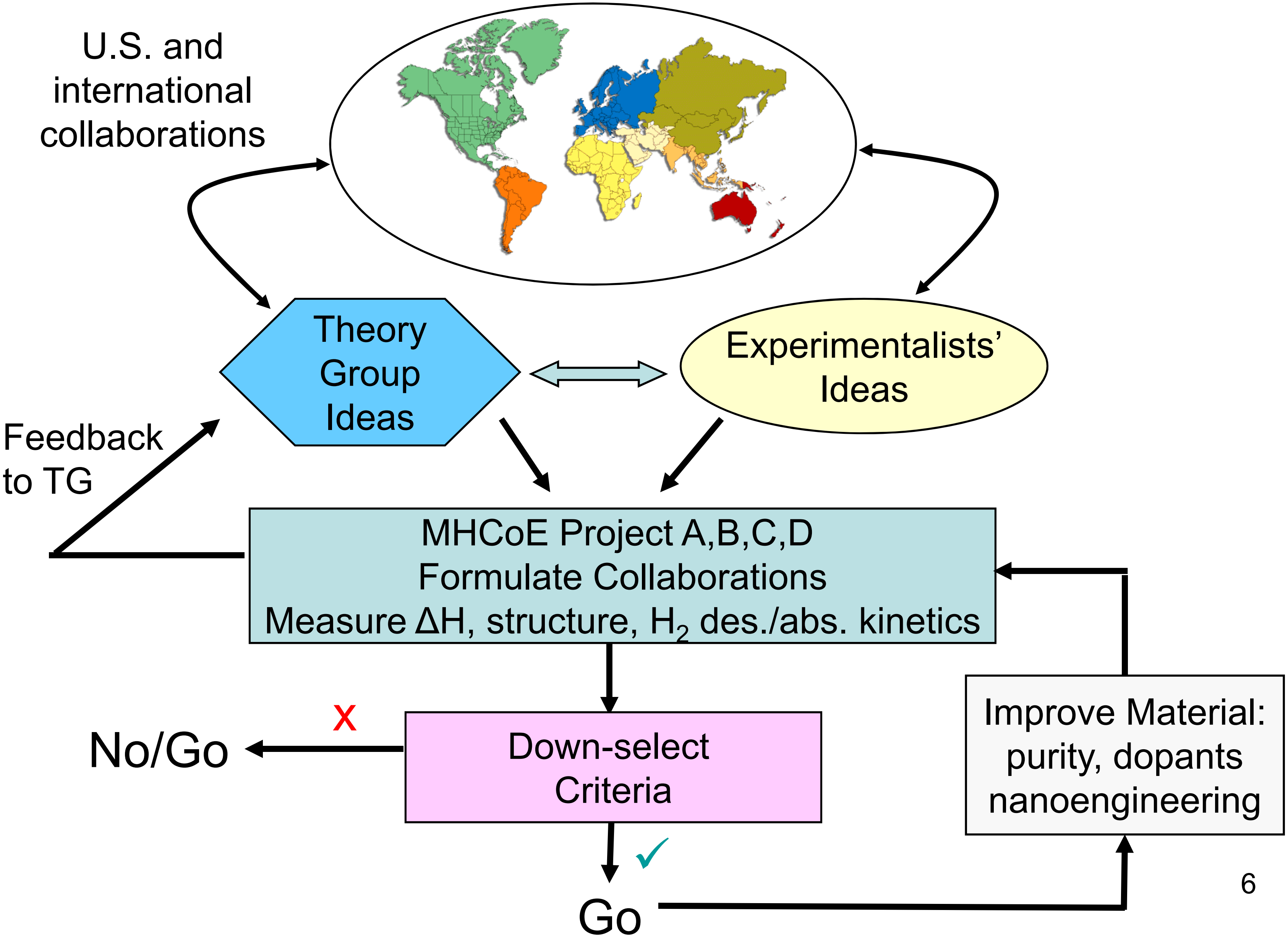
- GE (J.-C. Zhao moved to OSU)
- Carnegie Mellon University (David Sholl moved to GT)
- Intematix (Jonathan Melman, Darshan Kundaliya)

New Leaders:

Craig Jensen is now Project B Lead, replacing Ewa Rönnebro who is now with PNNL (thank you Ewa for your contributions)

J.-C. Zhao was elected to the Coordinating Council by the partners

MHCoE Approach to R&D: Flow of Ideas, Studies and Collaborations



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

No/Go

x

Down-select Criteria

✓

Go

Improve Material: purity, dopants nanoengineering

Specific Example: LiMgN

MHCoE Theorists Predict:

$$MgH_2 + LiNH_2 \rightarrow LiMgN + 2H_2$$

ΔH = 32kJ/mole H_2
Wt. % = 8.2

GT/Pitt

MHCoE Project C (Amides, Imides)

Synthesis, PCT, TGA: Utah
In-situ XRD: GE/OSU
NMR Structure: Caltech/JPL

Down-select Criteria

Reversible ✓, Capacity ✓
Kinetics ✓ , Thermo ?
Volatiles ✗

Go

"Modify theory to account for multistep rxns"
-- Tech Team

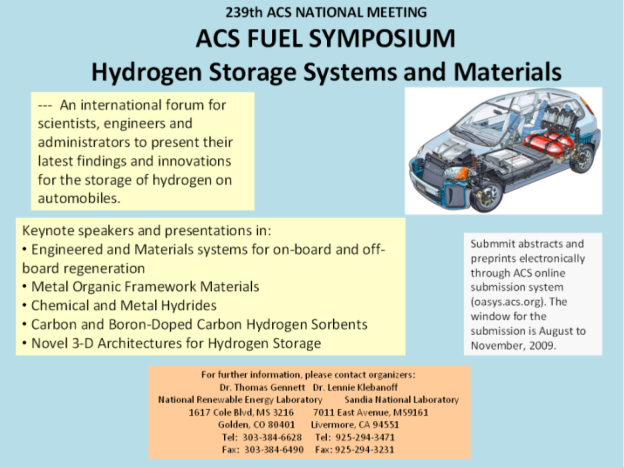
Pure LiMgN (Utah)
Kinetics (SRNL)
Measure ΔH (Utah)
Cat. screening (HRL)

Collaborations/Communications of the MHCoE with Others

At our December 2008 Face to Face meeting, we devoted a full morning to presentations and discussions with scientists outside the MHCoE:

1. Metal Ammonia Borane Derivatives, Tony Burrell, LANL
2. Computational Work in Chemical Hydrogen Storage, David Dixon, U. Alabama
3. Efficient Discovery of Novel Multicomp. Mixtures for Hydrogen Storage, Chris Wolverton, Northwestern U.
4. Boron Hydrides and Their Chemistry, Prof. Sheldon Shore, The Ohio State University

Other: Tom Gennett (NREL, Sorption Center) and Lennie Klebanoff (MHCoE) are co-organizers for the 2010 ACS Symposium on Hydrogen Storage, March 21-25, 2010 San Francisco, CA



239th ACS NATIONAL MEETING

ACS FUEL SYMPOSIUM

Hydrogen Storage Systems and Materials

--- An international forum for scientists, engineers and administrators to present their latest findings and innovations for the storage of hydrogen on automobiles.

Keynote speakers and presentations in:
- Engineered and Materials systems for on-board and off-board regeneration
- Metal Organic Framework Materials
- Chemical and Metal Hydrides
- Carbon and Boron-Doped Carbon Hydrogen Sorbents
- Novel 3-D Architectures for Hydrogen Storage

Submmit abstracts and preprints electronically through ACS online submission system (oasys.acs.org). The window for the submission is August to November, 2009.

For further information, please contact organizers:

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We Collaborate Nationally

MHCoE Partner	US Institution (not MHCoE)	US Collaborator and Topic
BNL	UC Davis	P. Power (solution chemistry of alane complexes)
UH	UOP, LLC	L. Knight, G. Lewis, J. Low, A. Sachtler (XRD and MS)
UH	U. Nevada LV	R. Kumar (neutron diffraction)
UH	U. South Florida	S. Srinivasan (DSC)
UH, HRL	PNNL	T. Autrey (Synthesis, mesoporous carbon)
HRL	LLNL	T. Baumann (porous carbon materials)
HRL	U. Conn	L. Shaw (optimizing kinetics using milling)
NIST	U. Maryland	M. Yousufuddin, J.-H. Her, J. Rush, H. Wu and W. Zhou (synth., neutron and x-ray measurements, DFT calculations)
NIST	GM	F. Pinkerton, M. Meyer (Li-B-N-H phases)
NIST	Penn	T. Yildirim (DFT calculations)
NIST	Michigan	M. Hartman (isotopically labelled hydrogen storage compounds)
SNL	UCLA	V. Ozolins (theory)
SNL	LLNL	J. Herberg (NMR)
SNL	Northwestern	C. Wolverton (theory)
SNL	U. Maryland	J-H Her (Neutron)
SRNL	U. South Carolina	H. zur Loye (XRD analysis)
UTRC	Albemarle Corp.	F.-J. Wu, J. Strickler (nanoconfinement)

-- we collaborate with 16 US institutions that are not partners in the MHCoE

We Collaborate Internationally

MHCoE Partner	International Institution	International Collaborator and Topic
BNL	IFE (Norway)	V. Yartys, B. Hauback (AlH_3 chem., structure)
BNL	U. Geneva (Switzerland)	K. Yvon, (oxidation of AlH_3, synchrotron)
UH	KEK	R. Kuboto (muon spin resonance)
UH	AIST (*Japan*)	E. Akiba, K. Sakaki (positron annihilation studies)
UH	Tohoku University (*Japan*)	S. Orimo, Y. Nakamori (synthesis, DSC and XRD)
UH/UNR	U. Rome *(Italy*)	R. Cantelli (analastic spectroscopy)
UH	IFE (*Norway*)	B. Hauback, M. Sorby; (Sync. X-ray, Neutron Diff.)
UH	U. Geneva (*Switzerland*)	H. Hagmann, R. Černý; (XRD, IR, Raman Spec.)
UNR	U. Geneva (*Switzerland*)	K. Yvon (sabbatical host, XRD studies)
GA Tech/Pitt	U. Geneva (*Switzerland*)	R. Černý (High res. XRD, neutron scattering)
SNL/UNR	ESRF (*France*)	Y. Filinchuk (Synchrotron X-ray Diffraction)
U. Utah	U. Singapore (*China*)	P. Chen (amide synthesis)

-- we collaborate with 8 foreign institutions that are not partners in the MHCoE

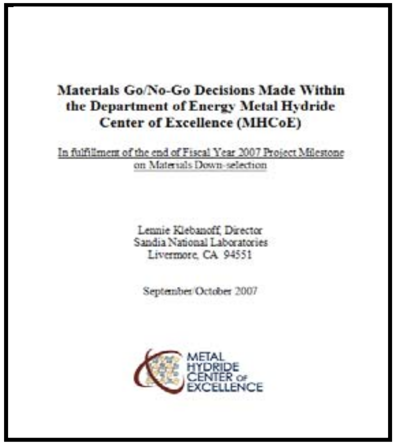
Materials Downselect Procedures Provide R&D Focus

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 wt%**
2) **The material should be at least 50% reversible after 3 cycles**
3) **The material should release its H_2 for $T < 350$ °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 are used as guidelines in determining if specific material systems have 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.

9/07 Down-select Report



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

Materials Down-selects: from 3/2008 - Present

During the past year, the following materials were synthesized and characterized, but are not being pursued further (have been down-selected):

$Ca(BH_4)_2$	(too high desorption T)
$Ca(BH_4)_2 \cdot NH_3$	(ammonia release)
$LiCa(BH_4)_3 \cdot NH_3$	(ammonia release)
$Na_2Zr(BH_4)_6$	(not reversible)
$K_2Zr(BH_4)_6$	(not reversible)
$LiMn(BH_4)_6$	(not reversible)
$Li_2Zr(BH_4)_6$	(not reversible)
$NaMn(BH_4)_6$	(not reversible)
$Li_3AlH_6/LiNH_2$	(LiMgN better)
ScH_2-$LiBH_4$	(no destabilization rxn.)
$LiSc(BH_4)_4$	(not reversible)

We are still pursuing the following bulk materials:

$Mg(BH_4)_2$
LiMgN
$Mg(BH_4)_2 \cdot (NH_3)_2$
MgH_2-Ti
AlH_3
$LiAlH_4$
$LiBH_4/Mg_2NiH_4$
New NH_2/BH_4 compounds
New borohydrides
New BH_4/NH_3 adducts
New BH_4/AlH_4 materials

Note: Some “downselected” bulk materials being used in nanoconfinement studies, for example $LiBH_4/MgH_2$ (HRL, Hawaii)

Technical Accomplishments: By The Numbers….

From 3/2008 to 3/2009:

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

26 -- **Collaborative Publications (between partners)**
(43% of total)

71 -- **MHCoE Talks**

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

<u>*Published in:</u>

Phys. Rev. Lett. (2)
Phys. Rev. B
J. Amer. Chem. Soc.
J. Phys. Chem. (A, B, C)
Scripta Materialia
Inorg. Chem.
Chem. Mat.
J. Appl. Phys.
Nanotechnology
Appl. Phys. Lett.

Key Technical Accomplishments From 3/2008 – 3/2009

Charge/Discharge Rates (Kinetics):

Developed a successful liquid phase procedure for incorporating metal hydride materials into nanoscaffolds, observed significant (up to 60X) increase in desorption rates (see ST07 by Hawaii and ST09 HRL). Successfully incorporated a mixed metal borohydride at high loadings into an inorganic aerogel, found stability enhancement (see ST10 by UTRC)

Hydrogen Capacity and Reversibility:

Discovered a method to fully reverse $Mg(BH_4)_2$, thereby demonstrating a fully reversible 14 wt.% system, the highest level of reversibility achieved thus far in a practical material (see ST07 by Hawaii and ST03 by Sandia). Also, significantly advanced AlH_3 off-board regeneration by electrochemical means (see ST06 by SRNL)

Hydrogen Purity/Cycle Lifetime:

Developed first theoretical approaches to understand impact of volatile species on reaction pathways, purity of hydrogen release, and the cycle life (see ST03 by Sandia, ST08 by PITT/GT)

Summary of Key MHCoE Accomplishments 3/08 – 3/09 (For Review after Presentations)

1. Developed capability to include important gas-phase species in phase equilibrium calculations for H_2 release from $LiNH_2$, $LiBH_4/C$ (SNL, Pitt, GT)

2. Synthesized pure LiMgN, found ΔH desorption to be ~20 - 30kJ/moleH_2 , in overall agreement with MHCoE theory (Utah)

3. Found that slurry AlH_3 H_2 release rates are greater than for AlH_3 alone (BNL)

4. Achieved full destabilized system ($LiBH_4/MgH_2$) in C-aerogel (HRL)

5. Achieved breakthrough in electrochemical regeneration of AlH_3, producing gram quantities of high purity AlH_3 with high H_2 content (SRNL).

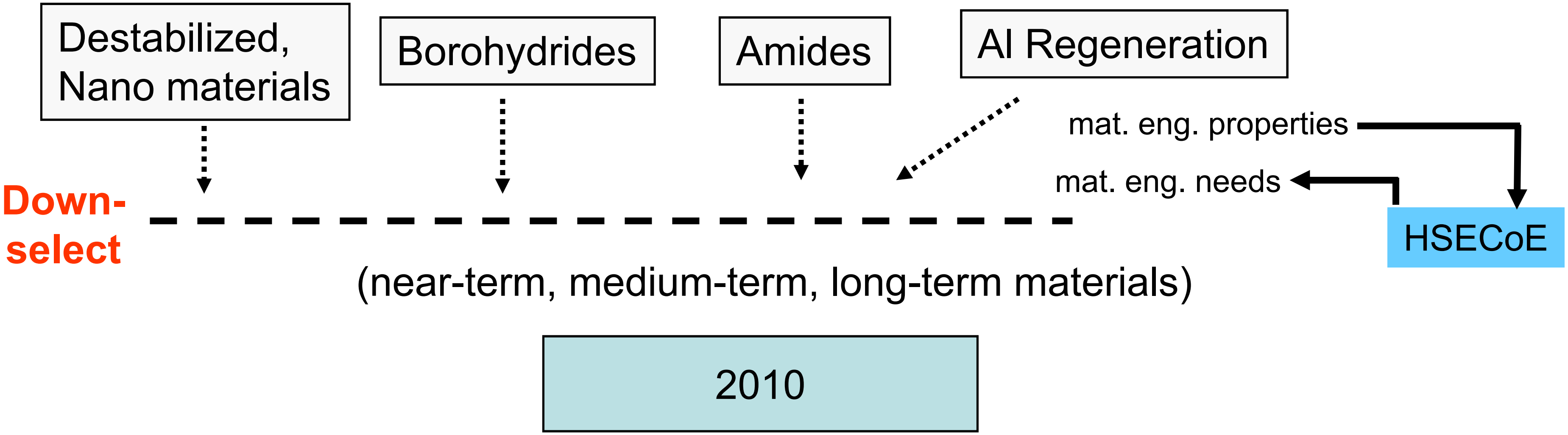
6. Found that discharged $LiAlH_4$ (LiH, Al[Ti]) can be conveniently regenerated at room temperature in 100 bar of Me_2O/H_2 (UNB, UH)

7. Demonstrated high loading of $NaTi(BH_4)_4$ in SiO_2 aerogel, with the aerogel improving hydride stability (UTRC, Albemarle)

8. Found that an additive allows $Mg(BH_4)_2$ to reverse at 700bar H_2, 350 °C (UH, SNL)

9. Advanced our understanding of $M_xB_{12}H_{12}$ (M = Li, Na, Ca, Mg) compounds, which are important intermediates during H_2 release from borohydrides (NIST, OSU, SNL, Caltech/JPL)

MHCoE Path Forward



Destabilized, Nano materials

Borohydrides

Amides

Al Regeneration

mat. eng. properties

mat. eng. needs

HSECoE

Down-select

(near-term, medium-term, long-term materials)

2010

3 High-Level MHCoE Goals For The Final Project Year: Focus for the Future

1. Identify a near-term material for collaboration and subsystem testing in the HSECoE (in progress)
2. Identify a medium-term material that needs more R&D, but would also be of eventual interest for HSECoE examination and subsystem testing
3. Identify areas of further R&D that in the long-term have promise for fulfilling the 2015 targets (pursued in a follow-on materials CoE)

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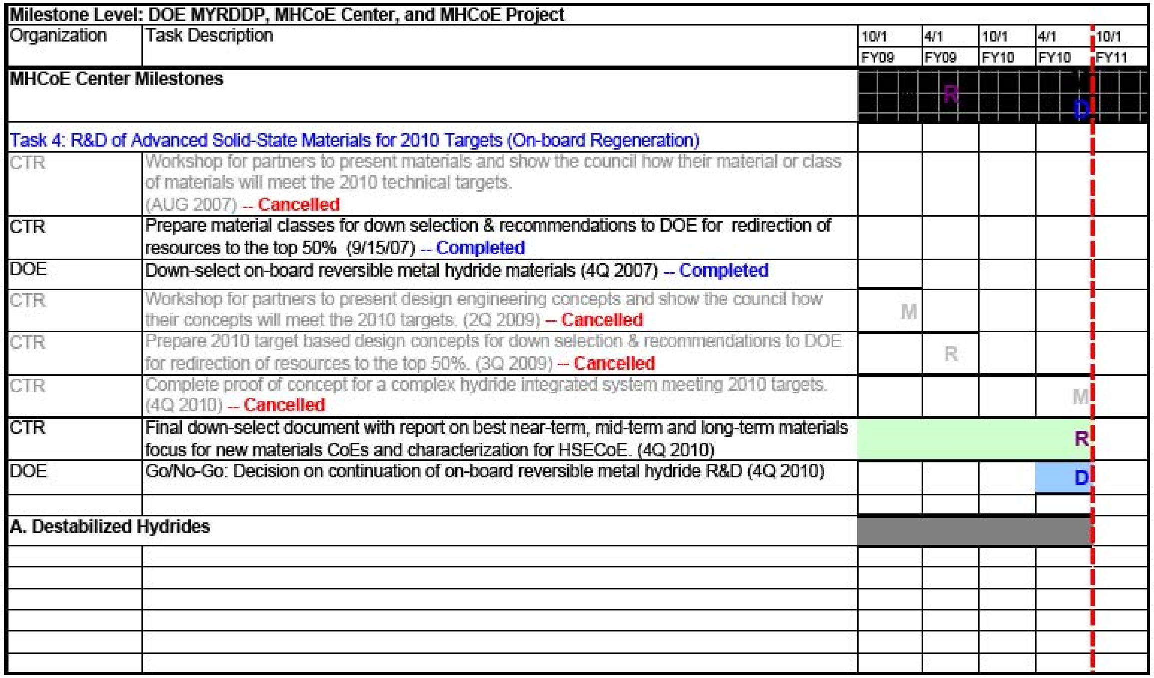
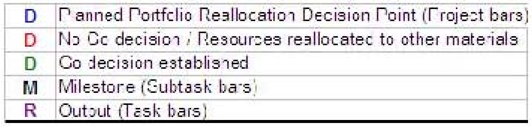
Proposed Future Work and Relevance: By Projects

Under the guidance of the Project Leads, the 4 MHCoE Projects have discussed their final-year MHCoE goals. The final-year milestones have been captured in our Milestone Chart, which ties us organizationally to the MYRDDP Milestones:



Milestone Level: DOE MYRDDP, MHCoE Center, and MHCoE Project						
Organization	Task Description	10/1 FY09	4/1 FY09	10/1 FY10	4/1 FY10	10/1 FY11
MHCoE Center Milestones			R		D	
Task 4: R&D of Advanced Solid-State Materials for 2010 Targets (On-board Regeneration)						
CTR	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) -- Cancelled					
CTR	Prepare material classes for down selection & recommendations to DOE for redirection of resources to the top 50% (9/15/07) -- Completed					
DOE	Down-select on-board reversible metal hydride materials (4Q 2007) -- Completed					
CTR	Workshop for partners to present design engineering concepts and show the council how their concepts will meet the 2010 targets. (2Q 2009) -- Cancelled	M				
CTR	Prepare 2010 target based design concepts for down selection & recommendations to DOE for redirection of resources to the top 50%. (3Q 2009) -- Cancelled		R			
CTR	Complete proof of concept for a complex hydride integrated system meeting 2010 targets. (4Q 2010) -- Cancelled				M	
CTR	Final down-select document with report on best near-term, mid-term and long-term materials focus for new materials CoEs and characterization for HSECoE. (4Q 2010)	🟩	🟩	🟩	🟩 R	
DOE	Go/No-Go: Decision on continuation of on-board reversible metal hydride R&D (4Q 2010)				D	
A. Destabilized Hydrides		▨	▨	▨	▨	



D	Planned Portfolio Reallocation Decision Point (Project bars)
D	No Go decision / Resources reallocated to other materials
D	Go decision established
M	Milestone (Subtask bars)
R	Output (Task bars)

Future Work and Relevance: Project A (Destabilized Hydrides)

Remaining Project A Goals: **Advance Kinetics, High H_2 Capacity**

- Optimize the procedures for introducing $LiBH_4/MgH_2$ into C aerogel
- Introduce a catalyst into the combined $LiBH_4/MgH_2$ in C aerogel
- Demonstrate the simultaneous incorporation of $LiBH_4/MgH_2$ and catalyst into an aerogel, to ensure intermixing within the nanocavity.

HRL, UH, Caltech, JPL

- Explore the $LiBH_4$/metal hexaboride destabilized systems which have been predicted by MHCoE theory (HRL, Caltech, JPL)
- Fully characterize the thermodynamics of ternary Li-Mg-Ni-B systems (HRL, Caltech)
- Attempt to synthesize M-B-C (M = Li, Mg) based on MHCoE Theory (HRL, Pitt, GT)
- Utilize thin-film model systems to probe effects of the nanoscale on MH thermodynamics (Stanford and NIST)

Project B: Complex Anionic Materials
Project C: Amides/Imides

Remaining Project B Goals: Advance H Capacity, Reversibility

- Investigate the reversibility of alkali and transition metal borohydrides (SNL, UH)

- Determine if reversibility can be achieved in the new $(BH_4)/(NH_3)$ class of materials (OSU, SNL, SRNL)

- Experimentally test predictions by Theory Group (SNL, HRL, NIST, OSU, Pitt, GT)

- Demonstrate incorporation of a reversible complex MH into an inorganic aerogel (UTRC, SNL, HRL)

Remaining Project C Goals: Advance Reversibility, H_2 Purity

- Comprehensive study of phase diagrams for LiMgN to understand reaction path, dependence on composition, T and P (UNR)

- Continue to study kinetics of LiMgN and the effect of catalysts/additives. Understand and mitigate NH_3 evolution from hydrogenated LiMgN (Utah, SNL, HRL, SRNL)

- Synthesis and characterization of new ABH_4/ANH_2 materials (SNL)

Future Work and Relevance: Project D (AlH_3)

Remaining Project D Goals: **Improve Reversibility (Off-board)**

- Select adducts for the recovery of AlH_3 and lower aluminum hydride-slurry decomposition temperatures to less than 120 °C (BNL)

- Optimize AlH_3 electrochemical regeneration process, work with ANL on system analysis of implementation (SRNL)

- Improve cycling of $LiAlH_4$-DME (UH, UNB)

- Experimentally evaluate the potential of ionic liquids to promote regeneration (ORNL)

- Predict trends in alane stabilization by ethers and amines (SNL)

- Complete processing studies on spent Al using amines and LiH for regenerating AlH_3 and work with ANL on system analysis (BNL)

Summary

Much progress has been made, but more is needed. The MHCoE continues to push hard to:

Improve our ability to predict new hydrogen storage materials

Synthesize predicted materials and quickly assess their characteristics

Advance hydrogen storage properties such as purity, kinetics, thermodynamics and cycle life in bulk and nanoengineered materials

Understand reaction pathways and test if catalysts/additives can improve materials performance

Make definitive down-select decisions after sufficient information is gathered so as not to waste time and resources

MHCoE Partners Meeting, December 18-19, 2007
California Institute of Technology, Pasadena, CA

The MHCoE thanks the AMR Reviewers for very valuable feedback and guidance

Extra Slides

Summary of Selected MHCoE Materials Properties

Properties	MgH_2/ Ni^{nano}	$NaAlH_4$	$LiBH_4$ /MgH_2	$Ca(BH_4)_2$	$LiBH_4$/ Mg_2NiH_4	AlH_3 (regenerated with amine)	$LiAlH_4$ (regenerated with THF)	$Mg(BH_4)_2$	LiMgN
Theoretical reversible wt% H_2 (without catalyst)	7.6	5.6	11.6	9.6	8.3	10.1	7.9	14.9	8.2
Volumetric density (g/L) (without catalyst)	112	92	95	TBD	TBD	149	72	TBD	107 (estimated)
Demonstrated reversible wt% H_2 (with catalyst)	6.5	~5	8 - 10	4.5	6.5	TBD	7.1	~14	6.6 (PCT)
Desorption Temp (°C) (with catalyst)	150-250 (low P)	100-160	400	330	280-360	< 100	115	200	160-240
Adsorption Temp (°C) (with catalyst)	150	120	300	330	300	25 (with amine)	25 (with THF)	350	160-300
Isothermal Plateau Pressure, with catalyst, (Bar) (temp °C)	1 (280)	1st step 1(~40) 10 (~90)	8 (360) Est 1(225)	TBD	1st Step 1bar (65 °C)	2 bar (88) (with amine)	1 bar (25) (with THF)	TBD	1, and 20 (240 °C)

-- MHCoE Materials in blue

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**).